JC-2 Examination Papers

2012

Chemistry

<table>
<thead>
<tr>
<th>College</th>
<th>H2</th>
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<tbody>
<tr>
<td>Anderson Junior College</td>
<td>P1</td>
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<tr>
<td>Catholic Junior College</td>
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<td>Serangoon Junior College</td>
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<td>Temasek Junior College</td>
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</table>
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

There are forty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D.
Choose the one you consider correct and record your choice in soft pencil on the Multiple Choice Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.

Multiple Choice Answer Sheet

Write your name, PDG and NRIC/FIN number, including the reference letter.
Shade the NRIC / FIN number.
Exam Title: JC 2 Prelim
Exam Details: H2 Chem / Paper 1
Date: 19/09/2012

This document consists of 17 printed pages.
Section A

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

1. The first stage in the manufacture of nitric acid is the oxidation of ammonia by oxygen.
   \[ a\text{NH}_3(g) + b\text{O}_2(g) \rightarrow c\text{NO}(g) + d\text{H}_2\text{O}(g) \]
   What are the values for \( a, b, c \) and \( d \)?

<p>| | | | |</p>
<table>
<thead>
<tr>
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</thead>
</table>
   A | 4 | 5 | 4 | 6 |
   B | 4 | 6 | 4 | 5 |
   C | 5 | 6 | 5 | 4 |
   D | 6 | 5 | 6 | 4 |

2. The nickel–cadmium rechargeable battery is based on the following overall reaction.
   \[ \text{Cd} + 2\text{NiOOH} + 4\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + 2\text{Ni(OH)}_2\cdot\text{H}_2\text{O} \]
   What is the oxidation number of nickel at the beginning and at the end of the reaction?

<p>| | | |</p>
<table>
<thead>
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<th></th>
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</thead>
</table>
   A | +1.5 | +2 |
   B | +2 | +3 |
   C | +3 | +2 |
   D | +3 | +4 |

3. Which element has an equal number of paired and unpaired electrons in its orbitals with principal quantum number 2?

   A. Beryllium
   B. Carbon
   C. Nitrogen
   D. Oxygen
4 Americium–241 is commonly used in smoke detectors. It works by emitting a constant stream of alpha particles which are similar to the nucleus of $^4$He.

Strontium–90 is another radioactive substance which can be used as a tracer for medicinal or agriculture uses. On decaying, it emits beta particles which can be considered as electrons.

A small amount of Americium–241 and Strontium–90 are separately placed in an ionisation chamber to emit a constant stream of radiation and the emitted particles are passed through an electric field.

![Ionisation Chamber Diagram](image)

What would be the path of the emitted particles in an electric field?

<table>
<thead>
<tr>
<th></th>
<th>Americium–241 ($\alpha$–particles)</th>
<th>Strontium–90 ($\beta$–particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>D</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

5 Which of the following is **not** a feature in the corresponding ion?

<table>
<thead>
<tr>
<th>Ion</th>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $\text{HF}_2^-$</td>
<td>Hydrogen bond</td>
</tr>
<tr>
<td>B $\text{NO}_2^-$</td>
<td>Unpaired electron</td>
</tr>
<tr>
<td>C $\text{CO}_3^{2-}$</td>
<td>Delocalised electrons</td>
</tr>
<tr>
<td>D $\text{C}_6\text{H}_5\text{O}^-$</td>
<td>All bond angles are 120°</td>
</tr>
</tbody>
</table>
Two gas bulbs, E and F, are connected by a stopcock. Bulb E contains argon and bulb F contains oxygen gas. The pressure and volume of gas in each bulb at 25 °C is shown below.

<table>
<thead>
<tr>
<th></th>
<th>Bulb E</th>
<th>Bulb F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume / dm³</td>
<td>v</td>
<td>7v</td>
</tr>
<tr>
<td>Pressure / kPa</td>
<td>p</td>
<td>5p</td>
</tr>
</tbody>
</table>

The stopcock is then opened and the gases were allowed to mix at 25 °C. Subsequently, the temperature of the mixture is raised and the final pressure is found to be 9p.

What is the temperature of the gases in the mixture that gives a pressure of 9p?

A  50 °C  B  596 °C  C  50 K  D  596 K

Solutions of hydrogencarbonates can react with acids as follows.

\[ \text{HCO}_3^- (aq) + \text{H}^+ (aq) \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2(g) \]

\[ \Delta H^\circ = +12.7 \text{ kJ mol}^{-1} \]

Given the following enthalpy changes:

<table>
<thead>
<tr>
<th>species</th>
<th>( \Delta H^\circ ) / kJ mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}(l) )</td>
<td>-285.8</td>
</tr>
<tr>
<td>( \text{CO}_2(g) )</td>
<td>-393.5</td>
</tr>
<tr>
<td>( \text{HCO}_3^- (aq) )</td>
<td>-692.0</td>
</tr>
</tbody>
</table>

What is the standard enthalpy change of formation of \( \text{H}^+ (aq) \)?

A  -25.4 kJ mol\(^{-1} \)  B  0.0 kJ mol\(^{-1} \)  C  +25.4 kJ mol\(^{-1} \)  D  +1384 kJ mol\(^{-1} \)

The Gibbs free energy change of a system determines whether a reaction is spontaneous, while the equilibrium constant indicates the extent of reaction.

What does the following pair of values for a reaction system indicate?

<table>
<thead>
<tr>
<th>values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta G^\circ )</td>
</tr>
<tr>
<td>( K_c )</td>
</tr>
</tbody>
</table>

A  No reaction  B  Position of equilibrium lies to the left  C  Some extent of reaction  D  Reaction goes to completion
9 The electrolysis of a highly concentrated aqueous solution of potassium hydroxide was carried out using an iron anode and a platinum cathode. After a current was passed through the cell for some time, 360 cm³ of gas was collected at the cathode (measured at r.t.p.) while there was a loss of mass of 0.279 g at the anode.

Which of the following ions is a likely product at the anode?

A $\text{Fe}^{2+}$  
B $\text{Fe}^{3+}$  
C $\text{FeO}_4^{4-}$  
D $\text{FeO}_4^{2-}$

10 The percentage of ammonia obtainable, if equilibrium was established during the Haber process, is plotted against the operating pressure for two temperatures, 400 °C and 500 °C.

Which diagram correctly represents the two graphs?
11 Water dissociates into H\(^+\) and OH\(^-\) as shown.

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \]

At 25 °C, the equilibrium [H\(^+\)] is 10\(^{-7}\) mol dm\(^{-3}\); [H\(_2\)O] = 55.6 mol dm\(^{-3}\).

What is the order of increasing numerical value of pH, pK\(_a\) and pK\(_w\) for this equilibrium at this temperature?

<table>
<thead>
<tr>
<th></th>
<th>smallest</th>
<th>largest</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>pH</td>
<td>pK(_w)</td>
</tr>
<tr>
<td>B</td>
<td>pH</td>
<td>pK(_a)</td>
</tr>
<tr>
<td>C</td>
<td>pK(_w)</td>
<td>pK(_a)</td>
</tr>
<tr>
<td>D</td>
<td>pK(_a)</td>
<td>pH</td>
</tr>
</tbody>
</table>

12 Bromocresol green is an acid–base indicator with a pH range of 3.8 to 5.4. The acidic colour of the indicator is yellow and the alkaline colour is blue.

Two drops of the indicator are added to each of the four aqueous solutions listed below.

Which solution has its colour **not** correctly stated?

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aqueous solution of MgCl(_2)</td>
<td>blue</td>
</tr>
<tr>
<td>B</td>
<td>Equal proportions of sodium ethanoate and ethanoic acid [pK(_a) of ethanoic acid = 4.7]</td>
<td>green</td>
</tr>
<tr>
<td>C</td>
<td>Dilute HC(_l) of concentration 3.0 (\times) 10(^{-5}) mol dm(^{-3})</td>
<td>yellow</td>
</tr>
<tr>
<td>D</td>
<td>Aluminium oxide in aqueous solution</td>
<td>blue</td>
</tr>
</tbody>
</table>

13 Lead is the final product formed by a series of changes in which the rate–determining step is the radioactive decay of uranium–238. The radioactive decay is a first order reaction with a half–life of 4.5 \(\times\) 10\(^9\) years.

What would be the age of a rock sample, originally lead–free, in which the molar proportion of uranium to lead is now 1:3?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.25 (\times) 10(^9) years</td>
</tr>
<tr>
<td>B</td>
<td>4.5 (\times) 10(^9) years</td>
</tr>
<tr>
<td>C</td>
<td>9.0 (\times) 10(^9) years</td>
</tr>
<tr>
<td>D</td>
<td>13.5 (\times) 10(^9) years</td>
</tr>
</tbody>
</table>
14 \( \text{Na}_2\text{S}_2\text{O}_3 \) reacts with dilute \( \text{HCl} \) to give a pale yellow precipitate. If 1 cm\(^3\) of 0.1 mol dm\(^{-3}\) \( \text{HCl} \) is added to 10 cm\(^3\) of 0.02 mol dm\(^{-3}\) \( \text{Na}_2\text{S}_2\text{O}_3 \) the precipitate forms slowly. If the experiment is repeated with 1 cm\(^3\) of 0.1 mol dm\(^{-3}\) \( \text{HCl} \) and 10 cm\(^3\) of 0.05 mol dm\(^{-3}\) \( \text{Na}_2\text{S}_2\text{O}_3 \) the precipitate forms more quickly.

Which of the following helps to explain this observation?

A The activation energy of the reaction is lower when 0.05 mol dm\(^{-3}\) \( \text{Na}_2\text{S}_2\text{O}_3 \) is used.
B The reaction proceeds by a different pathway when 0.05 mol dm\(^{-3}\) \( \text{Na}_2\text{S}_2\text{O}_3 \) is used.
C The collisions between reactant particles are more violent when 0.05 mol dm\(^{-3}\) \( \text{Na}_2\text{S}_2\text{O}_3 \) is used.
D The reactant particles collide more frequently when 0.05 mol dm\(^{-3}\) \( \text{Na}_2\text{S}_2\text{O}_3 \) is used.

15 Consecutive elements G, H and I are in the third period of the Periodic Table. Element H has the highest first ionisation energy and the lowest melting point.

What could be the identities of G, H and I?

A Aluminium, silicon, phosphorus
B Magnesium, aluminium, silicon
C Silicon, phosphorus, sulfur
D Sodium, magnesium, aluminium

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

A 5.00 g sample of an anhydrous Group II metal nitrate loses 3.29 g in mass when heated strongly.

Which metal is present?

A Magnesium
B Calcium
C Strontium
D Barium

17 Which suggestion concerning the element astatine (proton number 85) is consistent with its position in Group VII?

A The element is a solid at room temperature and pressure.
B Hydrogen astatide is more stable to heat than hydrogen iodide.
C Silver astatide is soluble in aqueous ammonia.
D Hydrogen astatide is a weak acid.
18 The structures of two complexes are as shown.

Which of the following statements is correct?

A Both complexes contain two different ligands.
B Co in the complex has four unpaired d-electrons.
C The oxidation number of Co in the complex is +2.
D The electronic configuration of nickel in the complex is [Ar] 3d⁷.

19 Platinum(IV) chloride combines with ammonia to form compounds in which the coordination number of platinum is 6. A formula unit of one of the compounds contains a cation and only one chloride ion.

What is the formula of this compound?

A Pt(NH₃)₆Cl₄
B Pt(NH₃)₅Cl₄
C Pt(NH₃)₄Cl₄
D Pt(NH₃)₃Cl₄

20 Limonene occurs in oil of lemons and is used to flavour some citrus drinks. The structure of limonene is shown below.

How many optical isomers will be formed when limonene is reacted with cold acidified potassium manganate(VII)?

A 2  B 4  C 16  D 32
21 When heated with chlorine, 2,2–dimethylbutane undergoes free radical substitution.

In a propagation step, the free radical $X^\cdot$ is formed.

$$\ce{CH3CH2-C-CH3 + C/\cdot \rightarrow X^\cdot + HCl}$$

How many different forms of $X^\cdot$ are possible?

A 1  B 2  C 3  D 4

22 A compound has the following structure.

Which of the following is obtained when alcoholic sodium ethoxide is added to this compound?

A  

B  

C  

D
23 Use of the Data Booklet is relevant to this question.

2.76 g of ethanol were mixed with an excess of aqueous acidified potassium dichromate(VI). The reaction mixture was then boiled under reflux for one hour. The organic product was then collected by distillation.

The yield of product was 75.0 %.

What mass of product was collected?
A 1.98 g  B 2.07 g  C 2.70 g  D 4.80 g

24 The ‘Grignard Reaction’ is the addition of an organomagnesium halide, R–MgX (Grignard reagent) to a carbonyl compound to form an alcohol. For example, the reaction with methanal leads to the formation of a primary alcohol as shown.

\[
\text{H_2C=O} \xrightarrow{1. \text{CH}_3\text{MgBr}} \text{CH}_3\text{OH} \xrightarrow{2. \text{H}_2\text{O}} \text{H}_2\text{C(OH)CH}_3
\]

Which of the following pairs of reagents could be used to produce \( \text{H}_2\text{C(OH)CH}_3 \)?
A  \( \text{H}_2\text{C}=\text{O} \) and \( \text{CH}_3\text{MgBr} \)
B  \( \text{H}_2\text{C}=\text{O} \) and \( \text{CH}_3\text{MgBr} \)
C  \( \text{H}_2\text{C}=\text{O} \) and \( \text{CH}_3\text{MgBr} \)
D  \( \text{H}_2\text{C}=\text{O} \) and \( \text{CH}_3\text{MgBr} \)

25 Which of the following, in aqueous solutions of equal concentration, is arranged in order of decreasing pH value?
A  \( \text{CH}_3\text{CH}_2\text{OH}, \text{C}_6\text{H}_5\text{OH}, \text{CH}_3\text{CO}_2\text{H}, \text{C}/\text{CH}_2\text{CO}_2\text{H}, \text{CH}_3\text{CO}/ \)
B  \( \text{CH}_3\text{CH}_2\text{OH}, \text{C}_6\text{H}_5\text{OH}, \text{C}/\text{CH}_2\text{CO}_2\text{H}, \text{CH}_3\text{CO}_2\text{H}, \text{CH}_3\text{CO}/ \)
C  \( \text{CH}_3\text{CO}/, \text{C}/\text{CH}_2\text{CO}_2\text{H}, \text{CH}_3\text{CO}_2\text{H}, \text{C}_6\text{H}_5\text{OH}, \text{CH}_3\text{CH}_2\text{OH} \)
D  \( \text{CH}_3\text{CO}/, \text{CH}_3\text{CH}_2\text{OH}, \text{C}_6\text{H}_5\text{OH}, \text{CH}_3\text{CO}_2\text{H}, \text{C}/\text{CH}_2\text{CO}_2\text{H} \)
26 Two isomers, L and M, C₆H₁₂O, react with alkaline aqueous iodine to form a yellow precipitate. However, unlike L, M can also react with both PCl₅ and ethanoyl chloride. M undergoes oxidation to form two compounds, both of which also form a yellow precipitate with alkaline aqueous iodine.

Which combination could L and M be?

A \((\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_3\) \(\text{CH}_2\text{CH}={\text{CH}}(\text{OH})(\text{CH}_3)_2\)

B \(\text{CH}_3\text{COCH}((\text{CH}_3)_2\text{CH}_3\) \(\text{CH}_3\text{CH}={\text{C}}(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}_3\)

C \(\text{CH}_3\text{COCH}_2\text{CH}((\text{CH}_3)_2\) \((\text{CH}_3)_2\text{C}={\text{CH}}(\text{OH})\text{CH}_3\)

D \((\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_3\) \((\text{CH}_3)_2\text{C}={\text{C}}(\text{CH}_3)_2\text{CH}_2\text{OH}\)

27 The reaction scheme below outlines the production of 3–amino–2–methylbutylamine from compound J.

\(\text{J} \xrightarrow{\text{alcoholic NaCN}} \text{K} \xrightarrow{\text{H}_2(g), \text{Ni catalyst}} \text{3-amino-2-methylbutylamine}\)

Which compound could J be?

A \((\text{CH}_3)_2\text{C(Br)CHBrCH}_3\)

B \(\text{CH}_3\text{CH(Br)CHBrCH}_3\)

C \(\text{CH}_3\text{CH(NH}_2\text{)C(CH}_3)_2\text{Br}\)

D \(\text{CH}_3\text{CH(NH}_2\text{)CHBrCH}_3\)

28 The reaction conditions for four different transformations are given below.

Which transformation has a set of conditions that is not correct?

A \(\text{CF}_3\text{CH}_2\text{Cl} + \text{Br}_2 \xrightarrow{\text{uv light}} \text{CF}_3\text{CHBrCl} + \text{HBr}\)

B \(\text{CH}_2=\text{CHCH}≡\text{CH}_2 + 11[\text{O}] \xrightarrow{\text{heat}} 4\text{CO}_2 + 3\text{H}_2\text{O}\)

C \(\text{CH}_3 + \text{HNO}_3 \xrightarrow{\text{heat}} \text{CH}_3\text{NO}_2\)

D \(\text{Cl} / \text{CHCl}_2 + 2\text{OH}^- \xrightarrow{\text{heat}} \text{Cl} / \text{C}^\circ\text{H}_4\text{CHO} + 2\text{Cl}^- + \text{H}_2\text{O}\)
Cannabinoids are active chemicals in the Cannabis plant that cause drug–like effects throughout the body including the central nervous system and the immune system.

*Nabilone*, a synthetic cannabinoid, has therapeutic use as adjunct analgesic for neuropathic pain while *Cannabidiol*, a naturally occurring cannabinoid in the plant, is effective as a typical antipsychotics in treating schizophrenia.

Which reagent would not react with either of these two cannabinoids?

A. An aqueous solution of ammoniacal silver nitrate
B. Alkaline potassium manganate(VII) solution
C. 2,4-dinitrophenylhydrazine
D. Aqueous bromine
30 Penicillin is widely used to kill bacteria. The general structure of a penicillin molecule is given below.

\[
\begin{align*}
\text{R} & \quad \text{O} \\
\text{R} & \quad \text{N} \\
\text{R} & \quad \text{H} \\
\text{R} & \quad \text{C} \quad \text{N} \\
\text{R} & \quad \text{O} \\
\end{align*}
\]

\[\text{CO}_2 \text{H} \quad \text{R} = \text{an aryl group}\]

What is produced when penicillin is boiled with excess aqueous sodium hydroxide?

A

B

C

D

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{Na}^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{Na}^+ & \quad \text{O}_2 \text{C} \\
\text{H}_2 \text{N} & \quad \text{HN} \\
\text{S} & \quad \text{CO}_2 \text{Na}^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{Na}^+ & \quad \text{O}_2 \text{C} \\
\text{H}_2 \text{N} & \quad \text{HN} \\
\text{S} & \quad \text{CO}_2 \text{Na}^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{O} & \quad \text{Na}^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{R} \\
\text{O} & \quad \text{Na}^+ \\
\end{align*}
\]
Section B

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

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

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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 Sodium hydrogensulfide, NaSH, is used to remove hair from animal hides.

Which statements about the SH– ion are correct?

1. It contains 18 electrons.
2. 3 lone pairs of electrons surround the sulfur atom.
3. Sulfur has an oxidation state of +2.

32 Which physical properties are due to hydrogen bonding between molecules?

1. Water has a higher boiling point than H₂S.
2. Ice floats on water.
3. The H–O–H bond angle in water is approximately 104°.

33 Use of the Data Booklet is relevant to this question.

An electrochemical cell is set up using a Fe²⁺(aq)|Fe(s) half–cell and a VO₂⁺(aq),VO₂⁺(aq)|Pt(s) half–cell.

Which of the following gives a correct effect on the $E^{\circ}$ cell and a correct explanation for the effect when each of the changes is made to the cell separately?

<table>
<thead>
<tr>
<th>Change</th>
<th>Effect on $E^{\circ}_{\text{cell}}$</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Add KCN(aq) to the Fe²⁺(aq)</td>
<td>Fe(s) half–cell</td>
</tr>
<tr>
<td>2</td>
<td>Add water to the VO₂⁺(aq),VO₂⁺(aq)</td>
<td>Pt(s) half–cell</td>
</tr>
<tr>
<td>3</td>
<td>Increase temperature of the Fe²⁺(aq)</td>
<td>Fe(s) half–cell</td>
</tr>
</tbody>
</table>
34 Which of the following processes will result in an increase in entropy?

1. The sublimation of solid carbon dioxide.
2. The decomposition of dinitrogen tetraoxide.
3. The formation of calcium carbonate from calcium oxide and carbon dioxide.

35 X, Y and Z are elements in the same period of the Periodic Table. The oxide of X is amphoteric, the oxide of Y is basic and the oxide of Z is acidic.

What is the correct order of trend for these elements?

1. Proton number: Y < X < Z
2. Atomic radius: Z < X < Y
3. Melting point: X < Z < Y

36 A student observed the reactions when sodium chloride and sodium iodide were each reacted separately with concentrated sulfuric acid and concentrated phosphoric acid. The observations were recorded in the table.

<table>
<thead>
<tr>
<th></th>
<th>Sodium chloride</th>
<th>Sodium iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>conc. H₂SO₄</td>
<td>steamy fumes</td>
<td>purple fumes</td>
</tr>
<tr>
<td>conc. H₃PO₄</td>
<td>steamy fumes</td>
<td>steamy fumes</td>
</tr>
</tbody>
</table>

Which of the following deductions can be made from these observations?

1. Concentrated sulfuric acid is a stronger oxidising agent than iodine.
2. Concentrated sulfuric acid is a weaker oxidising agent than chlorine.
3. Concentrated phosphoric acid is a stronger oxidising agent than concentrated sulfuric acid.

37 Which of the following reactions will form a product that rotates plane–polarised light?

1. \[
\begin{align*}
\text{CH₃} & \text{CH} \text{CH₂Br} \\
\text{heated under reflux with aqueous KOH}
\end{align*}
\]

2. \[
\begin{align*}
\text{CH₃} & \text{CH₃} \\
\text{CH₃} & \text{C} \text{CH₃} \\
\text{with cold alkaline KMnO₄(aq)}
\end{align*}
\]

3. \[
\text{CH₃COCH₃ with HCN in trace amounts of a base at 10 °C.}
\]
38 The following route shows the acid–catalysed reaction of an alkene with hydrogen azide, HN₃, to form an imine.

Which of the following types of reaction occur in the synthesis of imine?

1. Elimination
2. Electrophilic addition
3. Nucleophilic substitution

39 Milk, red meat, liver and egg white are sources of Vitamin B₂.

Which of the following statements about Vitamin B₂ are incorrect?

1. It is soluble in water.
2. 1 mol of Vitamin B₂ reacts with excess metallic sodium to produce 4 mol of hydrogen gas.
3. A yellow precipitate is formed when acidified 2,4-DNPH is added to Vitamin B₂.
The diagram below shows two segments of a protein molecule.

Which of the following, when added to the protein, will cause the interactions which exist between the two segments to be broken?

1. hot water
2. 0.100 mol dm$^{-3}$ sodium hydroxide
3. 0.100 mol dm$^{-3}$ lead(II) nitrate
<table>
<thead>
<tr>
<th>Question Number</th>
<th>Key</th>
<th>Question Number</th>
<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>21</td>
<td>C</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>22</td>
<td>C</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>23</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>24</td>
<td>D</td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>25</td>
<td>A</td>
</tr>
<tr>
<td>6</td>
<td>D</td>
<td>26</td>
<td>C</td>
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<tr>
<td>7</td>
<td>B</td>
<td>27</td>
<td>D</td>
</tr>
<tr>
<td>8</td>
<td>D</td>
<td>28</td>
<td>C</td>
</tr>
<tr>
<td>9</td>
<td>D</td>
<td>29</td>
<td>A</td>
</tr>
<tr>
<td>10</td>
<td>A</td>
<td>30</td>
<td>B</td>
</tr>
<tr>
<td>11</td>
<td>A</td>
<td>31</td>
<td>B</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>32</td>
<td>B</td>
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<td>13</td>
<td>C</td>
<td>33</td>
<td>D</td>
</tr>
<tr>
<td>14</td>
<td>D</td>
<td>34</td>
<td>B</td>
</tr>
<tr>
<td>15</td>
<td>C</td>
<td>35</td>
<td>B</td>
</tr>
<tr>
<td>16</td>
<td>B</td>
<td>36</td>
<td>B</td>
</tr>
<tr>
<td>17</td>
<td>A</td>
<td>37</td>
<td>D</td>
</tr>
<tr>
<td>18</td>
<td>B</td>
<td>38</td>
<td>B</td>
</tr>
<tr>
<td>19</td>
<td>D</td>
<td>39</td>
<td>A</td>
</tr>
<tr>
<td>20</td>
<td>C</td>
<td>40</td>
<td>A</td>
</tr>
</tbody>
</table>
ANDERSON JUNIOR COLLEGE

Preliminary Examinations 2012

CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs or rough working.
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 brackets [ ] at the end of each question or part question.

For Examiner’s Use

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>

This document consists of 20 printed pages.
1 Planning (P)

Suppose you are given a solution containing Zn$^{2+}$, Al$^{3+}$, Cl$^-$ and I$^-$ ions.

You are also provided with the following:

- NaOH(aq),
- NH$_3$(aq),
- HNO$_3$(aq),
- HCl(aq),
- AgNO$_3$(aq) and
- distilled water

(a) (i) Name the reagent, from the list provided, that can be used to convert both the Cl$^-$ and I$^-$ ions to precipitates.

(ii) Name another reagent, from the list provided, that can be used to dissolve one of the precipitates formed in (a)(i).

(b) Using the reagents you have identified in (a), you are to devise a sequence of steps, by which the halides in the mixture could be separated such that each halide is present in a separate precipitate.

In your plan, you need to include details on the reagents you will use, expected observations and state the location of each anion (i.e. in a solution or precipitate) after each step. You may present your answer in the form of a table or flow chart.
(c) A small amount of dilute nitric acid is usually added before the addition of the reagent you have chosen in (a)(i).

Suggest a reason why this is done.

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

(d) One of the cations present in the above mixture, Zn^{2+} or Al^{3+}, can be removed as a precipitate, on reaction with excess of either NaOH(aq) or NH_{3}(aq).

Identify the reagent to be added in excess and which cation, Zn^{2+} or Al^{3+}, can be removed as a precipitate. Explain your answer using relevant equations.

Reagent to be added in excess .................................................................................................................................

Cation precipitated ..................................................................................................................................................

Explanation..............................................................................................................................................................

........................................................................................................................................................................[2]

You are provided with 3 unlabeled bottles each containing one of the following organic halogen derivatives.

- bromobenzene, C_{6}H_{5}Br
- (bromomethyl)benzene, C_{6}H_{5}CH_{2}Br
- ethanoyl bromide, CH_{3}COBr

You are also provided with the following:

- NaOH(aq),
- NH_{3}(aq),
- HNO_{3}(aq),
- HCl(aq),
- AgNO_{3}(aq) and
- distilled water

- test tubes,
- filter funnel,
- filter paper and
- Bunsen burner

(e) Outline a logical sequence of chemical tests that would enable you to identify each of the compounds.

You need to describe in a clear, stepwise manner, the tests used to identify each compound.

For each test, you need to include

- details on the reagents and conditions you will use,
- their quantities and
- the expected observations for each compound tested in that particular step.

You may present your answer in the form of a table or flow chart.
2 (a) (i) The value of \( pV \) is plotted against \( p \) for the following three gases, where \( p \) is the pressure and \( V \) is the volume of the gas.

- 1 mol \( \text{CO}_2 \) at 298 K
- 1 mol \( \text{CO}_2 \) at 473 K
- 1 mol \( \text{SO}_2 \) at 298 K

Given that graph A represents the graph for 1 mol of \( \text{CO}_2 \) at 298 K, identify and explain what graphs B and C represent.

Graph B: ……………………………..  
Graph C: ……………………………..
The van der Waals’ equation as shown below is often used to account for the discrepancies between experimental and theoretical behaviour of real gases.

\[(p + \frac{n^2a}{V^2})(V - nb) = nRT\]

\(p\) is the pressure, \(V\) the volume, \(T\) the temperature, \(n\) the amount of substance (in mol), and \(R\) the gas constant. The van der Waals’ constants \(a\) and \(b\) are characteristic of the substance and are independent of temperature.

(ii) Given that the van der Waals’ constants \(a\) and \(b\) for \(SO_2\) is 0.687 Pa m\(^6\) mol\(^{-2}\) and 5.68 x 10\(^{-5}\) m\(^3\) mol\(^{-1}\) respectively, calculate the actual pressure exerted by 1 mol of \(SO_2\) in a 0.5 dm\(^3\) container at 25 °C.

(iii) Calculate the pressure exerted by \(SO_2\) as described in (a)(ii) if it obeys the ideal gas law.

(iv) Suggest a reason for the discrepancy in the pressures obtained in (a)(ii) and (a)(iii).
(b) A wide range of sulfur oxoanions exist and many of them are widely used in laboratory synthesis. Four of such oxoanions have two sulfur (S) atoms. The average oxidation number of S and number of oxygen in the anions are shown in the table below.

<table>
<thead>
<tr>
<th>oxoanion</th>
<th>average oxidation number of S</th>
<th>number of oxygen atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>+2</td>
<td>3</td>
</tr>
<tr>
<td>E</td>
<td>+3</td>
<td>4</td>
</tr>
<tr>
<td>F</td>
<td>x</td>
<td>6</td>
</tr>
<tr>
<td>G</td>
<td>+6</td>
<td>y</td>
</tr>
</tbody>
</table>

All four sulfur oxoanions have a negative charge of 2–.

Only D has one central atom.

In D, E and F only,
- the sulfur atoms are bonded directly to each other and
- no oxygen atom is attached to another oxygen atom.

(i) Suggest a value for \( x \) and \( y \) in the table.

Value of \( x \): ......................  Value of \( y \): ......................

(ii) Suggest the structural formulae of D and E.

(iii) Using VSEPR theory, suggest the shape of oxoanion E with respect to each S atom.
(iv) Oxoanion $G$ is a powerful oxidising agent.

\[ G + 2e^- \rightarrow 2SO_4^{2-} \quad E^o = +2.01 \text{ V} \]

Using the above data and information given in the question, draw the dot-and-cross diagram of oxoanion $G$.

---

(c) Thionyl halides such as $\text{SOCl}_2$ are commonly used in the halogenation of organic compounds. The reaction also results in the production of hydrogen halide vapour.

The following sketch shows the trend of vapour pressure exerted by the different thionyl halides at a given temperature.

(i) Explain the above trend in terms of structure of, and bonding in, each of these thionyl halides.
(ii) The mark ‘X’ indicates the vapour pressure exerted by hydrogen fluoride at a given temperature.

On the same axes, indicate the expected vapour pressure exerted by each of the other two hydrogen halides at the same temperature.

(iii) Explain why the vapour pressure exerted by hydrogen fluoride is lower than that exerted by thionyl fluoride at the given temperature.

[Total: 16]
In a typical laboratory, gas phase reactions are difficult to control and hence not common. Industrial production utilising gas phase reactions are similarly difficult to control and typically only used for manufacture of organic chemicals, sulfuric acid (Contact process) or ammonia (Haber process).

The Contact process used to produce sulfuric acid involves a three-stage process. Using V$_2$O$_5$ as a catalyst, reaction II achieves 99.5% conversion of sulfur dioxide to sulfur trioxide. The essential reactions are as follows:

I: \[ \text{S(g)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \quad \Delta H = -308 \text{ kJ mol}^{-1} \]

II: \[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H = -192 \text{ kJ mol}^{-1} \]

III: \[ \text{SO}_3(g) + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4(l) \quad \Delta H = -130 \text{ kJ mol}^{-1} \]

(a) (i) Write an expression each for $K_c$ and $K_p$ of reaction II.

Hence show that $K_p = K_c \left(\frac{1}{RT}\right)$. 
The following graph shows how the concentration of SO₃ varies with time in reaction II.

(ii) A change in condition was introduced to the reaction mixture at t₁ such that the concentration of SO₃ increases at a different rate after t₁. The dotted line in the graph above illustrates how the concentration of SO₃ would vary with time if no change in condition was introduced at t₁.

Suggest what this change could be and explain your answer.

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

(iii) The equilibrium mixture at t₂ was suddenly heated to a higher temperature.

Sketch on the graph above to show how the concentration of SO₃ would change from t₂ till equilibrium is reached.

(iv) Suggest and explain whether reaction II should be conducted at high or low pressure.

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

[6]
(b) Using the *Data Booklet*, calculate the average bond energy of the S=O bond in reaction II.
4 (a) Aspartic acid is a non-essential amino acid that can be synthesised by the human body. It plays a vital role in the construction of other amino acids and biochemicals in the citric acid cycle. It is also needed for stamina and assists the liver by removing excess ammonia and other toxins from the bloodstream.

\[
\text{HO}_2\text{C} - \text{CO}_2\text{H} \\
\text{NH}_2
\]

**aspartic acid**

The three \(pK_a\) values associated with aspartic acid are given in the following table.

<table>
<thead>
<tr>
<th></th>
<th>(pK_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-carboxyl</td>
<td>1.88</td>
</tr>
<tr>
<td>(R) group</td>
<td>3.65</td>
</tr>
<tr>
<td>(\alpha)-amino</td>
<td>9.60</td>
</tr>
</tbody>
</table>

(i) Using the protonated form of aspartic acid, suggest a reason why the \(pK_a\) value of the \(R\) group of aspartic acid is higher than that of the \(\alpha\)-carboxyl group.

(ii) Sketch the pH–volume added curve you would expect to obtain when 30 cm\(^3\) of NaOH is added to 10 cm\(^3\) of the protonated form of aspartic acid of the same concentration. Show clearly on your curve where the three \(pK_a\) values occur.
(iii) Explain what is meant by the term *isoelectric point* of an amino acid. Hence suggest the structure of aspartic acid at its isoelectric point.

Indicate clearly the isoelectric point of aspartic acid on your curve obtained in (a)(ii) with an "X".

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

Structure of aspartic acid at isoelectric point

(iv) With the aid of an equation, explain how aspartic acid can maintain the pH of a solution at pH 3.65 on the addition of a small amount of H⁺(aq). Show clearly the structure of aspartic acid in your equation.

Equation:

..............................................................................................................................................
..............................................................................................................................................
(v) Using your answers to (ii) and (iv), calculate the change in pH when 50.0 cm\(^3\) of 0.0200 mol dm\(^{-3}\) HCl(aq) is added to 100.0 cm\(^3\) solution of 0.100 mol dm\(^{-3}\) aspartic acid at pH 3.65.

You may represent the acid as HA and the conjugate base as A\(^-\) in your working.
(b) (i) Describe the reagents and conditions needed to hydrolyse a protein in the laboratory to form a mixture of its constituent amino acids.

(ii) A polypeptide H was analysed and found to contain the following amino acids.

<table>
<thead>
<tr>
<th>amino acid</th>
<th>abbreviation</th>
<th>number of residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>aspartic acid</td>
<td>Asp</td>
<td>1</td>
</tr>
<tr>
<td>glycine</td>
<td>Gly</td>
<td>1</td>
</tr>
<tr>
<td>serine</td>
<td>Ser</td>
<td>2</td>
</tr>
<tr>
<td>tyrosine</td>
<td>Tyr</td>
<td>1</td>
</tr>
<tr>
<td>valine</td>
<td>Val</td>
<td>1</td>
</tr>
</tbody>
</table>

Analysis gave the following results:
- The N–terminal was shown to be ser.
- On reaction with the enzyme chymotrypsin, which hydrolyses at the carboxylic acid end of tyr, H gave two tripeptides.
- On reaction with a special reagent which digests at the carboxylic acid end of val, H gave two peptides. One of these two was a dipeptide of sequence gly–ser.

Use the above information to determine the amino acid sequence of polypeptide H. Justify your answer.
[You should use the same 3–letter abbreviations as shown above to write out the amino acid sequence.]
5 (a) Compound J, is a non-narcotic analgesic commonly sold in pharmacy. Refluxing J in the presence of dilute sulfuric acid produces K and ethanoic acid.

Table 1 and Table 2 below show results of the analysis of compound K.

<table>
<thead>
<tr>
<th>Elemental Analysis (%)</th>
<th>Melting point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>60.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reagent</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Excess aqueous Br₂</td>
<td>White solid, L formed which has $M_r = 295.8$.</td>
</tr>
<tr>
<td>2</td>
<td>Aqueous Na₂CO₃</td>
<td>Effervescence of gas.</td>
</tr>
<tr>
<td>3</td>
<td>Excess Na metal</td>
<td>About 174 cm³ of a colourless gas is evolved when 1 g of K is used at room temperature.</td>
</tr>
</tbody>
</table>

(i) When vaporised in a suitable apparatus, 0.12 g of K occupies a volume of 37.5 cm³ at 250 °C and a pressure of 101 kPa. Calculate the molar mass of K.

Molar mass of K: ........................................

(ii) Hence using your answer in (a)(i) and Table 1, deduce the molecular formula of K.

Molecular formula of K: ........................................

(iii) Name the functional group that reaction 1 shows to be present in K.

(iv) Name the functional group present in K that is confirmed by reaction 2.
(v) Use your answers to (a)(ii) – (a)(iv) to account for the result in reaction 3.

(vi) State the molecular formula of L in reaction 1.

Molecular formula of L:…………………………..

(vi) Hence suggest two possible structural formulae of K. Draw the displayed formulae of your compounds in the boxes below.

![Compound 1](image1.png) ![Compound 2](image2.png)

(vii) Given that one of the compounds in (a)(vi) has a melting point of 214 °C, state the identity of K and explain your choice.

K is compound ………

Explanation: ………………………………………………………………………………………………

(viii) Hence deduce the structure of compound J.

![Structure of J](image3.png)
(b) Glycolic acid, HOCH$_2$CO$_2$H, is a colourless, odourless and hygroscopic crystalline solid that is highly soluble in water. It is commonly used in various skin-care products. It can be prepared from ethanedial by the Cannizzaro reaction, discovered in 1853.

When ethanedial, CHOCHO is reacted with aqueous NaOH and the product treated with dilute sulfuric acid, the following reaction sequence in the Cannizzaro reaction takes place.

**Stage I**  
CHOCHO + NaOH $\rightarrow$ HOCH$_2$CO$_2$Na

**Stage II**  
HOCH$_2$CO$_2$Na + H$^+$ $\rightarrow$ HOCH$_2$CO$_2$H + Na$^+$

(i) What is unusual about the overall reaction?

(ii) The following shows part of the mechanism in stage I where hydroxide ion attacks ethanedial in an aqueous medium.

Using the intermediates given above, propose a further 3–step mechanism to form HOCH$_2$CO$_2$Na.

In your answer, show relevant charges, lone pairs of electrons and movement of electrons.

(iii) What is the role of the H$^-$ produced in (b)(ii)?
(iv) When a similar experiment is carried out using benzaldehyde as the starting material, two organic products are obtained.

\[
\text{CHO} \\
\text{benzaldehyde}
\]

Write the structural formulae of the two products and state the ratio in which they might be produced.

<table>
<thead>
<tr>
<th>Structure of product</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ratio of products</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[Total: 20]
1 (a) (i) AgNO$_3$(aq)  
(ii) NH$_3$(aq)  

(b)  

<table>
<thead>
<tr>
<th>Step</th>
<th>Expected Observations</th>
<th>Location of each anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Add excess AgNO$_3$(aq). Filter the mixture.</td>
<td>Yellow ppt</td>
<td>Cl$^-$ and I$^-$ exists as AgX in the ppt</td>
</tr>
<tr>
<td>2. Add excess NH$_3$(aq) to the residue. Filter the mixture.</td>
<td>Yellow residue Colourless filtrate</td>
<td>I$^-$ exists as AgI in residue Cl$^-$ remains in filtrate</td>
</tr>
<tr>
<td>3. Add HNO$_3$(aq) to the filtrate.</td>
<td>White ppt</td>
<td>Cl$^-$ exists as AgCl in the ppt</td>
</tr>
</tbody>
</table>

Filter the mixture after adding excess AgNO$_3$(aq) and after adding excess NH$_3$ to the residue.

Correct identification of ions:

Yellow ppt with AgNO$_3$ in step 1. White ppt negates the mark. (Note: white ppt is obscured by the yellow ppt.)

Yellow residue and colourless filtrate in step 2.

White ppt with acid in step 3.

FYI

The mixture has to be filtered after adding AgNO$_3$ to separate AgCl and AgI from the cations so that insoluble metal hydroxides would not be formed when NH$_3$(aq) is added.

(c) To remove other anions (e.g. CO$_3^{2-}$ and SO$_3^{2-}$) that form insoluble compound with Ag$^+(aq)$. (All nitrates are soluble).

(d) Reagent: NH$_3$(aq) and cation: A/$_{3}^{3+}$

Al(OH)$_3$ is insoluble while Zn(OH)$_2$ is soluble in excess NH$_3$(aq) due to complex formation.

\[
\text{A/}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3(s) \\
\text{Zn(OH)}_2 + 4\text{NH}_3 \rightarrow [\text{Zn(NH}_3)_4]^{2+}(aq) + 2\text{OH}^-
\]

[allow 2 separate equations showing dissolving of Zn(OH)$_2$]

\[
\text{Zn(OH)}_2 \rightleftharpoons \text{Zn}^{2+} + 2\text{OH}^- \\
[\text{Zn(H}_2\text{O)}_6]^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Zn(NH}_3)_4]^{2+} + 6\text{H}_2\text{O}
\]
(e) Step 1: To 2 cm depth of each of the unknown in a test tube, add a few drops of AgNO₃(aq). (allow distilled water – gives white fumes)

<table>
<thead>
<tr>
<th>C₆H₅Br</th>
<th>C₆H₅CH₂Br</th>
<th>CH₃COBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ppt</td>
<td>No ppt</td>
<td>Cream ppt</td>
</tr>
</tbody>
</table>

Step 2: To fresh samples of 2 cm depth each of the other 2 compounds in a test tube, add NaOH(aq) and heat gently for 5 minutes.

Step 3: To the cooled samples of each of the remaining 2 compounds in a test tube, add excess HNO₃(aq), followed by AgNO₃(aq).

<table>
<thead>
<tr>
<th>C₆H₅Br</th>
<th>C₆H₅CH₂Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ppt</td>
<td>Cream ppt</td>
</tr>
</tbody>
</table>

Appropriate reagents: AgNO₃(aq), NaOH(aq), HNO₃(aq)
Appropriate conditions: heat (not reflux, warm), (cool), excess
Quantities mentioned in all 3 steps: 2 cm depth / 1 – 5 cm³, (a few drops)
Correct observations in steps 1 and 3

Alternatives:
Add distilled water or dil HCl. Only ethanoyl bromide gives white fumes.
Add aqueous silver nitrate and heat. Only ethanoyl bromide and (bromomethyl)benzene give cream ppt.
2 (a) (i) Graph B is CO$_2$ at 473 K whilst graph C is SO$_2$ at 298 K. SO$_2$ deviates more than CO$_2$ at 298 K. SO$_2$ molecules are held by stronger permanent dipole–permanent dipole attractions (or van der Waals forces of attraction) as compared to weaker instantaneous dipole–induced dipole attractions (or van der Waals forces of attraction) between CO$_2$ molecules.

CO$_2$ at 473 K deviates less than CO$_2$ at 298 K. At higher temperature, CO$_2$ molecules possess higher average kinetic energy and are more able to overcome forces of attraction between the molecules.

(ii) 
\[ p = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} \]
\[ = \frac{(1)(8.31)(298)}{(0.5\times10^{-3} - 5.68\times10^{-3})} - \frac{(1)^2(0.687)}{(0.5\times10^{-3})^2} \]
\[ = 5.588 \times 10^6 - 2.748 \times 10^6 \]
\[ = 2.84 \times 10^6 \text{ Pa} \]

(iii) Using the ideal gas equation,
\[ p = \frac{nRT}{V} \]
\[ = \frac{(1)(8.31)(298)}{(0.5\times10^{-3})} \]
\[ = 4.95 \times 10^6 \text{ Pa} \]

(iv) The actual pressure exerted is much lower than the pressure calculated from the ideal gas equation as forces of attraction between SO$_2$ molecules are not negligible.

(b) (i) $x$: +5; $y$: 8

(ii) 
\[ [\text{S} \quad \text{O} \quad \text{S} \quad \text{O}]^{2-} \quad [\text{O} \quad \text{O} \quad \text{S} \quad \text{S}]^{2-} \]

D

E

(iii) Trigonal pyramidal w.r.t. to each S atom.

(iv) 
\[ [\text{S} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{O}]^{2-} \]
(c) (i) Thionyl halides exist as simple covalent molecules held together by van der Waals’ forces of attractions. Across the series from SOF$_2$ to SOBr$_2$, as the no. of electrons / size of the electron cloud increases, the strength of van der Waals’ forces of attractions (id–id) between the molecules also increases.

As the boiling point increases, the vapour pressure decreases.

(ii) vapour pressure

![Graph showing the relationship between electron cloud size and vapour pressure]

2 points must be above SOC$_2$ and SOBr$_2$
2 points must be above HF

(iii) HF molecules are held together by stronger hydrogen bonds. Thus, the vapour pressure of HF is lower than that of SOF$_2$. 
### 3 (a) (i)

\[
K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \\
K_p = \frac{(p_{\text{SO}_3})^2}{(p_{\text{SO}_2})^2(p_{\text{O}_2})}
\]

Using \(pV = nRT\)

\[
\rho = \frac{n}{V}RT = cRT
\]

\[
K_p = \frac{([\text{SO}_3]RT)^2}{([\text{SO}_2]RT)^2([\text{O}_2]RT)}
\]

\[
= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]RT}
\]

\[
= \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \left( \frac{1}{RT} \right)
\]

\[
= K_c \left( \frac{1}{RT} \right) \quad \text{(shown)}
\]

(ii) The equilibrium \([\text{SO}_3]\) does not change but equilibrium is reached faster. Hence the effect is due to the addition of a catalyst at \(t_1\).

(iii) A higher temperature will favour the reverse endothermic reaction. Hence the position of equilibrium will shift to the left. The equilibrium concentration of \(\text{SO}_3\) will thus be lower.
(iv) The reaction should be conducted at a **high pressure**.

The forward reaction results in a decrease in the number of moles of gaseous molecules. Hence the **position of equilibrium will shift to the right** to decrease pressure by producing fewer gas molecules. Thus, increasing the yield of SO$_3$ produced.

(b) SO$_2$ has 2 S=O bonds and SO$_3$ has 3 S=O bonds.

From reaction II:

\[
4S=O + O=O \rightarrow 6S=O
\]

Let $x$ be the bond energy of S=O

\[
(4x + (+496)) - 6x = -192
\]

\[
-2x = -192 - 496
\]

\[
x = 344 \text{ kJ mol}^{-1}
\]

4 (a) (i) \[
\text{HO}_2\text{C}^\alpha \text{CO}_2^- \quad \text{NH}_3^+ \\
\]

$\alpha$–NH$_3^+$ group is electron–withdrawing.

$\alpha$–CO$_2^-$ group being closer/nearer to the $\alpha$–NH$_3^+$ group is more stabilised as the negative charge is dispersed to a greater extent.

(ii)

<table>
<thead>
<tr>
<th>pH</th>
<th>Volume of NaOH added / cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.88</td>
<td>5</td>
</tr>
<tr>
<td>3.65</td>
<td>10</td>
</tr>
<tr>
<td>9.60</td>
<td>25</td>
</tr>
</tbody>
</table>

- correct shape
- correctly labeled 3 pH values (that correspond to the 3 pK$_a$ values)
- correctly labeled equivalence volumes & volumes at MBC

(iii) Isoelectric point is the pH at which the amino acid carries no net charge.

*Accept pH at which the amino acid exists as zwitterionic form.*
Isoelectric point correctly indicated (with an “X”) on curve.

(iv)

\[
\begin{array}{c}
\text{HO}_2\text{C} \quad \text{CO}_2^- \\
\uparrow \\
\text{NH}_3 \\
\end{array} + \quad \text{H}^+ \\
\begin{array}{c}
\text{HO}_2\text{C} \\
\downarrow \\
\text{CO}_2^- \\
\text{NH}_3 \\
\end{array}
\]

The (conjugate) base reacts with the added H\(^+\) thus maintaining the pH of the solution.

(v)

\[n_{(\text{aspartic acid})\ \text{present}} = 0.100 \times 100/1000 = 0.01 \text{ mol}\]

At pH = 3.65 (\(= \text{p}K_a\) of R–group)

\[\left[\text{HA}\right] = \left[\text{A}^-\right]\]

\[n_{\text{HA}} = n_{\text{A}^-} = 0.01/2 = 0.005 \text{ mol}\]

\[n_{\text{H}^+,\ \text{added}} = 0.0200 \times 50/1000 = 0.001 \text{ mol}\]

\[\text{A}^- + \text{H}^+ \rightarrow \text{HA}\]

\[n_{\text{HA}}\ \text{present after \text{HCl} is added} = 0.005 + 0.001 = 0.006 \text{ mol}\]

\[n_{\text{A}^-\ \text{present after \text{HCl} is added}} = 0.005 - 0.001 = 0.004 \text{ mol}\]

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

\[10^{-3.65} = \frac{[\text{H}^+](0.004)}{0.150}\]

\[[\text{H}^+] = 3.358 \times 10^{-4} \text{ mol dm}^{-3}\]

\[\text{pH} = 3.474\]

Change in pH = 3.474 – 3.65 = –0.176

(b) (i)

\text{aq NaOH or dilute HCl / H}_2\text{SO}_4\]

heat under reflux for a prolonged period / several hours

- correct sequence with 6 a.a. residues

Justification of answer:

```
N–terminal
gene

enzyme ⇒ 2 tripeptides obtained:
ser–asp–tyr & val–gly–ser

special reagent ⇒ 2 peptides obtained; one of these is a dipeptide gly–ser
```

- Any 2 points

```
For students:
1. special reagent digests at carboxylic end of val giving gly–ser ⇒ val–gly–ser
2. enzyme hydrolyses at carboxylic end of tyr ⇒ tyr–val–gly–ser
```
(a) (i) \[(101\ 000) \times (37.5 \times 10^{-6}) = (0.12/M) \times (8.31) \times (250+273)\]
Molar mass = 137.7 g mol\(^{-1}\)

\[M_r = 138\]

(ii) | Elemental Analysis (%) |
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>60.8</td>
</tr>
<tr>
<td>5.06</td>
</tr>
<tr>
<td>2.32</td>
</tr>
</tbody>
</table>

\[n(12 \times 2.32 + 2 + 16) = 137.7 \implies n = 3\]

\[C_7H_6O_3\]

(iii) Phenol

(iv) Carboxylic acid

(v) 1 mol of K contains 2 mol of –OH group, hence produces 1 mol H\(_2\) gas.

Volume of gas expected to produce from 1 g of K:
\[
\frac{1}{138} \times 24000 = 174 \text{ cm}^3
\]

(vi) L: C\(_7\)H\(_4\)O\(_3\)Br\(_2\)

Possible K:

\[
\begin{array}{c}
\text{COOH} \\
\text{OH}
\end{array}
\begin{array}{c}
\text{H} \\
\text{O}
\end{array}
\begin{array}{c}
\text{COOH} \\
\text{OH}
\end{array}
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

(vii) K can form intramolecular hydrogen bonding leading to less extensive intermolecular hydrogen bonding resulting in lower melting point.

(viii) K

(b) (i) Disproportionation has taken place.
(ii) \[ \text{H}^+ + \text{HO-} + \text{O-} \rightarrow \text{HO-C-OH} + \text{OH}^- \]

Curly arrows, charges and intermediate

\[ \text{HO-C-C-H} + \text{NaOH} \rightarrow \text{NaO-C-C-H} + \text{H}_2\text{O} \]

(iii) Nucleophile or reducing agent

(iv) \[
\begin{array}{c}
\text{COOH} \\
\text{CH}_2\text{OH}
\end{array}
\]

Ratio: 1:1
ANDERSON JUNIOR COLLEGE

Preliminary Examinations 2012

CHEMISTRY

Higher 2

Paper 3 Free Response Questions

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing paper
Graph paper

READ THESE INSTRUCTIONS FIRST

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

Answer any four questions.

Start each question on a fresh sheet of paper.

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

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

This document consists of 12 printed pages.
1 (a) Sodium dichromate(VI), Na$_2$Cr$_2$O$_7$, is used widely in organic synthesis as well as in the process of leather tanning. The principal ore of chromium called chromite, FeCr$_2$O$_4$, is used in the manufacture of sodium dichromate(VI) via a 2–stage process.

In the first stage of the process, the ore is fused with soda ash (sodium carbonate) and air at a temperature of 1000 °C. The following equation represents this stage.

$$4\text{FeCr}_2\text{O}_4 + a\text{Na}_2\text{CO}_3 + b\text{O}_2 \rightarrow c\text{Fe}_2\text{O}_3 + d\text{Na}_2\text{CrO}_4 + e\text{CO}_2$$

(i) Complete the balancing of the above equation by deducing the values for $a$, $b$, $c$, $d$ and $e$.

In the second stage, the products are extracted with hot water. Orange crystals of sodium dichromate(VI) separate out during the evaporation stage of the process.

(ii) Suggest a reagent that can be added to the hot water extract to produce the dichromate(VI) solution in the second stage of the process.

[2]

(b) Draw a fully labeled diagram to show how the standard electrode potential of the Cr$_2$O$_7^{2–}$(aq)/Cr$^{3+}$(aq) system could be measured by a standard hydrogen electrode. Show the direction of electron flow in the circuit.

[3]

(c) When zinc metal is added to an acidified solution of aqueous chromium(III) solution, the solution turns from green to blue. When the excess zinc is filtered off and the blue solution is left to stand for several hours in the absence of air, it slowly turned back to green and a colourless gas is evolved.

Explain these observations, quoting appropriate $E^o$ values from the Data Booklet.

[3]

(d) A chromium–containing ion, CrO$_x^{n–}$, disproportionates in acid solution to produce a mixture of chromium(III) ions and dichromate(VI) ions.

A solution containing 7.5 x 10$^{-3}$ mol of CrO$_x^{n–}$ ions was acidified and the disproportionation occurred. The resulting solution contained 2.5 x 10$^{-3}$ mol of dichromate(VI) ions.

Using the information given, calculate the oxidation number of chromium in the ion CrO$_x^{n–}$.

[2]
(e) Transition metals such as chromium, iron and zinc and their compounds have found wide applications in electrical energy–storage technology. New technologies involving the inventions of redox flow batteries and metal–air batteries have emerged in recent years.

Electrolytes containing chromium ions and iron ions are used in a redox flow battery called iron–chrome battery (ICB). Electricity is generated from the battery by the half–cell reactions of these electrolytes that flow into a cell. The two electrolytes in the cell are separated by an ion selective membrane. Inert electrodes with optimum power acceptance are used in this battery.

(i) Using the *Data Booklet*, select appropriate half–cell reactions of chromium ions and iron ions that would produce the largest standard cell potential in the ICB.

Write a balanced equation for the overall reaction that takes place when the battery discharges.

(ii) Explain the role of the ion selective membrane in the operation of the ICB.

An example of a metal–air battery is the zinc–air battery, commonly used as small button cells in watches and hearing aids. When a gas–permeable, liquid–tight membrane sealing tab in the button cell is removed, oxygen in the air is absorbed into an alkaline electrolyte. The positive electrode is made of porous carbon and the negative electrode consists of zinc. The electrolyte used is a paste containing potassium hydroxide.

(iii) A zinc–air button cell has a cell potential of 1.59 V.

Using relevant data from the *Data Booklet*, calculate the electrode potential for the reaction at the anode. Suggest an equation for the reaction that takes place at this electrode.

(iv) The zinc electrode of a new zinc–air button cell weighs 1.9 g. The cell can run until 80 % of the zinc is consumed.

Calculate the maximum amount of current that can be drawn from the cell if it is expected to last for 30 days.
(v) Considering the cell reactions in the two batteries described above, suggest the battery that would be expected to discharge electricity at a faster rate. Give a reason for your answer.

(vi) Common alkaline batteries contain zinc and manganese(IV) oxide in a paste of potassium hydroxide. The overall cell reaction is shown below.

\[ \text{Zn(s)} + \text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)} \rightarrow \text{ZnO(s)} + \text{Mn(OH)}_2(\text{s}) \]

Based on this information, suggest an advantage, other than lower cost, that the zinc–air battery has over the common alkaline battery of similar weight. Explain your answer.

[10]
[Total: 20]
2 (a) Data concerning some Group II sulfates and hydroxides, at 298 K, are given in the table below. Further data may be found in the Data Booklet.

<table>
<thead>
<tr>
<th></th>
<th>solubility / mol dm(^{-3})</th>
<th>– lattice energy / kJ mol(^{-1})</th>
<th>(\Delta H_{\text{hydration}}) of (\text{M}^{2+}) / kJ mol(^{-1})</th>
<th>(\Delta H_{\text{hydration}}) of (\text{SO}_4^{2-}) / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{MgSO}_4)</td>
<td>2.2</td>
<td>2959</td>
<td>–1890</td>
<td>–1160</td>
</tr>
<tr>
<td>(\text{CaSO}_4)</td>
<td>1.5 x 10(^{-2})</td>
<td>2704</td>
<td>–1562</td>
<td>–1160</td>
</tr>
<tr>
<td>(\text{SrSO}_4)</td>
<td>7.1 x 10(^{-3})</td>
<td>2572</td>
<td>–1414</td>
<td>–1160</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>solubility / mol dm(^{-3})</th>
<th>– lattice energy / kJ mol(^{-1})</th>
<th>(\Delta H_{\text{hydration}}) of (\text{M}^{2+}) / kJ mol(^{-1})</th>
<th>(2 \times \Delta H_{\text{hydration}}) of (\text{OH}^-) / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg(OH)}_2)</td>
<td>1.6 x 10(^{-4})</td>
<td>2993</td>
<td>–1890</td>
<td>–1100</td>
</tr>
<tr>
<td>(\text{Ca(OH)}_2)</td>
<td>2.5 x 10(^{-2})</td>
<td>2644</td>
<td>–1562</td>
<td>–1100</td>
</tr>
<tr>
<td>(\text{Sr(OH)}_2)</td>
<td>3.4 x 10(^{-2})</td>
<td>2467</td>
<td>–1414</td>
<td>–1100</td>
</tr>
</tbody>
</table>

(i) Define the term lattice energy.

(ii) Explain the following:

I The magnitude of the lattice energy of Group II sulfates decreases from \(\text{MgSO}_4\) to \(\text{SrSO}_4\).

II The \(\Delta H_{\text{hydration}}\) of \(\text{M}^{2+}\) becomes less exothermic from \(\text{Mg}^{2+}\) to \(\text{Sr}^{2+}\).

(iii) Hence, suggest qualitatively why the solubility of Group II sulfates decreases from \(\text{MgSO}_4\) to \(\text{SrSO}_4\), while the solubility of Group II hydroxides increases from \(\text{Mg(OH)}_2\) to \(\text{Sr(OH)}_2\).

(b) Many metal sulfates have very different industrial uses. For example, the mercury(I) sulfate reference electrode (MSRE) is the second most commonly used reference electrode while calcium sulfate products are used as an economical and FDA–approved source of supplemental calcium.

The numerical values of the solubility product, \(K_{\text{sp}}\), for these two sulfates at 298 K are:

\[K_{\text{sp}} \text{ of mercury(I) sulfate, } \text{Hg}_2\text{SO}_4 = 7.4 \times 10^{-7}\]
\[K_{\text{sp}} \text{ of calcium sulfate, } \text{CaSO}_4 = 2.4 \times 10^{-5}\]

During a Chemistry experiment, a student mixed 25.0 cm\(^3\) of 0.1 mol dm\(^{-3}\) Hg\(^+\) with 25.0 cm\(^3\) of 0.1 mol dm\(^{-3}\) \(\text{Ca}^{2+}\) ions and labeled it as solution J.

(i) The student was then instructed to add solid potassium sulfate to solution J slowly.

Calculate the minimum concentrations of sulfate ions required to precipitate the first trace of mercury(I) sulfate and first trace of calcium sulfate, respectively.

(ii) Using your answers to (b)(i), state and explain which metal sulfate will be precipitated first when solid potassium sulfate was added slowly to solution J.

Hence, calculate the maximum mass of this metal sulfate precipitated, without precipitating the other.
(c) Calcium oxide is commonly known as quicklime. Since it reacts readily with water, it does not occur naturally and has to be produced by heating limestone.

(i) By using relevant data from the Data Booklet and the following data, construct a labeled energy level diagram, showing clearly all the enthalpy changes involved and the chemical species at each stage. Hence, use it to calculate the lattice energy of calcium oxide.

<table>
<thead>
<tr>
<th>Reaction/Magnitude</th>
<th>Enthalpy Change (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First electron affinity of oxygen</td>
<td>$-147$</td>
</tr>
<tr>
<td>Second electron affinity of oxygen</td>
<td>$+753$</td>
</tr>
<tr>
<td>Enthalpy change of atomisation of calcium</td>
<td>$+178$</td>
</tr>
<tr>
<td>Enthalpy change of formation of calcium oxide</td>
<td>$-635$</td>
</tr>
</tbody>
</table>

(ii) Suggest and explain how the magnitude of the lattice energy of Ca$_3$N$_2$ might compare with that of CaO.
3 (a) Aromatic sulfonic acids are useful intermediates in the preparation of dyes and pharmaceuticals. The sulfonic acid group has the same structure as part of the sulfuric acid molecule. 4–methylbenzenesulfonic acid can be prepared by treating methylbenzene with sulfur trioxide and concentrated sulfuric acid.

\[
\text{SO}_3\text{H} + \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3 \xrightarrow{c. \text{ H}_2\text{SO}_4 + \text{SO}_3 \text{ heat}} \text{SO}_3\text{H} + \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3
\]

4-methylbenzenesulfonic acid

(i) Identify and sketch the shapes of the hybrid orbitals around one carbon atom in the benzene molecule.

(ii) In the first step of this reaction, sulfur trioxide behaves as a Brønsted base. Write an equation to illustrate the reaction between concentrated sulfuric acid and sulfur trioxide.

(iii) Hence, name and describe the mechanism for the reaction involved in the preparation of 4–methylbenzenesulfonic acid, including curly arrows to show the movement of electrons, and all charges.

Another sulfonic acid derivative, 4–aminobenzenesulfonic acid, is used in the manufacture of sulfonamide drugs, which are used to treat pneumonia and related diseases. Its structure is given below.

\[
\text{SO}_3\text{H} + \text{C}_6\text{H}_4\text{NH}_2
\]

(iv) Explain why 4–aminobenzenesulfonic acid is a weaker acid than sulfuric acid.

(v) Describe a simple chemical test to distinguish between 4–aminobenzenesulfonic acid and 4–methylbenzenesulfonic acid. [You may ignore the reactivity of –SO_3H group in both molecules.]
(b) Compound K has a molecular formula C₈H₉NO₃. Treating compound K with hot acidified potassium manganate(VII) gives compound L, C₇H₇NO₄, which produces effervescence with sodium hydrogencarbonate.

Heating compound K under reflux with acidified potassium dichromate(VI) gives compound M, C₈H₇NO₄. When compound M is treated with tin and concentrated hydrochloric acid, followed by careful neutralisation using an aqueous alkali, compound N, C₈H₉NO₂, is obtained.

1 mol of compound N reacts with 2 mol of aqueous bromine. Treatment of compound N with anhydrous phosphorus pentachloride produces compound O, C₈H₇NO.

(i) Deduce the structures of compounds K – O and explain the chemistry of the reactions involved.

(ii) Compound O can be separated from any unreacted compound N that is left in the product mixture. This can be done by shaking the product mixture with cold dilute hydrochloric acid. The two layers (organic and aqueous layers) formed are then allowed to stand.

In which layer will compounds N and O be present, respectively? Hence, explain why compounds N and O can be separated in this process.

[12]

[Total: 20]
Four different chromium(III) complexes with the formula $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ can be prepared under various conditions. Each complex contains a cation in which the coordination number of chromium is 6. The complexes may be distinguished by their colours and by the amount of lead(II) chloride precipitated when aqueous lead(II) nitrate is added to aqueous solutions containing each of the complexes.

<table>
<thead>
<tr>
<th>complex</th>
<th>colour</th>
<th>no. of moles of PbCl$_2$ precipitated per mole of complex</th>
<th>does the complex have a dipole moment?</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>violet</td>
<td>1.5</td>
<td>no</td>
</tr>
<tr>
<td>U</td>
<td>pale green</td>
<td>1.0</td>
<td>yes</td>
</tr>
<tr>
<td>V</td>
<td>dark green</td>
<td>0.5</td>
<td>yes</td>
</tr>
<tr>
<td>W</td>
<td>dark green</td>
<td>0.5</td>
<td>no</td>
</tr>
</tbody>
</table>

(i) What do you understand by the term complex ion?

(ii) Explain why an aqueous solution of T is coloured.

(iii) Using the results of the reaction with lead(II) nitrate, suggest, with reasons, the structural formulae for the cation present in T, U and V.

(iv) Describe the shape of and bonding in the cation in W. Illustrate your answer with a full structure of this cation in W, showing the disposition of the atoms.

(v) Explain the presence or absence of a dipole moment for complexes V and W respectively.

(b) The arrangement of electrons in the d–orbitals depends on the spin states of complexes.

The following diagram shows how the d–orbitals are split in an octahedral environment.

In a ‘high spin’ state, the electrons occupy all the d–orbitals singly, before starting to pair up in the lower energy d–orbitals.

In a ‘low spin’ state, the lower energy d–orbitals are filled first, by pairing up if necessary, before the higher energy d–orbitals are used.

(i) Use diagrams like the one above to show the electronic distribution of a Fe$^{2+}$ ion in a high spin state, and in a low spin state. Show in your diagram, the relative size of the energy gap E for each spin state.
Many transition elements and their compounds are paramagnetic, which means that they are attracted to a magnetic field. This property is due to the presence of un paired electron(s) in the d–orbitals.

The table below shows the relative paramagnetisms of some iron complexes.

<table>
<thead>
<tr>
<th>formula of complex</th>
<th>relative paramagnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}(\text H_2\text O)_6]^{2+})</td>
<td>4</td>
</tr>
<tr>
<td>([\text{Fe}(\text H_2\text O)_6]^{3+})</td>
<td>5</td>
</tr>
<tr>
<td>([\text{Fe}(\text{CN})_6]^{4-})</td>
<td>0</td>
</tr>
<tr>
<td>([\text{Fe}(\text{CN})_6]^{3-})</td>
<td>1</td>
</tr>
</tbody>
</table>

(ii) Using your answer to (b)(i) and the information given above concerning paramagnetisms of the different complexes, state and explain which ligand, \(\text{H}_2\text{O}\) or \(\text{CN}^-\), will cause a larger energy gap \(E\) between its d–orbitals.

(iii) Hence, suggest an explanation for the relative paramagnetisms of the hydrated \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) complexes.

(c) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, \(K_{\text{stab}}\) of the new complex.

The following table lists two stability constants for the following reaction.

\[
[\text{Fe}(\text H_2\text O)_6]^{3+} + n\text{L}^- \rightleftharpoons [\text{Fe}(\text H_2\text O)_{6-n}\text{L}_n]^{(3-n)+} + n\text{H}_2\text{O}
\]

(where \(n\) is a whole number)

<table>
<thead>
<tr>
<th>(\text{L}^-)</th>
<th>(n)</th>
<th>(K_{\text{stab}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SCN}^-)</td>
<td>1</td>
<td>(9 \times 10^2)</td>
</tr>
<tr>
<td>(\text{CN}^-)</td>
<td>6</td>
<td>(1 \times 10^{34})</td>
</tr>
</tbody>
</table>

(i) Write the expression for the stability constant, \(K_{\text{stab}}\), for \(\text{L} = \text{SCN}^-\) and state its units.

(ii) Use the data given in the table to predict the predominant complex formed when a solution containing equal concentrations of both \(\text{SCN}^-\) and \(\text{CN}^-\) ions was added to a solution containing \(\text{Fe}^{3+}(\text{aq})\) ions.

(d) Iron(III) ions catalyse the reaction between iodide ions and peroxodisulfate ions (\(\text{S}_2\text{O}_8^{2-}\)) in aqueous solution.

By considering relevant \(E^\circ\) values from the Data Booklet, explain how iron(III) ions function as a catalyst for the reaction between \(\text{I}^-\) and \(\text{S}_2\text{O}_8^{2-}\), writing equations where appropriate.
The oxidation of acidified iodide ions by hydrogen peroxide is represented by

\[ 2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l) \]

To determine the order of reaction, \( n \), with respect to iodide ions, the rate can be followed by adding a small but fixed volume of sodium thiosulfate solution to the constant volume system of reaction mixture together with 1 cm\(^3\) of starch solution and measuring the time taken for the blue black colour to appear. The results are given below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(<a href="aq">I^-</a>) / mol dm(^{-3})</th>
<th>Time (t) / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0040</td>
<td>74.0</td>
</tr>
<tr>
<td>2</td>
<td>0.0060</td>
<td>49.4</td>
</tr>
<tr>
<td>3</td>
<td>0.0080</td>
<td>37.0</td>
</tr>
<tr>
<td>4</td>
<td>0.010</td>
<td>30.0</td>
</tr>
<tr>
<td>5</td>
<td>0.012</td>
<td>25.0</td>
</tr>
</tbody>
</table>

(i) Explain the relationship between the time taken for the formation of the blue black colour and the initial rate of reaction.

(ii) In the experiments, the concentrations of hydrogen peroxide and hydrogen ions used are very much higher than that of the iodide solution. Explain why this is necessary.

(iii) Evaluate 1/t for each experiment and hence plot a suitable graph to determine the order of reaction, \( n \), with respect to iodide ions. State clearly your reasoning.

(iv) Further studies show that the rate equation for the reaction is

\[ \text{Rate} = k [I^-]^n [H_2O_2] \]

Based on this information and your answer to (a)(iii), state two conclusions you can make about the mechanism of this reaction.

(b) (i) 0.1 mol each of the four chlorides below is separately added to 1 dm\(^3\) of water. Copy the diagram below and sketch a graph showing the variation in pH of these resulting solutions.

(ii) Account for the pH of the aqueous solutions of carbon tetrachloride and phosphorus pentachloride. Write balanced equations for the reactions, if applicable.
(c) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

Describe what you would observe if concentrated sulfuric acid is added to separate samples of the solids KC{l} and K{I}. Suggest an explanation for the differences in reaction, and write equations illustrating the types of reaction undergone.

(d) There are three bottles labeled X, Y and Z in the laboratory. Each bottle contains one of the following reagents: C{l/2}(aq), K{I}(aq) and K{Br}(aq).

The following tests were carried out and the results were summarised in the table below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Procedure</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mixing reagent in bottle X with reagent in bottle Y</td>
<td>mixture remains colourless</td>
</tr>
<tr>
<td>2</td>
<td>mixing reagent in bottle X with reagent in bottle Z</td>
<td>mixture turns brown</td>
</tr>
<tr>
<td>3</td>
<td>mixing reagent in bottle Y with reagent in bottle Z</td>
<td>mixture turns brown</td>
</tr>
</tbody>
</table>

(i) Which bottle contains C{l/2}(aq)? Write a balanced equation to support your answer.

(ii) If hexane is also provided, how would you use it to identify the contents of the other two bottles? Include the observations in your answer.

[Total: 20]
2012 H2 Chemistry Preliminary Examination Paper 3 Solutions

1 (a)  (i)  \[4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{Na}_2\text{CrO}_4 + 8\text{CO}_2\]

\[a = 8, \ b = 7, \ c = 2, \ d = 8, \ e = 8\]

(ii) Any dilute acid e.g. dilute H\text{SO}_4 or dilute HCl

(b) \[
\begin{array}{c}
\text{Pt electrode} \\
\text{electron flow} \\
\text{voltmeter}
\end{array}
\]

\[
\begin{align*}
1.00 \text{ mol dm}^{-3} \text{Cr}_2\text{O}_7^{2-} (aq), \\
1.00 \text{ mol dm}^{-3} \text{Cr}^{3+} (aq), \\
1.00 \text{ mol dm}^{-3} \text{H}^+ (aq)
\end{align*}
\]

correct components of each half-cell

direction of electron flow

(c) \[
\begin{align*}
\text{Zn}^{2+} + 2e & \rightarrow \text{Zn} & -0.76 \text{ V} \\
\text{Cr}^{3+} + e & \rightarrow \text{Cr}^{2+} & -0.41 \text{ V}
\end{align*}
\]

Zn reduces Cr\text{3} to blue Cr\text{2}(aq); \[E_{\text{cell}}^o = +0.35 \text{ V} > 0,\]

\[2\text{H}^+ + 2e \rightarrow \text{H}_2 \quad 0.00 \text{ V}\]
The acid present in the solution oxidises blue Cr\text{2} back to green Cr\text{3}; \[E_{\text{cell}}^o = + 0.41 \text{ V},\]
producing H\text{2} gas.

(d) Mole ratio of CrO\text{x} to Cr\text{2}O\text{7} = 7.5 \times 10^{-3} : 2.5 \times 10^{-3} = 3 : 1

Thus, 3 mol of CrO\text{x} disproportionate to 1 mol of Cr\text{2}O\text{7} and 1 mol of Cr\text{3}

Let O.N. of Cr be y.

\[y - 3 = 2(6) - 2y\]

\[y = 5\]

O.N. of Cr in the ion CrO\text{x} = +5

(e)  (i) \[
\begin{align*}
\text{Fe}^{3+} + e & \rightarrow \text{Fe}^{2+} & +0.77 \text{ V} \\
\text{Cr}^{3+} + e & \rightarrow \text{Cr}^{2+} & -0.41 \text{ V}
\end{align*}
\]

\[E_{\text{cell}}^o = +1.18 \text{ V}\]

\[\text{Fe}^{3+} + \text{Cr}^{2+} \rightarrow \text{Fe}^{2+} + \text{Cr}^{3+}\]
(ii) When cell discharges, iron half–cell becomes less positive and the chromium half–cell becomes more positive. Passage of current would stop. Membrane allows anions to pass through to maintain electrical neutrality in the two half–cells. (not allowing the positive ions to pass through, otherwise self–discharge or short circuit occurs)  

$$E_{\text{cell}}^o = E_{\text{red}}^o - E_{\text{ox}}^o$$
1.59 = +0.40 – $$E_{\text{anode}}^o$$

$$E_{\text{anode}}^o = -1.19 \text{ V}$$

Anode: Zn + 4OH– $\rightarrow$ Zn(OH)$_4^{2–}$ + 2e (or Zn + 2OH$^-$ $\rightarrow$ Zn(OH)$_2$ + 2e)

(iv) $Q = 0.8 \times 1.9/65.4 \times 2 \times 96500 = 4486 \text{ C}$

Current = $4486 / (30 \times 24 \times 60 \times 60) = 1.73 \times 10^{-3} \text{ A}$

(v) ICB is expected to discharge faster as it involves simple electron transfer reactions, while energy is needed to break covalent bonds in O$_2$ (and H$_2$O) in the zinc–air battery.

(vi) Zn–air battery has higher energy density as it uses air as the oxidising agent, unlike the heavier oxidising agent, MnO$_2$, used in the alkaline battery. Thus, more zinc can be packed within a cell of similar weight.

2 (a) (i) It is the amount of energy evolved when 1 mole of solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 atm.

(ii) I: As the cationic radius increases down the group, inter–ionic distance increases

OR state that L.E. $\propto r^+ + r^-$ and cationic radius ($r^+$) increases down the group. Thus, the strength of electrostatic forces of attraction between the M$^{2+}$ and SO$_4^{2–}$ ions decreases. Hence, the magnitude of L.E. decreases.

II: $\Delta H_{\text{hydration}}$ of the cation $\propto \frac{q^+}{r^+}$

As the cationic radius increases down the group, OR the charge density of the cation decreases.

Thus, the strength of ion–dipole interactions formed between M$^{2+}$ and water molecules decreases and hence $\Delta H_{\text{hydration}}$ becomes less exothermic.

(iii) $\Delta H_{\text{solution}} = - \text{L.E.} + \Delta H_{\text{hydration}}$ of M$^{2+} + \Delta H_{\text{hydration}}$ of anion

For Group II sulfates, the decrease in |L.E.| is less than that of $|\Delta H_{\text{hydration}}$ of M$^{2+}|$. Thus, $\Delta H_{\text{solution}}$ becomes more positive down the group and solubility decreases

For Group II hydroxides, size of the OH$^-$ anion is much smaller than that of the SO$_4^{2–}$ anion. The decrease in |L.E.| is more than that of $|\Delta H_{\text{hyd}}$ of M$^{2+}|$. Thus, $\Delta H_{\text{solution}}$ becomes more negative down the group and solubility increases.

OR

The size of the cation is much smaller than that of the anion (SO$_4^{2–}$), thus the decrease in |L.E.| is less significant than the decrease in the $|\Delta H_{\text{hydration}}|$. 
Conversely, the size of the OH\(^{-}\) anion is much smaller than that of the \(\text{SO}_4^{2-}\) anion, thus the decrease in |L.E| is more significant than the decrease in the |\(\Delta H_{\text{hydration}}\)|.

(b) (i) For \(\text{Hg}_2\text{SO}_4\), min. \([\text{SO}_4^{2-}]\) = \(7.4 \times 10^{-7} / (0.1/2)^2 = 2.96 \times 10^{-4}\) mol dm\(^{-3}\)

For \(\text{CaSO}_4\), min. \([\text{SO}_4^{2-}]\) = \(2.4 \times 10^{-5} / (0.1/2) = 4.80 \times 10^{-4}\) mol dm\(^{-3}\)

(ii) Since min. \([\text{SO}_4^{2-}]\) required to precipitate first trace of \(\text{Hg}_2\text{SO}_4\) is lower, \(\text{Hg}_2\text{SO}_4\) will be precipitated first.

When max. \(\text{Hg}_2\text{SO}_4\) is precipitated, i.e. when first trace of \(\text{CaSO}_4\) appears, \([\text{SO}_4^{2-}]_{\text{in solution}} = 4.80 \times 10^{-4}\) mol dm\(^{-3}\)

\[ [\text{Hg}^+]_{\text{in solution}} = [7.4 \times 10^{-7} / (4.80 \times 10^{-4})]^{1/2} = 0.0393\) mol dm\(^{-3}\)

\(n(\text{Hg}^+)\) in 50 cm\(^3\) solution = \(0.0393 \times 50/1000 = 1.97 \times 10^{-3}\) mol

\(n(\text{Hg}^+)\) precipitated = \(0.1 \times 25.0/1000 - 1.97 \times 10^{-3} = 5.30 \times 10^{-4}\) mol

\[2\text{Hg}^+ + \text{SO}_4^{2-} \rightarrow \text{Hg}_2\text{SO}_4\]

\(n(\text{Hg}_2\text{SO}_4)\) precipitated = \(\frac{1}{2} \times n(\text{Hg}^+)\) precipitated = \(\frac{1}{2} \times 5.30 \times 10^{-4} = 2.65 \times 10^{-4}\) mol

Max. mass of \(\text{Hg}_2\text{SO}_4\) precipitated = \(2.65 \times 10^{-4} \times (2 \times 201 + 32.1 + 4 \times 16.0) = 0.132\) g

(c) (i) Energy / kJ mol\(^{-1}\)

\[
\begin{align*}
\text{Ca}^{2+}(g) + \text{O}^{2-}(g) & : -147 + 753 \\
\text{Ca}^{2+}(g) + 2\ e^- + \text{O}(g) & : +590 + 1150 \\
\text{Ca}(g) + \text{O}(g) & : \frac{1}{2} (+496) \\
\text{Ca}(g) + \frac{1}{2}\text{O}_2(g) & : +178 \\
\text{Ca}(s) + \frac{1}{2}\text{O}_2(g) & : -635 \\
\text{CaO}(s) &
\end{align*}
\]

L.E\ of \(\text{CaO} = -( -147 + 753 + 590 + 1150 + \frac{1}{2} (496) + 178) + (-635) = -3410\) kJ mol\(^{-1}\) (3 s.f.)
(ii) magnitude of the L.E. of Ca$_3$N$_2$ should be larger than that of CaO due to a larger charge on N$^{3-}$.

OR due to more ionic attractions between 5 mol of ions in 1 mol of Ca$_3$N$_2$ than between 2 mol of ions in 1 mol of CaO.

3 (a) (i) sp$^2$ hybrid orbitals

(ii) $\text{H}_2\text{SO}_4 + \text{SO}_3 \rightarrow \text{HSO}_4^- + \text{HSO}_3^+$

(iii) Electrophilic substitution [1]

(iv) The lone pair of electrons on N atom is delocalised into the benzene ring. This further intensifies the negative charge on the sulfonate anion, making it less stable.

(v) Add aqueous bromine to each compound.
Observation: orange solution of bromine turns colourless and a white precipitate is formed for 4–aminobenzenesulfonic acid. Bromine solution remains orange and no precipitate formed for 4–methylbenzenesulfonic acid

OR
Heat each compound with KMnO$_4$ in dilute $\text{H}_2\text{SO}_4$.
Observation: purple KMnO$_4$ turns colourless for 4–methylbenzenesulfonic acid. KMnO$_4$ remains purple for 4–aminobenzenesulfonic acid.

OR
Add cold $\text{HCl}$ / $\text{H}_2\text{SO}_4$.
Observation: 4–aminobenzenesulfonic acid dissolves in $\text{HCl}$ but 4–methylbenzenesulfonic gives two immiscible layers.
Treating compound **K**, C₈H₇NO₃, with hot acidified potassium manganate(VII) gives compound **L**, C₇H₅NO₄.

**L** produces effervescence with sodium hydrogen carbonate.

Heating compound **K** under reflux with acidified potassium dichromate(VI) gives compound **M**, C₈H₇NO₄.

Compound **M** is treated with tin and concentrated hydrochloric acid, followed careful neutralisation, compound **N**, C₈H₉NO₂ is obtained.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Type of reaction</th>
<th>Deduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treating compound <strong>K</strong>, C₈H₇NO₃, with hot acidified potassium manganate(VII) gives compound <strong>L</strong>, C₇H₅NO₄.</td>
<td>oxidation</td>
<td>loss of 1 C ⇒ side–chain oxidation occurred.</td>
</tr>
<tr>
<td><strong>L</strong> produces effervescence with sodium hydrogen carbonate.</td>
<td>acid–base reaction</td>
<td>Carboxylic acid group in <strong>L</strong> reacted with sodium hydrogen carbonate. \ L contains carboxylic acid group, –COOH.</td>
</tr>
<tr>
<td>Heating compound <strong>K</strong> under reflux with acidified potassium dichromate(VI) gives compound <strong>M</strong>, C₈H₇NO₄.</td>
<td>oxidation</td>
<td>gain in 1 O, loss of 2 H ⇒ 1° alcohol in <strong>K</strong> is oxidised to –COOH in <strong>M</strong>.</td>
</tr>
<tr>
<td>Compound <strong>M</strong> is treated with tin and concentrated hydrochloric acid, followed careful neutralisation, compound <strong>N</strong>, C₈H₉NO₂ is obtained.</td>
<td>reduction</td>
<td>–NO₂ group in <strong>M</strong> is reduced to –NH₂ group in <strong>N</strong>.</td>
</tr>
</tbody>
</table>
1 mole of compound N reacts with 2 moles of aqueous bromine. Electrophilic substitution. N is a phenylamine. -Br is substituted at positions 2, 4 or 2, 6 w.r.t the –NH₂ group.

Treatment of compound N with anhydrous phosphorus pentachloride produces compound O, C₈H₇NO. N is first converted to acyl chloride, by PC₅ via nucleophilic substitution. The acyl chloride formed then undergoes intra-molecular condensation with the –NH₂ group to form a cyclic amide O. The –CH₂COOH group must be adjacent to the –NH₂ group in N to enable ring formation/formation of a cyclic amide.

(ii) Compound N will dissolve in the aqueous layer while compound O will remain in the organic layer. The basic –NH₂ group in compound N will react with cold dilute HCl to give an ionic product which can form strong ion–dipole interactions with water molecules. Compound O is neutral and does not react with cold dilute HCl, hence remains in the organic layer.

4 (a) (i) Complex ion consists of a central metal ion or atom surrounded by ligands via dative bonds.

(ii) In the presence of ligands,
- the partially–filled 3d orbitals are split into two levels (non–degenerate) with a small energy gap
- energy is absorbed from the visible light region when an electron promotes from a lower level d orbital to a vacant higher energy d orbital, i.e. d–d transition,
- colour of the complex T is the complement of the colour absorbed.

(iii) Number of moles of free Cl⁻ per mole of complex = 2 x number of moles of PbCl₂ precipitated per mole of complex

T: 1.5 mol of PbCl₂ precipitated
=> 3 moles of free Cl⁻ per mole of complex
=> cation is [Cr(H₂O)₆]³⁺

U: 1 mol of PbCl₂ precipitated
=> 2 moles of free Cl⁻ per mole of complex and 1 mole of Cl⁻ as ligand per mole of complex
=> cation is [Cr(H₂O)₅Cl]²⁺

V: 0.5 mol of PbCl₂ precipitated
=> 1 mole of free Cl⁻ per mole of complex and 2 moles of Cl⁻ as ligand per mole of complex
=> cation is [Cr(H₂O)₄Cl₂]⁺
(iv) Octahedral with respect to Cr\(^{3+}\). \(\text{H}_2\text{O}\) and Cl\(^–\) ligands are dative bonded to the Cr(III) atom in the complex.

(v) The dipole moment of the 2 Cr–Cl bonds which are on the same side in V do not cancel each other so it has an overall dipole moment.

The dipole moment of the 2 Cr–Cl bonds which are on opposite sides in W cancel out each other so net dipole moment is zero.

(b) (i) Fe\(^{2+}\) ion: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 3d\(^6\)

\[
\begin{array}{c}
\text{energy gap} \\
\downarrow \uparrow \downarrow \uparrow \\
\text{low spin state} \\
\end{array}
\quad
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
\text{high spin state} \\
\end{array}
\]

(ii) CN\(^–\) will cause a larger energy gap E between its d–orbitals

In the presence of CN\(^–\) ligands, the relative paramagnetism is lower. This means that electrons are paired up and arranged in a low spin state. Hence, the energy gap is larger.

(iii) In the presence of water ligands, the electrons of Fe\(^{2+}\)(aq) and Fe\(^{3+}\)(aq) are arranged in a high spin state

where there are 4 unpaired electrons in the d–orbitals of Fe\(^{2+}\)(aq) and 5 unpaired electrons in the d–orbitals of Fe\(^{3+}\)(aq).

Hence the relative paramagnetism of the Fe\(^{2+}\)(aq) and Fe\(^{3+}\)(aq) ions is 4 : 5.

(c) (i) \(K_{\text{stab}} = \frac{[\text{Fe(SCN)}(\text{H}_2\text{O})_5]^{2+}}{[\text{Fe(H}_2\text{O})_6]^{2+}[\text{SCN}^-]}\)

units: mol\(^{-1}\) dm\(^3\)

(ii) Since \(K_{\text{stab}}\) for the complex formed by CN\(^–\) and Fe\(^{3+}\) ions (1 x 10\(^{-3}\)) is much larger than that by SCN\(^–\) and Fe\(^{3+}\) ions (9 x 10\(^{-2}\)). [Fe(CN)\(_6\)]\(^{3–}\) is more stable than [Fe(SCN)(H\(_2\)O)\(_5\)]\(^{2+}\), hence the predominant complex formed is [Fe(CN)\(_6\)]\(^{3–}\).

(d) \(\text{S}_2\text{O}_8^{2–}\)(aq) + 2e\(^–\) \(\rightarrow\) Error! Objects cannot be created from editing field codes. \(2\text{SO}_4^{2–}\)(aq) 

\(E^- = +2.01\text{V}\)

Fe\(^{3+}\)(aq) + e\(^–\) \(\rightarrow\) Error! Objects cannot be created from editing field codes. Fe\(^{2+}\)(aq) 

\(E^- = +0.77\text{V}\)

I\(^2\)(aq) + 2e\(^–\) \(\rightarrow\) Error! Objects cannot be created from editing field codes. 2I\(^–\)(aq) 

\(E^- = +0.54\text{V}\)
Step 1: Formation of intermediate
\[2\text{Fe}^{3+}(aq) + 2\text{I}^-(aq) \rightarrow 2\text{Fe}^{2+}(aq) + \text{I}_2(aq)\]
\[E_{\text{cell}}^\circ = +0.23\text{V}\]

Step 2: Regeneration of the catalyst
\[2\text{Fe}^{2+}(aq) + \text{S}_2\text{O}_8^{2-}(aq) \rightarrow 2\text{Fe}^{3+}(aq) + 2\text{SO}_4^{2-}(aq)\]
\[E_{\text{cell}}^\circ = +1.24\text{V}\]

5 (a) (i) Since a fixed volume of thiosulfate is used in each experiment, rate can be measured by the time taken for fixed amount of iodine liberated, i.e. rate \(\propto \frac{1}{t}\).

(ii) So that \([\text{H}_2\text{O}_2]\) and \([\text{H}^+]\) are kept effectively constant and will not affect the rate of reaction / rate is only affected by the concentration of \([\text{I}^-]\).

(iii) \text{evaluate} (1/t)

labelled axes: y–axis – (1/t); x-axis – [\text{I}^-]

best–fit straight line drawn through the origin correctly plotted points

Rate \(\propto [\text{I}^-]^n [\text{H}_2\text{O}_2]^y [\text{H}^+]^z\)

Since rate \(\propto \frac{1}{t}\) and \([\text{H}_2\text{O}_2]\) and \([\text{H}^+]\) are effectively constant, \(\frac{1}{t} \propto [\text{I}^-]^n\).

Since a straight line which passes through the origin is obtained when \((1/t)\) is plotted against \([\text{I}^-]\), \(n = 1\).

(iv) 1. It is a multi–step mechanism.
2. \(\text{H}^+\) is not involved in the rate–determining step.
3. 1 (mol) of \(\text{I}^-\) and 1 (mol) of \(\text{H}_2\text{O}_2\) are involved in the rate–determining step.

(b) (i) pH

7

\(\text{NaCl} \quad \text{AlCl}_3 \quad \text{CCl}_4 \quad \text{PCl}_5\)

(ii) \(\text{PCl}_5\) undergoes hydrolysis in water but not \(\text{CCl}_4\).

\(\text{CCl}_4\) has no vacant low–lying (energetically accessible) \(d\)–orbitals to accept the lone pair of electrons from the water molecules. Therefore, it will not undergo hydrolysis.

OR

\(\text{PCl}_5\) has vacant low–lying \(3d\)–orbitals to accept the lone pair of electrons from the water.
molecules. Hence, it will undergo hydrolysis to give $\text{H}_3\text{PO}_4$ and $\text{HCl}$, resulting in an acidic solution.

$$\text{PCl}_5 + 4\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 5\text{HCl}$$

(c) Steamy / white fumes of HCl observed for KCl, violet / purple fumes of I$_2$ observed for KI.

$$\text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{KHSO}_4 + \text{HCl}$$

$$\text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{HI} + \text{KHSO}_4$$

$$8\text{HI} + \text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O}$$

I$^-$ being a stronger reducing agent (than Cl$^-$) will reduce $\text{H}_2\text{SO}_4$ to $\text{H}_2\text{S}$ / itself oxidised to I$_2$.

(d) (i) Bottle Z

$$\text{Cl}_2 + X^- \rightarrow 2\text{Cl}^- + X_2$$ where $X = \text{Br}$ or I

(ii) Knowing that bottle X and Y is either KBr or KI, add hexane to the two brown mixtures obtained, separately.

If the organic layer is purple, bottle contains KI.
If the organic layer is red–brown, bottle contains KBr.
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write and/or shade your name, NRIC / FIN number and HT group on the Multiple Choice Answer Sheet in the spaces provided.

There are forty 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 in soft pencil on the separate Answer Sheet.

Read the instructions on the Multiple Choice Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
Calculators may be used.
Section A

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

1. Gallium (Aᵣ = 69.7) occurs naturally as two isotopes, $^{69}_{31}$Ga and $^{71}_{31}$Ga. What is the percentage of $^{71}_{31}$Ga atoms in a sample of naturally occurring gallium?
   A 33 %  
   B 35 %  
   C 60 %  
   D 65 %

2. The mineral tellurite, TeO₂ (Mᵣ = 160.0) is often used in the manufacture of optic fibres. It was found that 1.01 g of TeO₂ in an ore sample required exactly 60 cm³ of 0.035 mol dm⁻³ acidified K₂Cr₂O₇ for complete reaction. In this reaction, Cr₂O₇²⁻ is converted into Cr³⁺.

   What is the oxidation state of Te in the final product?
   A +2  
   B +3  
   C +5  
   D +6

3. Use of the Data Booklet is relevant to this question.

   What do the ions $^{35}$Cl⁻ and $^{40}$Ca²⁺ have in common?
   A Both ions have 18 neutrons.
   B Both ions have more protons than neutrons.
   C Both ions contain the same number of nucleons.
   D Both ions have an outer electronic configuration 3s² 3p⁶.

4. Carbodiimides are often used in organic synthesis as dehydrating agent to activate carboxylic acids towards amide or ester formation. Carbodiimides consist of the general structure, RN=C=NR where R is an alkyl group.

   What is the most likely bond angle at each nitrogen atom in carbodiimides?
   A 107°  
   B 118°  
   C 120°  
   D 180°

5. Myoglobin, Mb, is an oxygen-carrier protein that exists in the muscle fibres of most mammals. Each Mb molecule will bind to one O₂ molecule, according to the following equation.

   $$\text{Mb(aq)} + \text{O}_2(\text{aq}) \rightleftharpoons \text{MbO}_2(\text{aq}) \quad K_c = 1 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$$

   Given that the concentration of O₂ is 6.5 × 10⁻⁶ mol dm⁻³, what is the percentage of MbO₂ in a Mb-MbO₂ mixture?
   A 50.5 %  
   B 65.0 %  
   C 86.7 %  
   D 88.4 %
6 The enthalpy changes involving some oxides of nitrogen are given below:

\[
\begin{align*}
N_2(g) + O_2(g) & \rightarrow 2NO(g) \quad \Delta H = +180 \text{ kJ mol}^{-1} \\
2NO_2(g) + \frac{1}{2}O_2(g) & \rightarrow N_2O_5(g) \quad \Delta H = -55 \text{ kJ mol}^{-1} \\
N_2(g) + \frac{5}{2}O_2(g) & \rightarrow N_2O_5(g) \quad \Delta H = +11 \text{ kJ mol}^{-1}
\end{align*}
\]

What is the enthalpy change, in kJ mol\(^{-1}\), of the following reaction?

\[2NO(g) + O_2(g) \rightarrow 2NO_2(g)\]

A \(-235\)  
B \(-125\)  
C \(-114\)  
D \(-57\)

7 The Thermit Reaction involves mixing iron(III) oxide with aluminium powder in a crucible, with a suitable fuse to start the reaction. The reaction is as follows:

\[\text{Fe}_2\text{O}_3(s) + 2\text{Al}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2\text{Fe}(l)\]

The fuse is first ignited, where it will burn in oxygen, forming the oxide with a large release of heat required for the Thermit reaction to take place. The commonly used material for the fuse is a clean magnesium strip.

Which of the following does \textbf{not} help to explain why a strip of magnesium is suitable to be used as a fuse?

A The large amount of heat energy released on igniting the fuse enables the reactants to overcome the high activation energy involved.
B Magnesium removes the thin layer of oxide on aluminium, thus allowing aluminium to react with the iron(III) oxide.
C The numerical value of the enthalpy change of formation of magnesium oxide is very large.
D The strip increases the surface area for magnesium to react with the oxygen at a faster rate.

8 When a precipitate is formed, \(\Delta G_{\text{ppt}}^o\), in J mol\(^{-1}\), is given by the following expression

\[\Delta G_{\text{ppt}}^o = 2.303RT\log K_{sp}\]

Data about AgBr is as follows: \(K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}\), \(\Delta H_{\text{ppt}}^o = -84.4 \text{ kJ mol}^{-1}\)

What is the \(\Delta S_{\text{ppt}}^o\), in J mol\(^{-1}\) K\(^{-1}\), for the formation of AgBr(s) at 298 K?

A \(-47.8\)  
B \(-0.0478\)  
C \(+0.0478\)  
D \(+47.8\)
The secondary structure of DNA is the double helix. The formation of the double helix involves two DNA chains, where one has the bases Adenine (A) and Guanine (G), interacting with the bases Thymine (T) and Cytosine (C) on the other chain as shown below:

The two chains coil together in a helical fashion, and this process is an example of self-assembly.

What are the correct signs of $\Delta H$ and $\Delta S$ for the formation of the double helix?

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>B</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>C</td>
<td>+</td>
<td>–</td>
</tr>
<tr>
<td>D</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
10 The cell below is set up under standard conditions:

\[ \text{Pt(s) / Sn}^{2+}(aq), \text{Sn}^{4+}(aq) \parallel \text{HNO}_2(aq), \text{H}^+(aq) / \text{NO(g)} / \text{Pt(s)} \quad E_{\text{cell}}^\circ = +0.84 \text{ V} \]

Which of the following changes will cause the cell e.m.f. to be less than +0.84 V immediately after the cell is being set up?

A adding NaOH(aq) to the HNO\(_2\)(aq) / NO(g) half-cell  
B adjusting the partial pressure of NO(g) to be 0.5 atm  
C adding water to the Sn\(^{4+}\)(aq)/Sn\(^{2+}\)(aq) half-cell  
D adding SnCl\(_2\) to the Sn\(^{4+}\)(aq)/Sn\(^{2+}\)(aq) half-cell

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

The cell shown in the diagram is set up under standard conditions where X and Y are platinum electrodes.

\[
\begin{array}{c}
\text{Cl}_2(g) \\
\text{Cl}^-(aq) \\
X \quad \text{Y} \\
\end{array}
\]

Half-cell A  
Half-cell B  
Fe\(^{2+}\)(aq) and Fe\(^{3+}\)(aq)

Which of the following statements is correct?

A Changing X to Fe in half-cell A will not affect \(E_{\text{cell}}^\circ\).
B The voltmeter will show a reading of about 1.80 V.
C The electrons will flow from Y to X through the voltmeter.
D Y will be the positive electrode.

12 Ethyl ethanoate is a common ester formed during production of wines. It gives the aroma found in younger wines and contributes towards the “fruitiness” perception in wine. The formation of ester in wine can be illustrated by the following equation.

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} 
\]

\[ K_c = 4.0, \quad \Delta H = -20 \text{ kJ mol}^{-1} \]

Which of the following statement is correct about the above equilibrium?

A As water is removed from wine, [CH\(_3\)CO\(_2\)CH\(_2\)CH\(_3\)] and \(K_c\) increases.
B As temperature of the wine decreases, [CH\(_3\)CO\(_2\)CH\(_2\)CH\(_3\)] and \(K_c\) increases.
C As water is added to the wine, [CH\(_3\)CO\(_2\)CH\(_2\)CH\(_3\)] increases.
D As CH\(_3\)CO\(_2\)H is removed from the wine, [CH\(_3\)CO\(_2\)CH\(_2\)CH\(_3\)] increases.
13 HA is a weak acid and can have different degree of acidity in aqueous solution and in liquid ammonia. The respective equations that represent their dissociations are as follow.

\[
\begin{align*}
HA + H_2O &\rightleftharpoons A^- + H_3O^+ \\
HA + NH_3 &\rightleftharpoons A^- + NH_4^+
\end{align*}
\]

Which of the following statement is correct?

A. Ammonia is more polar than water, resulting in greater dissociation of HA.
B. Degree of dissociation of HA is identical in aqueous solution and liquid ammonia.
C. $pK_a$ of NH$_3$ is larger than that of H$_2$O, hence HA is a stronger acid in liquid ammonia.
D. $K_b$ of NH$_3$ is larger than that of H$_2$O, hence HA is a stronger acid in liquid ammonia.

14 Amylase is the first enzyme discovered and isolated. It acts as a catalyst in the hydrolysis of starch.

In a single experiment, the rate of hydrolysis of starch was monitored as the reaction proceeded and the following graph was obtained.

![Graph](image)

Which of the following statement about the reaction is not correct?

A. When [starch] is smaller than $x$, the rate changes as [starch] changes.
B. When [starch] is larger than $x$, the active sites of amylase are fully occupied.
C. The order of reaction with respect to starch is constant at all concentrations.
D. Throughout the experiment, [amylase] remains constant as it is not used up.

15 Oxides of two unknown elements of the third period have the following properties. Both can be dissolved in an alkali and when added separately to water, the resultant pH was approximately 7 and 3 respectively.

Which of the following pairs could have been the oxides?

A. Al$_2$O$_3$ and P$_4$O$_{10}$
B. Al$_2$O$_3$ and Na$_2$O
C. Na$_2$O and SiO$_2$
D. SO$_3$ and P$_4$O$_{10}$
Two students were tasked to prepare pure hydrogen iodide from solid potassium iodide. The first student used concentrated $\text{H}_2\text{SO}_4$ as the reagent, while the second student used concentrated $\text{H}_3\text{PO}_4$ instead. Only one student was successful in preparing pure hydrogen iodide.

Which of the following is the most likely explanation and/or observation?

A First student was unsuccessful, as hydrogen iodide formed further react to give purple fumes of iodine and hydrogen sulfide which contaminates the product.
B First student was successful, as hydrogen iodide can be quickly isolated due to its low boiling point.
C Second student was unsuccessful, as $\text{H}_3\text{PO}_4$ is a weaker acid than $\text{H}_2\text{SO}_4$, thus hydrogen iodide cannot be formed.
D Second student was successful, as $\text{H}_3\text{PO}_4$ is a weaker reducing agent than $\text{H}_2\text{SO}_4$.

Transition metals have many interesting properties.

Which statement correctly describes a property unique to transition metals?

A They form metal ions which form dative covalent bonds with ligands.
B They form compounds which can exhibit colours due to partially filled d-orbitals.
C They are the only metals which have high melting and boiling points.
D They are the only metals which have variable oxidation states.

The bond lengths in buta-1,3-diyne differs from those which might be expected. The carbon-carbon bond length in ethane ($\text{C}_2\text{H}_6$) is 0.154 nm and in ethyne ($\text{C}_2\text{H}_2$) is 0.120 nm. The single C2-C3 bond in buta-1,3-diyne, however is shorter than the single bond in ethane: it is 0.137 nm.

What helps to explain this C2-C3 bond length in buta-1,3-diyne?

A It is an sp-sp overlap.
B It is an sp²-sp overlap.
C The sp³-sp³ overlap is pulled shorter by a p-p (π-bond) overlap.
D The electrons in the filled p-orbitals on C2 and C3 repel each other.

Which of the following gases is not removed by catalytic converters from the exhaust fumes of cars?

A CO    B H₂O    C NO₂    D CH₄
Potassium sodium tartrate, also known as Rochelle salt, is used medicinally as a laxative and has the following structure.

\[
\text{OH} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{K}^+ \\
\text{Na}^- \\
\]

Which of the following could be part of the reaction sequence to synthesise Rochelle salt?

A. \((\text{CHO})_2\) + HCN(aq) + NaCN + KOH(aq) + NaOH(aq) → Rochelle salt

B. \(\text{CH}_2\text{BrCH}_2\text{Br}\) + KCN(alc) + KOH(aq) + NaOH(aq) → Rochelle salt

C. \(\text{CH}_3\text{COCH}_3\) + HCN(aq), NaOH(aq) + KMnO₄, OH⁻(aq) → Rochelle salt

D. \(\text{CH}_3\text{(CH}_2\text{)}_3\text{Cl}\) + KOH(aq) + KMnO₄, OH⁻(aq) → Rochelle salt

Phenylamine can be synthesised via a one-step reaction as shown below.

\[
\text{C} \quad \text{Cl} \quad \xrightarrow{\text{NaNH}_2, \text{NH}_3(l)} \quad \text{NH}_2 \quad \text{Cl} \quad + \quad \text{NaCl}
\]

What type of reaction has occurred?

A. Electrophilic substitution
B. Electrophilic addition
C. Nucleophilic substitution
D. Nucleophilic addition
22. A halogen derivative, X, was first warmed with aqueous sodium hydroxide, followed by adding excess of dilute nitric acid and aqueous silver nitrate. A precipitate was produced. Dilute aqueous ammonia was then added and a colourless solution is obtained. Which of the following could be the identity of compound X?

A \[\text{Br} \]

B \[\text{Cl} \]

C \[\text{I} \]

D \[\text{CH}_2\text{CH}_2\text{Cl} \]

23. Estrone, one of several natural estrogens, can be converted from cholesterol via steriodogenesis. The structures of both compounds are shown below.

\[\text{estrone} \]

\[\text{cholesterol} \]

Which of the following \textbf{cannot} be used to distinguish estrone from cholesterol?

A 2,4-dinitrophenylhydrazine, warm
B neutral \(\text{FeCl}_3\) (aq)
C \(\text{PCl}_5\)
D \(\text{Br}_2\) (aq)
24 Compound R was warmed with aqueous iodine in the presence of aqueous sodium hydroxide. After filtration and removal of unreacted iodine, the resultant organic product was heated with ethanol in the presence of concentrated sulfuric acid to give ethyl butanoate.

Which of the following could compound R be?

A  

B  

C  

D  

25 Which procedure gives the highest yield of ethyl benzoate?

A  refluxing CH$_3$CO$_2$H with SOCl$_2$, then adding phenol
B  refluxing CH$_3$CH$_2$OH with concentrated HCl, then adding C$_6$H$_5$CO$_2$H
C  refluxing C$_6$H$_5$CO$_2$H with SOCl$_2$, then adding CH$_3$CH$_2$OH
D  refluxing CH$_3$CH$_2$OH with concentrated H$_2$SO$_4$, then adding C$_6$H$_5$CO$_2$H

26 Antipyrine is a drug used in reducing fever. The synthesis of antipyrine involves the reaction between compound P and phenylhydrazine.

Which of the following statements regarding compound P is true?

A  P reacts with warm aqueous alkaline iodine to form one organic product.
B  P gives a silver mirror when heated with Tollens’ reagent.
C  P turns hot acidified potassium dichromate(VI) from orange to green.
D  P contains two carbonyl groups which can both react with cold alkaline HCN.
27 Cocaine is medicinally valued as a local anaesthetic. The structure of cocaine is shown below.

```
CH₃
| N
| CO₂CH₃
| C
| O
```

Which pair of compounds would produce cocaine when reacted together?

A.  
```
| CH₃
| N
| CO₂H
| CH₂OH
| O
```

B.  
```
| CH₃
| N
| CO₂H
| + CH₃OH
```

C.  
```
| CH₃
| N
| CO₂H
| + HCO₂H
```

D.  
```
| CH₃
| N
| CO₂H
| + HCO₂H
```

28 2-bromopropane, (CH₃)₂CHBr, W, may be used as the starting material for synthesising (CH₃)₂C(OH)CO₂H.

Which of the following sequences would result in the highest yield of (CH₃)₂C(OH)CO₂H?

A.  
W → (CH₃)₂C(OH)CN → (CH₃)₂C(OH)CO₂H

B.  
W → (CH₃)₂CH(CN) → (CH₃)₂CH(CO₂H) → (CH₃)₂C(OH)CO₂H

C.  
W → (CH₃)₂CH(OH) → CH₃COCH₃ → (CH₃)₂C(OH)CN → (CH₃)₂C(OH)CO₂H

D.  
W → (CH₃)₂CBr₂ → (CH₃)₂C(Br)CN → (CH₃)₂C(OH)CO₂⁻ → (CH₃)₂C(OH)CO₂H
29. What is the correct order of increasing $pK_b$ for the following four compounds?

![Chemical structures](image)

A. I, IV, III, II
B. II, III, IV, I
C. III, I, II, IV
D. IV, III, II, I

30. Tyrosine, a building block for several neurotransmitters, has the structure as shown below. Tyrosine has three $pK_a$ values of 2.20, 9.11 and 10.07, which correspond to the $–CO_2H$, $–NH_3^+$ and phenol groups respectively.

![Chemical structure](image)

In an aqueous solution at pH 9.5, how much charge will be carried on different parts of each molecule of Tyrosine?

<table>
<thead>
<tr>
<th></th>
<th>total number of positive charges</th>
<th>total number of negative charges</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct). The responses A to D should be selected on the basis of:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
<td></td>
</tr>
</tbody>
</table>

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

31 The titration curve of the protonated form of alanine, \( \text{NH}_2\text{CH(CH}_3\text{)}\text{CO}_2\text{H} \), is as shown.

![Titration curve diagram]

The two stages of this titration are associated with two different dissociation constants, \( pK_1 \) and \( pK_2 \).

\[
\begin{align*}
\text{H}_3\text{N}^+ \text{CH(CH}_3\text{)}\text{CO}_2\text{H} + \text{OH}^- & \rightleftharpoons \text{H}_3\text{N}^+ \text{CH(CH}_3\text{)}\text{CO}_2^- + \text{H}_2\text{O} & pK_1 = 2.4 \\
\text{H}_3\text{N}^+ \text{CH(CH}_3\text{)}\text{CO}_2^- + \text{OH}^- & \rightleftharpoons \text{H}_2\text{NCH(CH}_3\text{)}\text{CO}_2^- + \text{H}_2\text{O} & pK_2 = 9.7
\end{align*}
\]

Which statements are correct for alanine?

1. Equal concentrations of \( \text{H}_3\text{N}^+ \text{CH(CH}_3\text{)}\text{CO}_2\text{H} \) and \( \text{H}_3\text{N}^+ \text{CH(CH}_3\text{)}\text{CO}_2^- \) are present at \( \text{pH} = 2.4 \).
2. There is no net charge on alanine at the point when the slope of the curve is at maximum at its centre.
3. The form \( \text{H}_2\text{NCH(CH}_3\text{)}\text{CO}_2^- \) is the major species present at \( \text{pH} 9.7 \).
A | B | C | D
---|---|---|---
1, 2 and 3 are correct | 1 and 2 only are correct | 2 and 3 only are correct | 1 only is correct

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

32 Ketones react with HCN solution in the presence of NaCN catalyst to form cyanohydrins, which are useful intermediates in organic syntheses. In investigations of the reaction between propanone and HCN, the following results were obtained.

<table>
<thead>
<tr>
<th>Initial concentrations of reactants / mol dm(^{-3})</th>
<th>Relative initial rate / mol dm(^{-3}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CH}_3\text{CO}])</td>
<td>[HCN]</td>
</tr>
<tr>
<td>0.020</td>
<td>0.020</td>
</tr>
<tr>
<td>0.025</td>
<td>0.020</td>
</tr>
<tr>
<td>0.020</td>
<td>0.020</td>
</tr>
<tr>
<td>0.040</td>
<td>0.025</td>
</tr>
</tbody>
</table>

Which conclusions can be drawn about the kinetics of this reaction under these conditions?

1. The reaction is zero order with respect to HCN.
2. The rate-determining step involves only propanone and NaCN.
3. When the concentration of propanone used in the reaction is in large excess, the reaction appears to be first order with respect to NaCN.

33 Use of the Data Booklet is relevant to this question.

Which of the following are chemically stable when left to stand in the atmosphere?

1. a solution of K\(_3\)Fe(CN)\(_6\)
2. a solution of CrCl\(_2\)
3. a mixture of NaOH(aq) and FeSO\(_4\)(aq)
34 In which of the following pairs are the members, I and II,
• stereoisomers of each other and
• the overall dipole moment of I is larger than that of II?

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="c2-p15-1.png" alt="Image of I" /></td>
<td><img src="c2-p15-2.png" alt="Image of II" /></td>
</tr>
</tbody>
</table>

35 Solid magnesium hydroxide is typically added to paint coatings as fire retardant to prevent spread of fire. This is possible as solid magnesium hydroxide decomposes in a similar manner to Group II nitrates.

\[ \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \]

Magnesium hydroxide decomposes at about 300 °C to give water vapour which prevents oxygen from reaching the burning material. At the same time, it is an endothermic reaction that absorbs heat energy.

However, barium hydroxide is less suitable as flame retardants. Which of the following statements explain this?

1 Barium hydroxide when fully decomposed produces less amount of water vapour per mole of hydroxide, thus it is less effective.
2 Barium hydroxide decomposes at a much higher temperature, therefore it may not release enough water vapour at the start of a fire.
3 Barium hydroxides are much more soluble and may not remain on the painted material for a long period of time.
No other combination of statements is used as a correct response.

36 Citronella oil is a well-known plant-based insect repellent and one of the key chemical compounds found in the oil is citronellal.

![Citronellal structure](image)

Which of the following statements about citronellal are correct?

1. The bond length of C1-C2 is expected to be shorter than that of C2-C3 bond due to sp³-sp² overlap.
2. Optical and geometrical isomerism are both possible in citronellal.
3. Reaction of citronellal with hydrogen and a suitable catalyst will produce a compound with three chiral centres.

37 1-phenylethanol, C₆H₅CH(OH)CH₃, was reacted in a three-step reaction using the following reagents.

Step 1: Br₂, catalyst  
Step 2: K₂Cr₂O₇, H⁺, reflux  
Step 3: HCN, NaCN, 15 °C

Which of the following is true?

1. The final product has no effect on plane-polarised light.
2. Iron(III) bromide can be used as a catalyst for step 1.
3. Nucleophilic substitution has occurred in step 3.
38Lovastatin is a naturally occurring drug found in food such as oyster mushrooms and red yeast rice. It can lower cholesterol levels and thus prevent cardiovascular disease.

\[
\text{Lovastatin}
\]

Which of the following is true when lovastatin is refluxed with excess aqueous sodium hydroxide?

1. One of the organic products contains three hydroxyl groups.
2. 1 mol of lovastatin reacts with 3 mol of aqueous NaOH.
3. Three organic products are formed.

39Which of the following statements regarding compound $X$ is true?

\[
\text{compound } X
\]

1. 1 mol of compound $X$ reacts with 3 mol of cold dilute hydrochloric acid.
2. 1 mol of compound $X$ reacts with 2 mol of ethanoyl chloride.
3. 1 mol of compound $X$ reacts with aqueous bromine to give an acidic solution.
No other combination of statements is used as a correct response.

40 The structure of the herbicide *Karbutilate* is shown below.

What would be the products formed when *Karbutilate* is subjected to prolonged boiling with aqueous dilute hydrochloric acid?

1. CO₂
2. C₆H₅OH
3. (CH₃)₂NH
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READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes provided above.
Write in dark blue or black pen on both sides of the paper. [PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]
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 all questions. Write your answers in the space provided.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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

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This document consists of 17 printed pages and 0 blank page.

1 Planning (P)
Eggshells are rich in calcium carbonate and make good plant fertilisers to replenish calcium, an essential nutrient in plant growth. The eggshells are normally crushed and sprinkled around the plants. The shells will slowly decompose and enrich the soil. The decomposition of \( \text{CaCO}_3(\text{s}) \) may be represented as:

\[
\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})
\]

In the laboratory, all Group II carbonates, \( M\text{CO}_3 \), can be decomposed by heating to give the corresponding oxide, \( MO \), and carbon dioxide, \( \text{CO}_2 \).

You are to design an experiment to investigate how the rate of decomposition of Group II carbonates varies down the group.

In addition to the standard apparatus available in a school laboratory for gas collection, you are provided with the following materials,

- samples of carbonates of magnesium, calcium, strontium and barium,
- a stopwatch

(a) Briefly describe how you would measure the rate of decomposition of the different carbonates in order to enable comparison.

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

(b) Draw a diagram of the apparatus and experimental set up that you would use to carry out the experiment. Show clearly the following:
- the apparatus used to heat the carbonate, and
- how the carbon dioxide will be collected.

Label each piece of apparatus used, indicating its size or capacity.
(c) The temperature of the Bunsen flame varies depending on the ratio of the fuel to oxygen burnt. Besides keeping to the same fuel to oxygen ratio, suggest how you would control another factor in the heating to ensure a fair comparison of the rate of decomposition of different carbonates.

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

(d) Other than the use of safety goggles, state one hazard that must be considered when planning the experiment and suggest how you would keep this risk to a minimum.

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.................................................................................................................................................. [2]

(e) With reference to the apparatus in (b), show how you would calculate the mass of each carbonate used in the experiment.

\[ M_r: \text{MgCO}_3 = 84.3; \text{CaCO}_3 = 100.1; \text{SrCO}_3 = 147.6; \text{BaCO}_3 = 197.0 \]
(f) Draw a table with appropriate headings (and units) to show the data you would record and the values you would calculate in order to plot a suitable graph to show the variation in the rates of decomposition of the carbonates.

Sketch, and explain, the shape of the graph you would expect from your results. Label clearly the axes.

Explanation:

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……………………………………………………………………………………………………. [4]

[Total: 12]
2 (a) Carbon dioxide is used in beverage carbonation. Cylinders of pressurised carbon dioxide are used to produce carbonated drinks. One such cylinder has an internal volume of 3.0 dm$^3$ and contains 4.6 kg of carbon dioxide.

(i) Calculate the pressure (in Pascals) the carbon dioxide gas would exert inside the cylinder at 28 °C.

(ii) To find the pressure of a fixed amount of carbon dioxide gas under certain conditions, the van der Waals' equation given below should be used.

\[
\left( p + \frac{a n^2}{V^2} \right) (V - nb) = nRT
\]

Without further calculation, explain how the pressure obtained using the van der Waals' equation would differ from that in (a)(i).

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

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(b) Real gases like carbon dioxide can be liquefied at low temperatures just by applying pressure. Gases can be liquefied by pressure alone if the temperature is below their critical temperature, $T_c$. At temperatures above $T_c$, the gas cannot be liquefied, regardless of the pressure applied. The critical temperature of carbon dioxide is 31.1 °C.

(i) Explain why real gases like carbon dioxide can be liquefied just by applying pressure.

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(ii) By considering structure and bonding, suggest a value for the critical temperature of methane and give a reason for your choice.

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(c) Beyond the critical temperature and pressure, carbon dioxide exists as a supercritical fluid, a state that resembles a gas but has density closer to that in the liquid phase. Carbon dioxide is now well established as a solvent for use in extraction.

(i) Suggest a reason why supercritical carbon dioxide is preferred as a solvent to extract caffeine from solid coffee over organic solvents like benzene.

(ii) Suggest why small amounts of ethanol need to be added to supercritical carbon dioxide to increase the solubility of polyphenols for extraction. An example of a polyphenol is shown below.

![Polyphenol Structure](image)

(d) Ethanedioate ions, C$_2$O$_4^{2-}$, can be oxidised by hot acidified aqueous potassium manganate(VII) to form carbon dioxide.

(i) Draw the structure of ethanedioate ions, C$_2$O$_4^{2-}$, and give the bond angle around the central carbon atom.
(ii) Construct a balanced equation for the reaction between ethanedioate ions and hot acidified potassium manganate(VII).

(iii) 1.63 g of a salt, KHC$_2$O$_4$·H$_2$C$_2$O$_4$, was dissolved in distilled water and made up to 250 cm$^3$ solution. Calculate the volume of 0.020 mol dm$^{-3}$ KMnO$_4$ required to react with 20.0 cm$^3$ of the KHC$_2$O$_4$·H$_2$C$_2$O$_4$ solution.

$[M_r$ of KHC$_2$O$_4$·H$_2$C$_2$O$_4 = 218.1]\]

(e) (i) The reaction between acidified potassium manganate(VII) and ethanedioate ions is usually carried out at a higher temperature of 60 °C. Suggest why the rate of this reaction is slow at room temperature.

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The graph of rate against time for the reaction between acidified potassium manganate(VII) and ethanedioate ions is shown below.

(ii) Suggest the species responsible for the increase in rate of reaction before point A, and identify the property which enables it to act as a catalyst in this reaction.

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[2]
[Total: 13]
Iron is the fourth most common element in the Earth’s crust, and has many applications throughout the history of mankind. In nature, iron exists in many different mineral ores, consisting of iron in either +2 or +3 oxidation state. In prehistoric era, iron compounds were more commonly used as pigment without further purification. Limonite, which has the general formula of FeO(OH)·nH₂O, was used as a yellow pigment as early as 10 000 B.C.

(a) (i) Complete the electronic configuration of Fe³⁺.

1s² ..............................................

(ii) Briefly explain why iron in mineral ores is found in variable oxidation states, but for s-block elements, for example calcium, there is usually only one oxidation state.

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............................................................................................................................
............................................................................................................................
............................................................................................................................
............................................................................................................................
............................................................................................................................ [3]

(b) A mineralogist dissolved 100 g of a certain pure limonite in concentrated HCℓ to form a yellow solution. It was found that 3.2 mol of HCℓ had reacted based on the equation,

FeO(OH)·nH₂O + 4HCℓ → FeCl₄⁻ + (n+2)H₂O + H⁺

(i) State the formula of this limonite (with n as an integer): .........................

(ii) Suggest the shape of FeCl₄⁻: .................................

(iii) Explain, with reference to FeCl₄⁻, why transition element complexes are coloured.

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............................................................................................................................ [5]
In recent times, with much better understanding of chemistry, iron and its compounds are widely used as catalysts and reagents in synthesis of chemicals. In particular, the ferrate(VI) ion, FeO$_4^{2-}$, is a strong oxidising agent that is used in green chemistry and water purification due to its non-toxic by-products.

Ferrate(VI) ions are not stable in acidic conditions and easily oxidise water to give oxygen. Hence, they are often produced in an alkaline medium.

Some $E^\circ$ data of chlorate(I) and ferrate(VI) ions are given below.

\[
\begin{align*}
\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- & \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O} & E^\circ = +2.20 \text{ V} \\
\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- & \rightleftharpoons \text{Fe(OH)}_3 + 5\text{OH}^- & E^\circ = +0.80 \text{ V} \\
2\text{ClO}^- + 4\text{H}^+ + 2\text{e}^- & \rightleftharpoons \text{Cl}_2 + 2\text{H}_2\text{O} & E^\circ = +1.63 \text{ V} \\
\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- & \rightleftharpoons \text{Cl}^- + 2\text{OH}^- & E^\circ = +0.89 \text{ V}
\end{align*}
\]

(i) By selecting relevant $E^\circ$ data from the *Data Booklet* and using the information above, explain with suitable calculation,

I why ferrate(VI) ions are not stable in acidic conditions,

II why it is feasible to form potassium ferrate(VI), K$_2$FeO$_4$, by reacting KC/0 with Fe(OH)$_3$ in the presence of KOH.

(ii) Hence write a balanced overall equation for the formation of K$_2$FeO$_4$.

(iii) Would you expect an acidified solution of K$_2$FeO$_4$ to be a stronger or weaker oxidising agent compared to an acidified solution of KMnO$_4$? Support your answer with relevant $E^\circ$ values from the *Data Booklet*.
(iv) Hence draw the structure of the possible organic product formed when hot acidified purple \( \text{K}_2\text{FeO}_4 \) reacts with the following compound and suggest the expected observations.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{OH} \\
\end{array}
\xrightarrow{\text{}}
\begin{array}{c}
\text{CH}_3 \\
\text{C} \\
\end{array}
\]

Observations: …………………………………………………………………………………

……………………………………………………………………………………………………

………………………………………………………………………………………………………

[8]

(d) White light contains all the colours in the visible spectrum. Each of these colours is associated with a certain wavelength, \( \lambda \). The formula relating energy and wavelength is,

\[
E = \frac{hc}{\lambda}
\]

where \( h = 6.626 \times 10^{-34} \text{ J s} \),

\( c = 3.00 \times 10^8 \text{ m s}^{-1} \)

\( \lambda \) has the unit of m.

<table>
<thead>
<tr>
<th>Wavelength, ( \lambda ) (10(^{-9}) m)</th>
<th>Colour of light</th>
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<tbody>
<tr>
<td>400</td>
<td>Violet</td>
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<tr>
<td>450</td>
<td>Blue</td>
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<tr>
<td>500</td>
<td>Green</td>
</tr>
<tr>
<td>550</td>
<td>Yellow</td>
</tr>
<tr>
<td>600</td>
<td>Orange</td>
</tr>
<tr>
<td>650</td>
<td>Red</td>
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</tbody>
</table>

(i) By considering the appearance of green iron(II) compounds and yellow iron(III) compounds, state the colour of light absorbed for these compounds.

Iron(II) ……………………………………… Iron(III) ………………………………………
(ii) Hence, calculate the energy associated with the respective colours absorbed.

Energy of colour absorbed by
Iron(II) compounds: ........................
Iron(III) compounds: ........................

(iii) Using your answer in (d)(ii), complete the diagram below to show the relative energies of the d-orbitals, and the electronic distribution of the metal ion in each compound. In each case, label clearly the energy required for the promotion of an electron from the lower energy d-orbitals to the higher energy d-orbitals.

Assume that all electrons occupy the lower energy orbitals before the higher energy orbitals.

Energy

Iron(II) compound  Iron(III) compound

[5]
[Total: 21]
4 Cymobarbatol is an antimutagenic agent isolated from the marine algae *Cymopolia barbata*. The structure of cymobarbatol is shown below.

![Cymobarbatol](image)

(a) Name two functional groups, other than phenyl and ether, which are present in the cymobarbatol molecule.

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

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

(b) Identify the chiral carbons in cymobarbatol molecule by placing an asterix (*) against each chiral carbon on the structure above.

(c) Draw the structural formula of each organic product formed when cymobarbatol is treated with the following reagents. In each reaction, assume that the ring remains unaltered.

(i) ethanolic NaOH, heated under reflux

(ii) concentrated ethanolic NH₃, heated in a sealed tube
(d) Cymobarbatol will also react with aqueous NaOH under reflux condition.

(i) Given that one mole of cymobarbatol reacts with two moles of aqueous NaOH, write a balanced equation for this reaction.

(ii) When the bromine atoms in cymobarbatol are replaced by iodine atoms, how would you expect the rate of its hydrolysis reaction to compare to that of cymobarbatol? Explain your answer.

(iii) Describe the expected observations when aqueous AgNO₃, followed by concentrated aqueous ammonia, is subsequently added to the resultant mixture in (d)(i). Explain your answer with relevant equations.
There are a number of structural isomers of molecular formula C\(_n\)H\(_n\)O\(_2\). In particular, one of the isomers, B, is used as a tincture in perfumes and as a food additive.

(a) To find the value of \(n\), a 1.00 g sample of B was burned in an excess of oxygen, and the gases produced were first passed through a U-tube containing P\(_4\)O\(_{10}\) (to absorb the water vapour) and then bubbled through concentrated NaOH(aq). The P\(_4\)O\(_{10}\) in the U-tube increased in mass by 0.529 g.

(i) Write an equation for the reaction of P\(_4\)O\(_{10}\) with water vapour and state the pH of the resultant solution.

(ii) Suggest why anhydrous CaCl\(_2\) cannot be used in place of P\(_4\)O\(_{10}\) in the U-tube.

(iii) Calculate the number of moles of water produced.

(iv) Use the above data to show that the value of \(n = 8\).
(b) A reaction scheme involving compound B is shown below.

\[ B, C_8H_8O_2 \xrightarrow{\text{LiA/H}_4 \text{ in dry ether}} \rightarrow \]
\[ \text{violet colouration} \]
\[ \text{heating with} \]
\[ \text{acidified K}_2\text{Cr}_2\text{O}_7(aq) \]
\[ \text{orange solution} \]

\[ C, C_8H_{10}O_2 \]
\[ \text{heating with} \]
\[ \text{conc. H}_2\text{SO}_4 \]

\[ D, C_8H_8O \]
\[ \text{HBr(g)} \]

\[ E, C_8H_9OBr \]

(i) Based on the above information, draw three possible structural isomers of B, which are labelled as B1, B2 and B3 in the boxes below.

\[ \text{B1} \quad \text{B2} \quad \text{B3} \]

(ii) Based on the structural isomer B1, draw the structural formulae of C, D and E.

\[ \text{C} \quad \text{D} \quad \text{E} \]
(c) A structural isomer of D, C₈H₈O, which is labelled as F, contains a C-O-C bond. F does not react with HBr(g).

(i) Suggest a structural formula of F.

(ii) Although F does not react with HBr(g), it can react with concentrated HBr(aq). The reaction of F with concentrated HBr(aq) is similar to the reaction of primary alcohols with concentrated HBr(aq). The process involves the following two stages:

\[
\begin{align*}
\text{Stage I} & \quad \text{RCH}_2\text{-OH} + \text{H}^+ & \rightarrow \quad \text{RCH}_2\text{-O}^- + \text{H}_2\text{O} \\
\text{Stage II} & \quad \text{RCH}_2\text{-O}^- + \text{Br}^- & \rightarrow \quad \text{RCH}_2\text{-Br} + \text{H}_2\text{O}
\end{align*}
\]

Suggest a mechanism for the Stage II process in the reaction of F with concentrated HBr(aq), including curly arrows to denote movement of electrons, and all charges. You do not need to draw the 3-dimensional representation of the molecules involved.
1 Planning (P)

Eggshells are rich in calcium carbonate and make good plant fertilisers to replenish calcium, an essential nutrient in plant growth. The eggshells are normally crushed and sprinkled around the plants. The shells will slowly decompose and enrich the soil. The decomposition of CaCO$_3$(s) may be represented as:

$$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO(\text{s})} + \text{CO}_2(\text{g})$$

In the laboratory, all Group II carbonates, $M\text{CO}_3$, can be decomposed by heating to give the corresponding oxide, $MO$, and carbon dioxide, $CO_2$.

You are to design an experiment to investigate how the rate of decomposition of Group II carbonates varies down the group.

In addition to the standard apparatus available in a school laboratory for gas collection, you are provided with the following materials,

- samples of carbonates of magnesium, calcium, strontium and barium,
- a stopwatch

(a) Briefly describe how you would measure the rate of decomposition of the different carbonates in order to enable comparison.

- …measure time taken to produce (collect) the same volume of CO$_2$(g) from …… each carbonate …………………………………………………………………………………………………………………………………………………………… [1]

(b) Draw a diagram of the apparatus and experimental set up that you would use to carry out the experiment. Show clearly the following:

- the apparatus used to heat the carbonate, and
- how the carbon dioxide will be collected.

Label each piece of apparatus used, indicating its size or capacity.
The temperature of the Bunsen flame varies depending on the ratio of the fuel to oxygen burnt. Besides keeping to the same fuel to oxygen ratio, suggest how you would control another factor in the heating to ensure a fair comparison of the rate of decomposition of different carbonates.

- Bunsen burner at same distance from the reaction vessel. [1]

Other than the use of safety goggles, state one hazard that must be considered when planning the experiment and suggest how you would keep this risk to a minimum.

1. “Hot” apparatus – use heat-proof gloves or let apparatus cool before handling
2. Potential suck back (if water allowed to suck back, hot boiling tube would crack and shatter) – remove delivery tube from water when heating is stopped. [2]

With reference to the apparatus in (b), show how you would calculate the mass of each carbonate used in the experiment.

\[ M_r: \text{MgCO}_3 = 84.3; \text{CaCO}_3 = 100.1; \text{SrCO}_3 = 147.6; \text{BaCO}_3 = 197.0 \]

Note: 1. Vol of CO\(_2\)(g) collected must not exceed capacity of collection device.
2. Mass of each carbonate used must contain the same number of moles.

Let volume of CO\(_2\)(g) collected = 40 cm\(^3\)

Since molar gas volume at r.t.p. = 24 dm\(^3\),

\[
\text{mol of CO}_2 = \frac{40}{24} = 1.67 \times 10^{-3} \text{ mol}
\]

\[ \text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2 \]

\[
\therefore \text{minimum mol of MCO}_3 = \text{mol of CO}_2 = 1.67 \times 10^{-3} \text{ mol}
\]

\[ M_r \text{ of MCO}_3 = (A_r \text{ of } M) + [12.0 + 3(16.0)] = (A_r \text{ of } M) + 60.0 \]

Let mol of carbonate = \(2.00 \times 10^{-3}\) mol

mass of \(\text{MCO}_3\) = \(nM_r\) = \(2.00 \times 10^{-3} \times [(A_r \text{ of } M) + 60.0] \)

\[
\therefore \text{mass of MgCO}_3 = (2.00 \times 10^{-3}) \times 84.3 = 0.169 \text{ g}
\]

mass of CaCO\(_3\) = \((2.00 \times 10^{-3}) \times 100.1 = 0.200 \text{ g}\)

mass of SrCO\(_3\) = \((2.00 \times 10^{-3}) \times 147.6 = 0.295 \text{ g}\)

mass of BaCO\(_3\) = \((2.00 \times 10^{-3}) \times 197.0 = 0.394 \text{ g}\) [2]
(f) Draw a table with appropriate headings (and units) to show the data you would record and the values you would calculate in order to plot a suitable graph to show the variation in the rates of decomposition of the carbonates.

<table>
<thead>
<tr>
<th></th>
<th>( M_r )</th>
<th>time / s</th>
<th>( \frac{1}{t_{\text{sec}}} ) / s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCO(_3)</td>
<td>84.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO(_3)</td>
<td>100.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrCO(_3)</td>
<td>147.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaCO(_3)</td>
<td>197.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sketch, and explain, the shape of the graph you would expect from your results. Label clearly the axes.

Explanation:

- Down the group, as the cation increases in size (while the charge remains unchanged), the charge density decreases and the polarising power of the cation also decreases.
- Hence, the larger cations polarise (distort) the carbonate anion less and the compound is thus relatively stable to heat.

[decrease in charge density of cation; less polarisation of anion]
(a) Carbon dioxide is useful in beverage carbonation. Cylinders of pressurised carbon dioxide are used to produce carbonated drinks. One such cylinder has an internal volume of 3.0 dm³ and contains 4.6 kg of carbon dioxide.

(i) Calculate the pressure (in Pascals) the carbon dioxide gas would exert inside the cylinder at 28 °C.

\[
pV = nRT
\]

\[
p \times (3 \times 10^{-3}) = \frac{4.6 \times 10^3}{44} (8.31)(28+273)
\]

\[
p = 8.72 \times 10^7 \text{ Pa}
\]

(ii) To find the pressure of a fixed amount of carbon dioxide gas under certain conditions, the van der Waals’ equation should be used.

\[
\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT
\]

Without further calculation, explain how the pressure obtained using the above equation would differ from that in (a)(i).

The pressure obtained would be lower since intermolecular forces of attraction exist between CO₂ molecules.

(b) Real gases like carbon dioxide can be liquefied at low temperatures just by applying pressure. Gases can be liquefied by pressure alone if their temperature is below their critical temperature, T_c. The critical temperature of carbon dioxide is 31.1 °C.

(i) Explain why real gases like carbon dioxide can be liquefied just by applying pressure.

At high pressure, the molecules are very close together, and the intermolecular forces of attraction become significant.

(ii) By considering structure and bonding, suggest a value for the critical temperature of methane and give a reason for your choice.

Any value less than that of carbon dioxide will be accepted as the answer. The van der Waals’ forces of attraction between methane molecules is weaker compared to that between carbon dioxide molecules because CH₄ has a smaller electron cloud.
Beyond the critical temperature and pressure, carbon dioxide exists as a supercritical fluid, a state that resembles a gas but has density closer to that in the liquid phase. Carbon dioxide is now well established as a solvent for use in extraction.

(ii) Suggest why supercritical carbon dioxide is preferred as a solvent to extract caffeine from solid coffee over organic solvents like benzene.

*Carbon dioxide is non-toxic while benzene is toxic and should be kept away from food and beverages.* OR

*The carbon dioxide can be easily removed as a gas by depressurizing.*

(iii) Suggest why small amounts of ethanol need to be added to supercritical carbon dioxide in the extraction of polyphenols. An example of a polyphenol is shown below.

![Polyphenol structure](image)

*The ethanol molecules added can form hydrogen bonds with the phenol groups present and this increase the solubility of polyphenols.*

(d) Ethanedioate ions, $C_2O_4^{2-}$, can be oxidised by hot acidified aqueous potassium manganate(VII) to form carbon dioxide.

(i) Draw the structure of ethanedioate ions, $C_2O_4^{2-}$, and give the bond angle around the central carbon atom.
(ii) Construct a balanced equation for the reaction between ethanedioate ions and hot acidified potassium manganate(VII).

\[ \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^- \]

\[ \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

Overall equation: \[ 5\text{C}_2\text{O}_4^{2-} + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O} \]

(iii) 1.63 g of a salt, KHC\textsubscript{2}O\textsubscript{4}⋅\textsubscript{H}\textsubscript{2}C\textsubscript{2}O\textsubscript{4}, was dissolved in distilled water and made up to 250 cm\textsuperscript{3} solution. Calculate the volume of 0.020 mol dm\textsuperscript{-3} of KMnO\textsubscript{4} required to react with 20.0 cm\textsuperscript{3} of the KHC\textsubscript{2}O\textsubscript{4}⋅\textsubscript{H}\textsubscript{2}C\textsubscript{2}O\textsubscript{4} solution. [M\textsubscript{r} of KHC\textsubscript{2}O\textsubscript{4}⋅\textsubscript{H}\textsubscript{2}C\textsubscript{2}O\textsubscript{4} = 218.1]

Amount of C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} ions present = \( 2 \times \frac{1.63}{218.1} \times \frac{20}{250} = 0.0011958 \) mol

Amount of MnO\textsubscript{4}\textsuperscript{-} required = \( \frac{2}{5} \times 0.0011958 = 0.0004783 \) mol

Volume of MnO\textsubscript{4}\textsuperscript{-} required = \( \frac{0.0004783}{0.020} = 0.0239 \text{ dm}^3 = 23.9 \text{ cm}^3 \)

[4]

The graph of rate against time for the reaction between acidified potassium manganate(VII) and ethanedioate ions is shown below.

(e) (i) The reaction between acidified potassium manganate(VII) and ethanedioate ions is usually carried out at a higher temperature of 60 °C. Suggest why the rate of this reaction is slow at room temperature.

Both C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} and MnO\textsubscript{4}\textsuperscript{-} are \textit{negatively charged} and the \textit{activation energy for...} the reaction is \textit{high due to repulsion between the ions.}
(ii) Suggest the species responsible for the increase in rate of reaction before point A, and identify the property which enables it to act as a catalyst in this reaction.

- Mn$^{2+}$. It can exist in variable oxidation states.

[Total: 13]

Iron is the fourth most common element in the Earth’s crust, and has many applications throughout the history of mankind. In nature, iron exists in many different mineral ores, consisting of iron in either +2 or +3 oxidation state. In prehistoric era, iron compounds were more commonly used as pigment without further purification. Limonite, which has the general formula of FeO(OH)-nH$_2$O, was used as a yellow pigment as early as 10 000 B.C.

(a) (i) Complete the electronic configuration of Fe$^{3+}$.

$1s^2 \ldots 2s^2 2p^6 3s^2 3p^6 3d^6$ .................

(ii) Briefly explain why iron in mineral ores are found in variable oxidation states, but for s-block elements, for example calcium, there is usually only one oxidation state.

Iron has valence electrons of similar energy in both the 3d and 4s orbitals, thus it can lose electrons from both the 4s and 3d orbitals, giving rise to variable oxidation states. However s-block elements can only lose valence electrons in the s orbitals, resulting in only 1 oxidation state.

[3]

(b) A mineralogist dissolved 100 g of a certain pure limonite in concentrated HCl to form a yellow solution. It was found that 3.2 mol of HCl had reacted based on the equation,

$$FeO(OH).nH_2O + 4HCl \rightarrow FeCl_4^- + (n+2)H_2O + H^+$$

(i) State the formula of this limonite (with n as an integer): $FeO(OH).2H_2O$

Suggest the shape of FeCl$_4^-$: Tetrahedral.[or square planar]
(ii) Explain, with reference to FeCl₄⁻, why transition element complexes are coloured.

When C⁻ ligands are bonded to the Fe³⁺ they will cause the originally partially-filled degenerate d-orbitals to split into 2 energy levels with small energy gap.

When electron from the lower d-orbitals absorbs energy in the visible light region, it will be excited to the higher d* orbital. Such transition is d-d* electronic transition. Complementary colours, yellow, which is not absorbed will be observed as the colour of FeCl₄⁻.

(c) In recent times, with much better understanding of chemistry, iron and its compounds are widely used as catalysts and reagents in synthesis of chemicals. In particular, the ferrate(VI) ion, FeO₄²⁻, is a strong oxidising agent that is used in green chemistry and water purification due to its non-toxic by-products.

Ferrate(VI) ions are not stable in acidic conditions and easily oxidise water to give oxygen. Hence they are often produced in an alkaline medium.

Some E° data of chlorate(I) and ferrate(VI) are given below.

\[
\begin{align*}
\text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^- & \rightleftharpoons \text{Fe}^{3+} + 4\text{H}_2\text{O} \quad E^o = +2.20 \text{ V} \\
\text{FeO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- & \rightleftharpoons \text{Fe(OH)}_3 + 5\text{OH}^- \quad E^o = +0.80 \text{ V} \\
2\text{ClO}^- + 4\text{H}^+ + 2\text{e}^- & \rightleftharpoons \text{Cl}_2 + 2\text{H}_2\text{O} \quad E^o = +1.63 \text{ V} \\
\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- & \rightleftharpoons \text{Cl}^- + 2\text{OH}^- \quad E^o = +0.89 \text{ V}
\end{align*}
\]

(i) By selecting relevant E° data from the Data Booklet and using the information above, explain with suitable calculation, why ferrate(VI) ions are not stable in acidic conditions.

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^o = +1.23 \text{ V} \\
E^o_{\text{rxn}} = +2.20 - 1.23 = +0.99 \text{ V}
\]

As \( E^o_{\text{rxn}} \) is positive, the reaction is feasible, and ferrate will oxidise water to give oxygen.
II why it is feasible to form potassium ferrate(VI), $\text{K}_2\text{FeO}_4$, by reacting $\text{KCIO}_3$ with $\text{Fe(OH)}_3$ in the presence of KOH.

\[
3\text{e}^- + 4\text{H}_2\text{O} + \text{FeO}_4^{2-} \rightleftharpoons \text{Fe(OH)}_3 + 5\text{OH}^- \quad \text{E}^\circ = +0.80 \text{ V}
\]

\[
\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{OH}^- \quad \text{E}^\circ = +0.89 \text{ V}
\]

\[
\text{E}^\circ_{\text{rxn}} = +0.89 - 0.80 = +0.09 \text{ V} > 0, \text{ hence the reaction is feasible.}
\]

(ii) Hence write a balanced overall equation for the formation of $\text{K}_2\text{FeO}_4$.

\[
4\text{KOH} + 2\text{Fe(OH)}_3 + 3\text{KCIO}_3 \rightarrow 3\text{KCl} + 5\text{H}_2\text{O} + 2\text{K}_2\text{FeO}_4
\]

(iii) Would you expect an acidified solution of $\text{K}_2\text{FeO}_4$ to be a stronger or weaker oxidising agent compared to an acidified solution of $\text{KMnO}_4$? Support your answer with relevant $\text{E}^\circ$ values from the Data Booklet.

\[
\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad \text{E}^\circ = +1.52 \text{ V}
\]

Comparing the $\text{E}^\circ$ values of +1.52 V and +2.20 V, $\text{FeO}_4^{2-}$ undergoes reduction more readily, thus it is a stronger oxidising agent compared to $\text{MnO}_4^-$.

(iv) Hence draw the structure of the possible organic product formed when hot acidified purple $\text{K}_2\text{FeO}_4$ reacts with the following compound and suggest the expected observations.

\[
\text{CH}_2\text{CH}_2\text{OH} \quad \xrightarrow{\text{effervesence of carbon dioxide}} \quad \text{CO}_2\text{H}
\]

Observations: Effervesence of carbon dioxide is observed, and the solution changes from purple $\text{FeO}_4^{2-}$ to yellow $\text{Fe}^{3+}$.  

[8]
(d) White light contains all the colours in the visible spectrum. Each of these colours is associated with a certain wavelength, \( \lambda \). The formula relating energy and wavelength is,

\[
E = \frac{hc}{\lambda}
\]

where \( h = 6.626 \times 10^{-34} \text{ J s} \),

\( c = 3.00 \times 10^8 \text{ m s}^{-1} \)

\( \lambda \) has the units of m.

<table>
<thead>
<tr>
<th>Wavelength, ( \lambda ) (10(^{-9}) m)</th>
<th>Colour of light</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>Violet</td>
</tr>
<tr>
<td>450</td>
<td>Blue</td>
</tr>
<tr>
<td>500</td>
<td>Green</td>
</tr>
<tr>
<td>550</td>
<td>Yellow</td>
</tr>
<tr>
<td>600</td>
<td>Orange</td>
</tr>
<tr>
<td>650</td>
<td>Red</td>
</tr>
</tbody>
</table>

(i) By considering the appearance of green iron(II) compounds and yellow iron(III) compounds, state the colour of light absorbed for these compounds.

Iron(II):…………………………… Iron(III):……………………………….

(ii) Hence, with the information above, calculate the energy associated with the respective colours absorbed.

For Red absorbed by iron (II),

\[
E = \frac{(6.626 \times 10^{-34}) (3.00 \times 10^8)}{650 \times 10^{-9}}
\]

\[
= 3.06 \times 10^{-19} \text{ J}
\]

For Violet absorbed by iron (III),

\[
E = \frac{(6.626 \times 10^{-34}) (3.00 \times 10^8)}{400 \times 10^{-9}}
\]

\[
= 4.97 \times 10^{-19} \text{ J}
\]

Energy of colour absorbed by

Iron(II) compounds: ……… 3.06 \times 10^{-19} \text{ J}

Iron(III) compounds: ………………………………. 4.97 \times 10^{-19} \text{ J}
(iii) Using your answer in (d)(ii), complete the diagram below to show the relative energies of the d orbitals, and the electronic distribution of the respective compounds. In each case, label clearly the energy difference required for the promotion of an electron upon absorption of light.

Assume all electrons occupy the lower energy orbitals before the higher energy orbitals.

Energy

Iron(II) compounds

Iron(III) compounds

4 Cymobarbatol is an antimutagenic agent isolated from the marine algae Cymopolia barbata. The structure of cymobarbatol is shown below.

(a) Name two functional groups, other than phenyl and ether, that are present in the cymobarbatol molecule.

**phenol, secondary bromoalkane, bromoarene**

(b) Identify the chiral carbons in cymobarbatol molecule by placing an asterix (*) against each chiral carbon on the structure above.

(c) Draw the structural formula of each organic product formed when cymobarbatol is treated with the following reagents.

In the following reactions, the ring remains unaltered.
(i) ethanolic NaOH, heated under reflux

(ii) concentrated ethanolic NH₃, heated in a sealed tube

(d) Cymobarbatol will also react with aqueous NaOH under reflux condition.

(i) Given that one mole of cymobarbatol reacts with two moles of aqueous NaOH, write a balanced equation for this reaction.

(ii) When bromine in cymobarbatol is replaced by iodine, how would you expect the rate of its hydrolysis reaction to compare to that of cymobarbatol? Explain your answer.

...When bromine in cymobarbatol is replaced by iodine, the rate of reaction is faster than cymobarbatol.
...This is because the C-I bond is longer and hence weaker than the C-Br bond (since I atom is larger than Br atom).

…………………………………………………………………………………………………...
(iii) Describe the expected observations when aqueous AgNO₃, followed by concentrated aqueous ammonia, is subsequently added to the resultant mixture in (d)(i). Explain your answer with relevant equations.

A cream ppt. of AgBr will be observed to form when aq. AgNO₃ is added. It will then dissolve in the concentrated aq. NH₃ solution to form a colourless solution.

\[
\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightarrow [\text{Ag(NH}_3)_2]^+(aq) \quad \text{equation I}
\]

\[
\text{Ag}^+(aq) \text{ reacts with NH}_3(aq) \text{ to form a soluble complex, } [\text{Ag(NH}_3)_2]^+ \text{ from equation I.}
\]

\[
\text{AgBr(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq) \quad \text{equilibrium II}
\]

As [Ag⁺] decreases, the position of equilibrium II shifts to the right, and hence more AgBr dissolves.

[OR]

When excess NH₃(aq) is added such that ionic product of AgBr < K_{sp} of AgBr, all the AgBr will dissolve completely.

\[
\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4, \quad \text{pH} = 1 \text{ to } 2
\]

5 There are a number of structural isomers of molecular formula CₙHₙO₂. In particular, one of the isomers, B, is used as a tincture in perfumes and as a food additive.

(a) To find the value of \( n \), a 1.00 g sample of B was burned in an excess of oxygen, and the gases that were produced were first passed through a U-tube containing P₄O₁₀ (to absorb the water vapour) and then bubbled through concentrated NaOH(aq). The P₄O₁₀ in the U-tube increased in mass by 0.529 g.

(i) Write an equation for the reaction of P₄O₁₀ with water vapour and state the pH of the resultant solution.

\[
P₄O₁₀ + 6H₂O \rightarrow 4H₃PO₄, \quad \text{pH} = 1 \text{ to } 2
\]

(ii) Suggest why anhydrous CaCl₂ cannot be used in place of P₄O₁₀ in the U-tube.

\[
\text{Calcium chloride will absorb water vapour to form a neutral solution, and would absorb some of the CO}_2 \text{ formed.}
\]

(iii) Calculate the number of moles of water produced.

\[
\text{Amount of H}_2\text{O} = \frac{0.529}{18} = 0.0294 \text{ mol}
\]
(iv) Use the above data to show that the value of \( n = 8 \).

\[
\text{Amount of B} = \frac{1.00}{12n + n + 32} = \frac{1.00}{13n + 32} \text{ mol}
\]

\[C_nH_nO_2 \equiv \frac{n}{2} H_2O\]

Thus \[\frac{1.00}{13n + 32} \times \frac{n}{2} = 0.0294\]

Therefore \( n = 8 \)

(b) A reaction scheme involving compound B and its related compounds, C to E, undergo the following reactions:

\[\text{B, C}_8\text{H}_8\text{O}_2 \xrightarrow{\text{LiA/H}_4 \text{ in dry ether}} \text{C, C}_8\text{H}_{10}\text{O}_2\]

\[\text{neutral FeC}_3(\text{aq}) \xrightarrow{\text{violet colouration}} \]

\[\text{heating with acidified K}_2\text{Cr}_2\text{O}_7(\text{aq}) \xrightarrow{\text{orange solution}} \]

\[\text{heating with conc. H}_2\text{SO}_4 \xrightarrow{\text{D, C}_8\text{H}_8\text{O}} \]

\[\text{E, C}_8\text{H}_9\text{OBr} \xrightarrow{\text{HBr}(\text{g})} \]

(i) Based on the above information, draw three possible structural isomers of B, which are labeled as B1, B2 and B3 in the boxes below.
(ii) Based on your structure of B1, draw the structures of C, D and E.

(c) A structural isomer of D, C₈H₈O, which is labelled as F, contains a C-O-C bond. F does not react with HBr(g).

(i) Suggest a structural formula of F.

(ii) Although F does not react with HBr(g), it can react with concentrated HBr(aq). The reaction of F with concentrated HBr(aq) is similar to the reaction of primary alcohols with concentrated HBr(aq). The process involves two stages:

**Stage I**  \( \text{RCH}_2\text{OH} + \text{H}^+ \xrightarrow{} \text{RCH}_2\text{O}^+\text{H} \)

**Stage II**  \( \text{RCH}_2\text{O}^+\text{H} \xrightarrow{} \text{RCH}_2\text{Br} + \text{H-OH} \)

Suggest a mechanism for the **Stage II** process in the reaction of F with concentrated HBr(aq), including curly arrows to denote movement of electrons, and all charges. You do not need to draw the 3-dimensional representation of the molecules involved.

[arrows, lone pair on Br⁻ indicated, SN2 mechanism]

[Total: 14]
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. [PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]
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
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of 14 printed pages and 0 blank page.
This question relates to the chemistry of Be, Mg, Al and their compounds.

(a) Beryllium compounds are toxic air pollutants. Inhalation of high levels of beryllium can cause inflammation of the lungs in humans and long-term exposure may cause chronic beryllium disease (*berylliosis*), in which granulomatous lesions develop in the lung.

(i) Given that charge density $\propto \frac{\text{ionic charge}}{\text{ionic radius}}$, calculate the relative charge densities of $\text{Be}^{2+}$, $\text{Mg}^{2+}$ and $\text{Al}^{3+}$, using relevant data from the Data Booklet.

(ii) Hence, predict what is observed when aqueous sodium hydroxide is gradually added to aqueous beryllium sulfate until the sodium hydroxide is in an excess. Write equations for all reactions that have taken place.

(iii) Suggest the pH of the solution formed when beryllium chloride is dissolved in water. Give your reasoning.

(iv) Magnesium ions are essential for the action of some enzymes (e.g. alkaline phosphatase found in the liver) by receiving electron pairs from oxygen and nitrogen atoms in the protein. It is thought that beryllium compounds are poisonous because they displace magnesium ions from these enzymes. Suggest a reason why beryllium ions should behave in this way.

(v) Beryllium chloride may be used as a catalyst in the chlorination of benzene. Suggest a reason why this is possible. Outline the mechanism to show how beryllium chloride is involved in this reaction.

[10]
(b) A student carried out a kinetics experiment using a roll of magnesium ribbon that had been exposed to air for some time. He placed a piece of magnesium ribbon of mass 0.12 g into a flask containing 15.0 cm$^3$ of 1.0 mol dm$^{-3}$ hydrochloric acid. The progress of the reaction was followed by measuring the pressure of the system at different times. The graph below shows the results of the experiment.

(i) Determine, by calculation, the limiting reagent for the experiment.

(ii) Account for the change in pressure of the system as shown in the graph at points A, B, and from C onwards.

(c) An alloy of aluminium and magnesium is used in boat-building.

A 1.75 g sample of the alloy was dissolved in the minimum volume of 4 mol dm$^{-3}$ hydrochloric acid and the solution was then made alkaline by the addition of aqueous sodium hydroxide until no further reaction occurred. The resultant mixture was filtered and the residue, X, rinsed with distilled water, all washings being added to the filtrate, Y. After air drying, 0.18 g of X was obtained. Carbon dioxide was passed into Y and a white solid, Z, which contained aluminium, was collected. Heating Z to constant mass gave a residue of mass 3.16 g.

Suggest the identities of X, Y and Z, and determine the percentage composition by mass of the alloy.

[Total: 20]
2-chlorobutane undergoes hydrolysis with NaOH(aq) via two different reaction pathways, in the same reaction, to form a mixture of two enantiomeric products.

$$\text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{CH}_3 + \text{NaCl}$$

In one of the hydrolysis reaction pathways, only one product is formed and inversion of configuration occurs in the product. In the other reaction pathway, a racemic mixture is formed.

(a) In an experiment, one optical isomer of 2-chlorobutane undergoes hydrolysis and two enantiomeric products in a ratio of 95%:5% are formed.

(i) Draw the structures of the two enantiomeric products.

(ii) One enantiomer is formed in a much higher percentage compared to the other. Explain clearly how this disparity arises by examining the mechanisms of both reaction pathways. You should name both mechanisms involved but an outline of the mechanism is not required.

(iii) Write a rate equation for the reaction pathway that results in the inversion of the configuration and draw its energy profile diagram, given that the enthalpy change of the hydrolysis is exothermic.

(iv) Suggest the percentage of 2-chlorobutane that undergoes hydrolysis via the reaction pathway in (a)(iii).

(v) Hence deduce how much faster the rate of this reaction pathway in (b)(ii) compares to that of the other reaction pathway.

(b) 2-chlorobutane is commonly produced from but-1-ene via reaction with hydrogen chloride.

$$\text{CH}_2=\text{CHCH}_3(g) + \text{HCl}(g) \rightleftharpoons \text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_3(l)$$

(i) Name the other possible product in the above reaction.

(ii) Predict the sign of $\Delta S$ for this reaction, showing your reasoning.

(iii) Using relevant bond energy values from the Data Booklet, calculate the approximate value of $\Delta H$ for the reaction in (b).

(iv) Bond energies quoted from the Data Booklet are average values. Other than this, explain why the method in (b)(iii) is not the most accurate for determining $\Delta H$ of the reaction.

(v) Deduce how the rate of reaction of but-1-ene with hydrogen halides will vary from H-F to H-I, and give your reasoning.
(vi) While HCl react readily with alkenes under room conditions, HCN does not. Based on concepts of chemical bonding, suggest possible reasons for this.

[10]

(c) HCl can be prepared by adding concentrated sulfuric acid to solid sodium chloride. However when concentrated sulfuric acid is added to sodium iodide, the yield of HI is very low. Explain.

[1]

[Total: 20]
This question explores the chemistry of zinc in biochemistry, organic chemistry and electrochemistry.

(a) Angiotensin I, a simple protein, undergoes hydrolysis with the aid of an enzyme, known as angiotensin-converting enzyme (ACE) to form angiotensin II. Angiotensin II is an important hormone that causes blood vessels to constrict, resulting in a rise in blood pressure.

(i) State how proteins can be hydrolysed to form a mixture of their constituent amino acids.

Some of the amino acids found in angiotensin II are shown below.

![Amino Acid Structures]

The side chains (R-groups) of angiotensin II could bind to targeted proteins through suitable R-group interactions. The R-group interactions are also used to maintain two specific protein structures.

(ii) Briefly describe one protein structure that involves R-group interactions.

(iii) Suggest three different types of R-group interactions in which the side chains of angiotensin II could bind to targeted proteins. Your answer should clearly indicate the side chains that might be involved.

(iv) Another enzyme that functions similarly as ACE is carboxypeptidase. The active site of carboxypeptidase contains $-$NH$_3^+$ group and a Zn$^{2+}$ ion, which are both crucial in binding to suitable proteins.

Below shows the hydrolysis of a protein (represented by RCONHCHR'CO$_2^-$) catalysed by this enzyme, where ------ represents interactions between the enzyme and the protein.
If there is a mutation such that carboxypeptidase does not contain Zn²⁺, the enzyme will fail to function effectively as a catalyst. By using the above information, suggest why. [6]

(b) Lucas reagent is used to distinguish primary, secondary and tertiary alcohols. It consists of a solution of anhydrous ZnCl₂ in concentrated HCl. Upon addition of Lucas reagent at 28 °C, tertiary alcohols give immediate cloudiness, secondary alcohols give cloudiness within 5 minutes and primary alcohols have no cloudiness. The overall reaction that has occurred can be represented as

\[ \text{ROH} + \text{HCl} \rightarrow \text{RCI} + \text{H₂O} \]

(i) Draw three structural isomers with molecular formula C₄H₁₀O that can be distinguished using Lucas reagent and state the observation for each isomer.

(ii) Hence from your observation in (b)(i), suggest a possible product that is responsible for the cloudiness of the mixture.

(iii) Four structural isomers of molecular formula C₃H₆O₂ are as follows:

- E: CH₃CH(OH)CHO
- F: CH₃COCH₂OH
- G: HOCH₂CH₂CHO
- H: HCO₂CH₂CH₃

Show how isomers E to H can be adequately distinguished from one another by the use of simple chemical tests. You should also give brief descriptions of the chemical tests and expected observations for each isomer. [7]
(c) About 12 million tonnes of zinc are produced every year, of which 70% are obtained through mining. The ore is first roasted to produce zinc oxide, which is then further processed to obtain pure zinc through a series of steps.

(i) In the first step, ZnO is reacted with dilute sulfuric acid. Write a balanced equation for this reaction.

The next step involves electrolysis of the resulting solution obtained in (c)(i). A current of 10 000 A is passed through the solution in a series of electrolytic cells and zinc is deposited on the cathode of each cell. After 24 hours, each cell is shut down, the zinc coated cathodes are rinsed and pure zinc is mechanically stripped from the cathode.

(ii) Write the half-equations for each electrode reaction and hence, construct the overall balanced equation.

(iii) Assuming that only one cell is involved in the production in a 24-hour period
   I Calculate the mass of zinc produced in 24 hours.
   II Hence, calculate the thickness, in cm, of the zinc sheet produced.
   Given: current density = 500 A m⁻² of zinc deposited
   density of zinc = 7.14 g cm⁻³.
   [Current density is defined as the current flowing per unit area.]

   [Total: 20]
Piperidines are widely-used building blocks in the synthesis of organic compounds in the pharmaceutical industry. A possible synthetic route to prepare 2-methylpiperidine is shown below.

(a) (i) State the type of reaction that has occurred in stage I and identify a suitable reagent used.

(ii) Explain why stage I has to be carried out in an anhydrous condition. Include in your answer any relevant equation.

(iii) Draw the “dot-and-cross” diagram of the reagent used in stage I.

(iv) Suggest the structure of compound L and state the reagent and conditions required in stage II.

(b) Benzoic acid and 2-methylpiperidine can be used to synthesise piperocaine, a local anaesthesia used for infiltration and nerve block, via a two-step reaction. Benzoic acid is first converted into an intermediate, R, which is then converted to piperocaine.

Suggest the reagents and conditions required for each step and draw the structure of intermediate R produced.
(c) Benzoic acid is used as an antiseptic due to its ability to inhibit the growth of bacteria. Salicylic acid, a monohydroxybenzoic acid, has a similar function. The structure and solubility of both compounds in water are given in the table below.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Solubility / mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>0.0238</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>0.0145</td>
</tr>
</tbody>
</table>

(i) By considering structure and bonding, explain the difference in solubility of benzoic acid and salicylic acid.

(ii) Suggest a simple chemical test that can be used to distinguish benzoic acid from salicylic acid. State the reagents and conditions used and describe clearly the observations for each of the compound. Write a balanced equation for any reaction that occurs.

[5]

(d) Salicylic acid is also an important active metabolite of aspirin, a drug to relieve minor aches and pains, to reduce fever, and as an anti-inflammatory medication.

![Aspirin](image3.png)

The synthesis of aspirin involves treating salicylic acid with ethanoic anhydride, an acid derivative, in the presence of concentrated phosphoric acid. This esterification process (shown below) yields aspirin and ethanoic acid, which is considered a by-product of this reaction.

![Reaction](image4.png)
(i) Suggest why salicylic acid will not react with itself to produce an ester given the conditions stated above.

(ii) Suggest another reagent that can be used in place of ethanoic anhydride in the synthesis of aspirin from salicylic acid.

(iii) The synthesis of aspirin from salicylic acid with ethanoic anhydride may occur as follows.

Suggest the types of reactions occurring in stages I and II.

[3]

[Total: 20]
The Gabriel synthesis is a chemical reaction that transforms primary alkyl halides into primary amines using potassium phthalimide. It gives a high yield of primary amines and an example of the Gabriel synthesis is shown below.

(i) Step I is unusual as the amide hydrogen is quite acidic, hence it can react with KOH to produce potassium phthalimide. Suggest why the amide hydrogen is acidic in this case.

(ii) What type of reaction is step III?

(iii) Suggest a structure for M.
(b) 1-phenylmethanamine \((\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2)\) is a versatile organic compound which is used as a raw material for the production of Vitamin H. It is also an active ingredient in the production of nylon fibres.

1-phenylmethanamine can be produced via a similar two-step Gabriel amine synthesis.

\[
\begin{array}{ccc}
\text{N} & \text{P} & 1\text{-phenylmethanamine} \\
\end{array}
\]

Suggest the structures of compounds N and P. \([2]\]

(c) Phenylamine, along with its chlorine-substituted derivatives, is widely used in biology, medicine, as well as the paint and varnish industry.

(i) Suggest a synthetic route to form 2-methylphenylamine from methylbenzene.

\[
\begin{array}{c}
\text{2-methylphenylamine} \\
\end{array}
\]

(ii) The reaction below can proceed in the absence of a catalyst. Explain why milder conditions are required for this reaction compared to chlorination of benzene.

\[
\begin{array}{c}
\text{2-methylphenylamine} \\
\end{array}
\]
The Hofmann rearrangement is another organic reaction used to synthesis primary amines. It involves the reaction of a primary amide with aqueous alkaline bromine to form a primary amine with one less carbon atom than the starting material.

\[
\text{Br}_2 + \text{OH}^- (\text{aq}) \rightarrow \text{H} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{O} \quad \text{NH}_2 \quad \text{CH}_3 \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{NH}_2
\]

1-phenylmethanamine (C_6H_5CH_2NH_2) can also be produced in a three-step sequence given below where the last step is a Hofmann reaction.

(i) Draw the structures of compounds Q and S.

(ii) Suggest reagents and conditions required for stages I and II.

(e) (i) Arrange the following compounds in order of decreasing basicity. Explain your answer.

\[
\text{CH}_3 \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{NH}_2 \quad \text{and} \quad \text{NH}_3
\]

(ii) Calculate the pH of the resulting solution when 25 cm^3 of 0.0200 mol dm\(^{-3}\) HCJ is added to 25 cm^3 of 0.0300 mol dm\(^{-3}\) 1-phenylmethanamine (C_6H_5CH_2NH_2).

(The K\(_b\) value of 1-phenylmethanamine is 2.19 \times 10^{-5} mol dm\(^{-3}\).)

(iii) A 0.0200 mol dm\(^{-3}\) solution of 1-phenylmethanamine was mixed with an equal volume of 0.00100 mol dm\(^{-3}\) of aqueous magnesium sulfate. Determine whether a precipitate would be formed in this experiment.

(The numerical K\(_{sp}\) value of magnesium hydroxide is 1.8 \times 10^{-12}).
CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY 9647/03
Paper 3 Free Response Friday 24 AUGUST 2012

Candidates answer on separate paper.

Additional Materials: Answer Paper Data Booklet

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. [PILOT FRIXION ERASABLE PENS ARE NOT ALLOWED]
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
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of 14 printed pages and 0 blank page.

[Turn over
1 This question relates to the chemistry of Be, Mg, Al and their compounds.

(a) Beryllium compounds are toxic air pollutants. Inhalation of high levels of beryllium can cause inflammation of the lungs in humans and long-term exposure may cause chronic beryllium disease (berylliosis), in which granulomatous lesions develop in the lung.

(i) Given that charge density $\propto \frac{\text{ionic charge}}{\text{ionic radius}}$, calculate the relative charge densities of Be$^{2+}$, Mg$^{2+}$ and Al$^{3+}$, using relevant data from the Data Booklet.

Be$^{2+}$: 64.5, Mg$^{2+}$: 30.8, Al$^{3+}$: 60.0

(ii) Hence, predict what is observed when aqueous sodium hydroxide is gradually added to aqueous beryllium sulfate until the sodium hydroxide is in an excess. Write equations for all reactions that have taken place.

- white ppt, which dissolves in excess NaOH to give a colourless solution

$$\text{Be}^{2+}(aq) + 2\text{OH}^-(aq) \rightarrow \text{Be(OH)}_2(s)$$

$$\text{Be(OH)}_2(s) + 2\text{OH}^-(aq) \rightarrow \text{Be(OH)}_4^{2-}(aq)$$

(iii) Suggest the pH of the solution formed when beryllium chloride is dissolved in water. Give your reasoning.

pH 3

Be$^{2+}$ ions have high charge density, which polarises neighbouring H$_2$O molecules; hence, weakening O—H and H$^+$ lost

(iv) Magnesium ions are essential for the action of some enzymes (e.g. alkaline phosphatase found in the liver) by receiving electron pairs from oxygen and nitrogen atoms in the protein. It is thought that beryllium compounds are poisonous because they displace magnesium ions from these enzymes.

Suggest a reason why beryllium ions should behave in this way.

Be$^{2+}$ ions have higher charge density (or greater polarising power) than Mg$^{2+}$; hence has greater tendency to receive electron pairs to form dative covalent bonds.

(v) Beryllium chloride may be used as a catalyst in the chlorination of benzene. Suggest a reason why this is possible. Outline the mechanism to show how beryllium chloride is involved in this reaction.

In BeCl$_2$, Be atom has only 4 outer electrons and so, is able to act as lone pair acceptor (to generate Cl$^-$ electrophile)

$$\text{BeCl}_2 + \text{Cl}_2 \rightarrow \text{BeCl}_2^+ + \text{Cl}^-$$
(b) A student carried out a kinetics experiment using a roll of magnesium ribbon that had been exposed to air for some time. He placed a piece of magnesium ribbon of mass 0.12 g into a flask containing 15.0 cm$^3$ of 1.0 mol dm$^{-3}$ hydrochloric acid. The progress of the reaction was followed by measuring the pressure of the system at different times. The graph below shows the results of the experiment.

(i) Determine, by calculation, the limiting reagent for the experiment.

\[ \text{Mg} + 2\text{HC}l \rightarrow \text{MgC}l_2 + \text{H}_2 \]

\[
\text{amt of Mg} = \frac{0.12}{24.3} = 0.00494 \text{ mol}
\]

\[
\text{amt of HC}l = 1.0 \times \frac{15.0}{1000} = 0.015 \text{ mol}
\]

since \( \text{Mg} \equiv 2 \text{ HC}l \),

\[
\text{hence, amt of HC}l \text{ required for reaction} = 2 \times 0.00494 = 0.00988 \text{ mol} < 0.015 \text{ mol} \text{ (initial amount of HC}l \text{ used)}
\]

Hence, \( \text{Mg} \) is the limiting reagent.

(ii) Account for the change in pressure of the system as shown in the graph at points A, B, and from C onwards.
At A – initially rate is slow; due to layer of oxide/MgO formed on the surface of Mg ribbon due to oxidation in air

At B – rapid increase in rate; reaction is exothermic, heat evolved increases rate of reaction

C onwards – decrease in rate; as Mg (limiting reagent) is used up

(c) An alloy of aluminium and magnesium is used in boat-building.

A 1.75 g sample of the alloy was dissolved in the minimum volume of 4 mol dm$^{-3}$ hydrochloric acid and the solution was then made alkaline by the addition of aqueous sodium hydroxide until no further reaction occurred. The resultant mixture was filtered and the residue, $X$, rinsed with distilled water, all washings being added to the filtrate, $Y$. After air drying, 0.18 g of $X$ was obtained. Carbon dioxide was passed into $Y$ and a white solid, $Z$, which contained aluminium, was collected. Heating $Z$ to constant mass gave a residue of mass 3.16 g.

Suggest the identities of $X$, $Y$ and $Z$, and determine the percentage composition by mass of the alloy.

On dissolution in HCl (aq):

\[
\text{Mg(s)} + 2\text{HCl (aq)} \rightarrow \text{MgCl}_2 (aq) + \text{H}_2 (g) \quad \text{(and)} \quad \text{Al} + 3\text{HCl} \rightarrow \text{AlCl}_3 (aq) + 3/2 \text{H}_2 (g)
\]

On addition of excess NaOH (aq) till no further reaction occurs:

\[
\text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 (s) \quad \text{Residue X: Mg(OH)}_2
\]

\[
\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 (s)
\]

\[
\text{Al(OH)}_3 (s) + \text{OH}^- (aq) \rightarrow \text{Al(OH)}_4^- (aq) \quad \text{Filtrate Y: NaAl(OH)}_4 [\text{not Al(OH)}_4^-]
\]

On addition of CO$_2$ into Y:

\[
2\text{NaAl(OH)}_4 (aq) + \text{CO}_2 \rightarrow 2\text{Al(OH)}_3(s) + \text{Na}_2\text{CO}_3 (aq) \quad \text{White solid Z: Al(OH)}_3
\]

Heating Z to constant mass:

\[
2\text{Al(OH)}_3(s) \rightarrow \text{Al}_2\text{O}_3 (s) + 3\text{H}_2\text{O (aq)} \quad \text{residue of mass 3.16g = Al}_2\text{O}_3 (s)
\]

$X$ – Mg(OH)$_2$

$Y$ – NaAl(OH)$_4$

$Z$ – Al(OH)$_3$

\[
\text{mass of Mg in Mg(OH)}_2 = \frac{24.3}{24.3 + 2(16.0 + 1.0)} \times 0.18 = \frac{24.3}{58.3} \times 0.18 = 0.0750 \text{ g}
\]

\[
\text{mass of Al in Al}_2\text{O}_3 = \frac{2(27.0)}{2(27.0) + 3(16.0)} \times 3.16 = \frac{54.0}{102.0} \times 3.16 = 1.67 \text{ g}
\]

\[
\% \text{ of Mg in alloy} = \frac{0.0750}{1.75} \times 100 = 4.29 \%
\]
\[
\% \text{ of Al in alloy} = \frac{1.67}{1.75} \times 100 = 94.4 \%
\]

2-chlorobutane undergoes hydrolysis with NaOH(aq) via two different reaction pathways in the same reaction to form a mixture of two enantiomeric products.

\[
\text{CH}_3\text{CHClCH}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{CH}_3 + \text{NaCl}
\]

In one of the hydrolysis reaction pathways, only one product is formed and inversion of configuration occurs in the product. For the other reaction pathway, a racemic mixture is formed.

(a) In an experiment, one optical isomer of 2-chlorobutane undergoes hydrolysis and two enantiomeric products in a ratio of 95%:5% are formed.

(i) Draw the structures of the two enantiomeric products.

Few students scored full marks for this part. Many students could not represent the enantiomers appropriately.

Common errors:
1. No mirror line drawn (or) mirror line drawn as solid line.
2. Enantiomers are not represented as mirror images of each other.
3. Enantiomers are not represented in terms of tetrahedral geometry / 3D configuration.
4. Wedge and dotted line of 3D configuration not drawn in correct direction.
5. -CH₂CH₃ often wrongly represented as H₃CHC- in enantiomer structures.

(ii) One enantiomer is formed in a much higher percentage compared to the other. Explain clearly how this disparity arises by examining the mechanisms of both reaction pathways. You should name both mechanisms involved but an outline of the mechanism is not required.
Hydrolysis of 2-chlorobutane occurs via both \( \text{S}_\text{N}2 \) and \( \text{S}_\text{N}1 \) mechanisms. A racemic product is formed via the \( \text{S}_\text{N}1 \) mechanism whereas only 1 chiral product is formed during the \( \text{S}_\text{N}2 \) mechanism. As such, one of the enantiomers is formed in a greater proportion compared to the other.

One of the enantiomers is formed in a much greater percentage as the reaction proceeds largely via the \( \text{S}_\text{N}2 \) mechanism that results in the formation of 1 chiral product.

(iii) Write a rate equation for the reaction pathway that results in the inversion of the configuration and draw its energy profile diagram, given that the enthalpy change of the hydrolysis is exothermic.

\[
\text{rate} = k[\text{CH}_3\text{CHC/CH}_2\text{CH}_3][\text{OH}^-]
\]
(iv) Suggest the percentage of 2-chlorobutane that undergoes hydrolysis via the reaction pathway in (a)(iii).

90%

(v) Hence deduce how much faster the rate of this reaction pathway in (b)(ii) compares to that of the other reaction pathway.

9 times faster

(b) 2-chlorobutane is commonly produced from but-1-ene via reaction with hydrogen chloride.

\[ \text{CH}_2=\text{CHCH}_2\text{CH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_3(\text{l}) \]

(i) Name the other possible product in the above reaction.

1-chlorobutane

(ii) Predict the sign of \( \Delta S \) for this reaction, showing your reasoning.

\[ \text{CH}_2=\text{CHCH}_2\text{CH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_3(\text{l}) \]

\( \Delta S < 0 \)

Since 1 mol of \( \text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_3(\text{l}) \) is formed from 1 mol of \( \text{CH}_2=\text{CHCH}_2\text{CH}_3(\text{g}) \) and 1 mol of \( \text{HCl}(\text{g}) \), number of gas molecules in the system decreases as reaction proceeds. As molecules in the gaseous state have more ordered arrangement, hence entropy of system decreases.

(iii) Using relevant bond energy values from the Data Booklet, calculate the approximate value of \( \Delta H \) for the reaction in (b).

\[ \text{CH}_2=\text{CHCH}_2\text{CH}_3(\text{g}) + \text{HCl}(\text{g}) \rightleftharpoons \text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_3(\text{l}) \]

<table>
<thead>
<tr>
<th>Bond broken</th>
<th>Bond Energy / kJ mol(^{-1})</th>
<th>Bond formed</th>
<th>Bond energy / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>+610</td>
<td>C-C</td>
<td>-350</td>
</tr>
<tr>
<td>H-Cl</td>
<td>+431</td>
<td>C-H</td>
<td>-410</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-Cl</td>
<td>-340</td>
</tr>
</tbody>
</table>

\( \Delta H = +610 + 431 -350 -410 – 340 = -59 \text{ kJ mol}^{-1} \)

(iv) Bond energies quoted from the Data Booklet are average values. Other than this, explain why the method in (b)(iii) is not the most accurate for determining \( \Delta H \) of the reaction.
CH$_3$CHCl/CH$_2$CH$_3$ formed in the reaction is a liquid, whereas the bond energy method is only applicable for a gaseous system / bond energy refers to the energy required to break 1 mole of a covalent bond between two atoms in the gaseous state whereas CH$_3$CHCl/CH$_2$CH$_3$ formed is in the liquid state.

(v) Deduce how the rate of reaction of but-1-ene with hydrogen halides will vary from H-F to H-I, and give your reasoning.

The rate of reaction will increase from H-F to H-I as the bond energy of H-X decreases from H-F to H-I.

As the rate determining step of the mechanism involves the breaking of the H-X bond, the weaker the H-X bond, the more readily it will break, thus increasing the rate of reaction with but-1-ene.

This question was generally well-answered.

(vi) While HC-I react readily with alkenes under room conditions, HCN does not. Based on concepts of chemical bonding, suggest possible reasons for this.

HCN is a weaker electrophile than HC-I.
C-H bond in HCN is non-polar in nature, hence C-H bond does not break readily to release H$^+$. [10]

(c) HC-I can be prepared by adding concentrated sulphuric acid to solid sodium chloride. However when concentrated sulphuric acid is added to sodium iodide, the yield of HI is very low. Explain.

I$^-$ is a stronger reducing agent compared to Cl$^-$ hence it is able to further react with H$_2$SO$_4$ by reducing it to H$_2$S while itself is oxidised to I$_2$. As such, small amount of HI remains. [1]

[Total: 20]

3  This question explores the chemistry of zinc in biochemistry, organic chemistry and electrochemistry.

(a) Angiotensin I, a simple protein, undergoes hydrolysis with the aid of an enzyme, known as angiotensin-converting enzyme (ACE) to form angiotensin II. Angiotensin II is an important hormone that causes blood vessels to constrict, resulting in a rise in blood pressure.

(i) State how proteins can be hydrolysed to form a mixture of their constituent amino acids.

6 mol dm$^{-3}$ HC-I or H$_2$SO$_4$ or NaOH, and heat for several hours (eg 6 hours)
Some of the amino acids found in angiotensin II are shown below.

\[
\begin{align*}
\text{valine} & : & 
H_2N-C-\text{CO}_2H & \quad \text{tyrosine} & : & 
H_2N-C-\text{CO}_2H & \quad \text{arginine} & : & 
H_2N-C-\text{CO}_2H \\
& & \text{CH}_3\text{CH}_3 & & \text{OH} & & \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2
\end{align*}
\]

The side chains (R-groups) of angiotensin II could bind to targeted proteins through suitable R-group interactions. The R-group interactions are also used to maintain two specific protein structures.

(ii) Briefly describe one protein structure that involves R-group interactions.

**Tertiary structure and its description (also accept quaternary structure)**

(iii) Suggest three different types of R-group interactions in which the side chains of angiotensin II could bind to targeted proteins. Your answer should clearly indicate the side chains that might be involved.

- van der waals' forces of attraction with \(-\text{CH}(\text{CH}_3)_2\) from valine or \(-\text{CH}_2\text{C}_6\text{H}_5\) from tyrosine or \(-\text{CH}_2\text{CH}_2\text{CH}_2\) from arginine (or non-polar alkyl side chain)
- hydrogen bonding with phenol from tyrosine or \(-\text{C}=\text{NH}\) or \(-\text{NH}_2\) from arginine
- ionic bonding with \(-\text{NH}_3^+\) group from arginine

(iv) Another enzyme that functions similarly as ACE is carboxypeptidase. The active site of carboxypeptidase contains \(-\text{NH}_3^+\) group and a \(\text{Zn}^{2+}\) ion, which are both crucial in binding to suitable proteins. Below shows the hydrolysis of a protein (represented by RCONHCH(R')CO_2−) catalysed by this enzyme.
If there is a mutation such that carboxypeptidase does not contain Zn$^{2+}$, it will fail to function effectively as a catalyst. By using the above information, suggest why.

**Protein cannot effectively bind to active site of enzyme due to absence of ion-dipole attractions between Zn$^{2+}$ ions and C=O group**

(b) Lucas reagent is used to distinguish primary, secondary and tertiary alcohols. It consists of a solution of anhydrous ZnCl$_2$ in concentrated HCl. Upon addition of Lucas’ reagent at 28 °C, tertiary alcohols give immediate cloudiness, secondary alcohols give cloudiness within 5 minutes and primary alcohols have no cloudiness. The overall reaction that has occurred can be represented as

$$\text{ROH} + \text{HCl} \rightarrow \text{RCI} + \text{H}_2\text{O}$$

(i) Draw three structural isomers with molecular formula C$_4$H$_{10}$O that can be distinguished using Lucas reagent and state the observation for each isomer.

- CH$_3$CH$_2$CH$_2$OH or (CH$_3$)$_2$CHCH$_2$OH: no cloudiness
- CH$_3$CH(OH)CH$_2$CH$_3$: cloudiness within 5 minutes
- (CH$_3$)$_3$COH: immediate cloudiness

(ii) Hence from your observation in part (i), suggest a possible product that is responsible for the cloudiness of the mixture.

CH$_3$CH(CI)CH$_2$CH$_3$ or (CH$_3$)$_3$CCI

(iii) Four structural isomers of molecular formula C$_3$H$_6$O$_2$ are:

- **E**: CH$_3$CH(OH)CHO
- **F**: CH$_3$COCH$_2$OH
- **G**: HOCH$_2$CH$_2$CHO
- **H**: HCO$_2$CH$_2$CH$_3$

Show how isomers **E** to **H** can be adequately distinguished from one another by the use of simple chemical tests. You should also give brief descriptions of the chemical tests and expected observations for each isomer.
<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E: CH₃CH(OH)CHO</td>
<td>F: CH₃COCH₂OH</td>
<td>G: HOCH₂CH₂CHO</td>
<td>H: HCO₂CH₂CH₃</td>
</tr>
<tr>
<td>1</td>
<td>Add Lucas’ reagent.</td>
<td>Cloudiness within 5 minutes</td>
<td>No cloudiness</td>
<td>No cloudiness</td>
</tr>
<tr>
<td>2</td>
<td>Add Na metal.</td>
<td>Effervescence (of H₂) observed</td>
<td>Effervescence (of H₂) observed</td>
<td>Effervescence (of H₂) observed</td>
</tr>
<tr>
<td>3</td>
<td>Add SO₂Cl₂ or PCl₅.</td>
<td>Steamy fumes (of HCl) observed</td>
<td>Steamy fumes (of HCl) observed</td>
<td>No fumes</td>
</tr>
<tr>
<td>4</td>
<td>Add alkaline I₂(aq) and heat.</td>
<td>Yellow ppt (of CH₁₃) formed.</td>
<td>Yellow ppt (of CH₁₃) formed.</td>
<td>No ppt</td>
</tr>
<tr>
<td>5</td>
<td>Add 2,4-dinitrophenyl-hydrazine and heat.</td>
<td>Orange ppt formed</td>
<td>Orange ppt formed</td>
<td>No ppt</td>
</tr>
<tr>
<td>6</td>
<td>Add Tollens’ reagent and heat.</td>
<td>Silver mirror formed</td>
<td>No silver mirror</td>
<td>Silver mirror formed</td>
</tr>
<tr>
<td>7</td>
<td>Add Fehling’s solution and heat.</td>
<td>Red ppt (of Cu₂O) formed</td>
<td>No ppt</td>
<td>Red ppt (of Cu₂O) formed</td>
</tr>
<tr>
<td>8</td>
<td>Add acidified KMnO₄ and heat.</td>
<td>Purple KMnO₄ decolourised.</td>
<td>Purple KMnO₄ decolourised.</td>
<td>Purple KMnO₄ decolourised and effervescence (of CO₂) observed. [due to formation of HCO₂H on acidic hydrolysis, which gets oxidised to CO₂ and H₂O.]</td>
</tr>
</tbody>
</table>

(c) About 12 million tonnes of zinc are produced every year, of which 70 % are obtained through mining. The ore is first roasted to produce zinc oxide, which is then further processed to obtain pure zinc through a series of steps.
(i) In the first step, ZnO is reacted with dilute sulfuric acid. Write a balanced equation for this reaction.

\[
\text{ZnO} + H_2SO_4 \rightarrow \text{ZnSO}_4 + H_2O \quad \text{or} \quad \text{ZnO} + 2H^+ \rightarrow \text{Zn}^{2+} + H_2O
\]

The next step involves electrolysis of the resulting solution obtained in (i). A current of 10 000 A is passed through the solution in a series of electrolytic cells and zinc is deposited on the cathode of each cell. After 24 hours, each cell is shut down, the zinc coated cathodes are rinsed and pure zinc is mechanically stripped from the cathode.

(ii) Write the half-equations for each electrode reaction and hence, construct the overall balanced equation.

At cathode: \( \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \)

At anode: \( 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \)

Overall: \( 2\text{Zn}^{2+} + 2H_2O \rightarrow 2\text{Zn} + O_2 + 4H^+ \)

(iii) Assuming that only one cell is involved in the production in a 24-hour period

I. Calculate the mass of zinc produced in 24 hours.

\[
\text{Zn}^{2+} \equiv 2e^- \equiv \text{Zn}
\]

Total charge passed through in 24 hours = \( 10 000 \times 24 \times 60 \times 60 = 8.64 \times 10^8 \text{ C} \)

Amount of electrons = \( \frac{8.64 \times 10^8}{9.65 \times 10^4} = 8.953 \times 10^3 \text{ mol} \)

Amount of Zn = \( \frac{1}{2} \times 8.953 \times 10^3 = 4.477 \times 10^3 \text{ mol} \)

Mass of Zn = \( 4.477 \times 10^3 \times 65.4 = 2.93 \times 10^5 \text{ g ( = 293 kg)} \)

II. Hence, calculate the thickness, in cm, of the zinc sheet produced.

Given: current density = 500 A m\(^{-2}\) of zinc deposited

density of zinc = 7.14 g cm\(^{-3}\).

[Current density is defined as the current flowing per unit area]

Total volume of Zn deposited = \( \frac{2.93 \times 10^5}{7.14} = 4.1036 \times 10^4 \text{ cm}^3 \)

Total surface area = \( \frac{10 000}{500} = 20 \text{ m}^2 = 2 \times 10^5 \text{ cm}^2 \)

Thickness = \( \frac{4.1036 \times 10^4}{2.00 \times 10^5} = 0.205 \text{ cm} \)
Piperidines are widely used building blocks in the synthesis of organic compounds in the pharmaceutical industry. A possible synthetic route of 2-methylpiperidine is shown below.

(a) (i) State the type of reaction that has occurred in stage I and identify a suitable reagent used.

Nucleophilic substitution

PCl₅ / PCl₃ / SOCl₂

(ii) Explain why stage I has to be carried out in an anhydrous condition. Include in your answer any relevant equation.

PCl₅ / PCl₃ / SOCl₂ undergoes hydrolysis when reacted with water.

PCl₅ + H₂O → POCl₃ + 2 HCl

OR PCl₃ + 3H₂O → H₃PO₃ + 3HCl

OR SOCl₂ + H₂O → SO₂ + 3HCℓ

(iii) Draw the dot-and-cross diagram of the reagent used in stage I.

(iv) Suggest the structure of compound L and state the reagent and conditions required in stage II.
LiA/H₄ in dry ether, r.t.p.
OR heat with H₂ over Ni catalyst at 140°C

(b) Benzoic acid and 2-methylpiperidine can be used to synthesise piperocaine (shown below), a local anaesthesia used for infiltration and nerve block, via a two-step reaction. Benzoic acid is first converted into an intermediate, R, which is then converted to piperocaine.

\[
\text{Benzoic acid} \xrightarrow{\text{H₂SO₄, reflux}} R \xrightarrow{\text{2-methylpiperidine, reflux}} \text{piperocaine}
\]

Suggest a synthetic route for piperocaine. State clearly the reagents and conditions required for each step and draw the structure of intermediate R produced.

(c) Benzoic acid is used as an antiseptic due to its ability to inhibit the growth of bacteria. Salicylic acid, a monohydroxybenzoic acid, has a similar function. The structure and solubility of both compounds in water are shown in the table below.

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Solubility / mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td><img src="image" alt="Benzoic acid structure" /></td>
<td>0.0238</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td><img src="image" alt="Salicylic acid structure" /></td>
<td>0.0145</td>
</tr>
</tbody>
</table>

(i) By considering structure and bonding, explain the difference in solubility of benzoic acid and salicylic acid.

Both compounds are simple covalent molecules and can form hydrogen bonding with water molecules.
However, **intramolecular hydrogen bonding** is present in salicylic acid due to the **close proximity** of the carboxyl group and hydroxyl group.

Thus, the hydrogen bonding between salicylic acid and water is **less extensive** than the hydrogen bonding between benzoic acid and water. This results in the lower solubility of salicylic acid in water.

(ii) Suggest a simple chemical test that can be used to distinguish benzoic acid from salicylic acid. State the reagents and conditions used and describe clearly the observations for each of the compound. Write a balanced equation for any reaction that occurs.

Add **$\text{Br}_2(\text{aq})$** to each compound separately at **room temperature**.

$\text{Br}_2(\text{aq})$ turned from **brown to colourless** when reacted with salicylic acid due to the presence of phenol.

$\text{Br}_2(\text{aq})$ **remained brown** when reacted with benzoic acid

$$\text{O} \quad \text{OH} \quad + \quad 2\text{Br}_2 \quad \rightarrow \quad \text{O} \quad \text{OH} \quad + \quad 2\text{HBr}$$

OR

Add **Neutral FeCl}_3(\text{aq})$** to each compound separately.

**Purple Coloration** when reacted with salicylic acid due to the presence of phenol.

**No such coloration** with benzoic acid

$$6 \text{O} \quad \text{OH} \quad + \quad \text{FeCl}_3 \quad \rightarrow \quad \left[\text{Fe}(\text{COOH})_6\right]^{2-} \quad + \quad 3\text{Cl}^- \quad + \quad 6\text{H}^+$$

(d) Salicylic acid is also an important active metabolite of aspirin(shown below), a drug to relieve minor aches and pains, to reduce fever, and as an anti-inflammatory medication.

![Aspirin Structure](attachment:aspirin.png)
The synthesis of aspirin involves treating salicylic acid with ethanoic anhydride, an acid derivative, in the presence of concentrated phosphoric acid. This esterification process (shown below) yields aspirin and ethanoic acid, which is considered a by-product of this reaction.

(i) Suggest why salicylic acid will not react with itself to produce an ester given the conditions stated above.

Phenol is too weak a nucleophile (as the lone pair of electrons on the oxygen can delocalised into the benzene ring, thus less available for donation) for esterification with benzoic acid to occur.

(ii) Suggest another reagent that can be used in place of ethanoic anhydride in the synthesis of aspirin from salicyclic acid.

Ethanoyl Chloride

(iii) The synthesis of aspirin from salicyclic acid with ethanoic anhydride may occur as follows.
Suggest the types of reactions occurring in stage I and II.

I. Acid-base reaction
II. Nucleophilic addition

5 (a) The Gabriel synthesis is a chemical reaction that transforms primary alkyl halides into primary amines using potassium phthalimide. It gives a high yield of primary amines and an example of the Gabriel synthesis is shown below.

(i) Step I is unusual as the amide hydrogen is quite acidic, hence it can react with KOH to produce potassium phthalimide. Suggest why the amide hydrogen is acidic in this case.

**Presence of two electron-withdrawing C=O groups increases polarisation of N-H bond and weakens the N-H bond, hence amide hydrogen is acidic.**

(ii) What type of reaction is step III?

**Step II: hydrolysis**

(iii) Suggest a structure for M.
(b) 1-phenylmethanamine ($C_6H_5CH_2NH_2$) is a versatile organic compound which is used as a raw material for the production of Vitamin H and is also an active ingredient in the production of nylon fibres.

1-phenylmethanamine can be produced via a similar two-step Gabriel amine synthesis.

\[
\begin{align*}
\text{N} & \quad \text{OH}^- / H_2O \\
\text{P} & \quad \text{CH}_2\text{NH}_2
\end{align*}
\]

1-phenylmethanamine

Suggest the structures of compounds N and P.

N: $\begin{align*}
\text{or } & \quad \text{CH}_2\text{Br} \\
\text{or } & \quad \text{CH}_2\text{Cl}
\end{align*}$

P: $\begin{align*}
\text{CH}_2\text{NH}_2
\end{align*}$

(c) Phenylamine, along with its chlorine-substituted derivatives, is widely used in biology, medicine as well as the paint and varnish industry.

(i) Suggest a synthetic route to form 2-methylphenylamine from methylbenzene.
(ii) The reaction below can proceed in the absence of a catalyst. Explain why milder conditions are required for this reaction compared to chlorination of benzene.

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{NH}_2 & \text{Cl}_2(\text{aq}) \\
\text{Cl} & \text{Cl} \\
\end{align*}
\]

Presence of electron-donating NH2 group increases electron-density on the benzene ring or activates the ring towards electrophilic substitution and thus milder conditions are required for the reaction to occur. Aqueous chlorine is used to allow polysubstitution to occur.

**Comments**

1. Many students lose this mark due to poor phrasing, using words like “charge density of the benzene” or “the negativity of the benzene ring” is increased. These are not accepted since it is not an ion to begin with!

(d) The Hofmann rearrangement is another organic reaction used to synthesis primary amines. It involves the reaction of a primary amide with aqueous alkaline bromine to form a primary amine with one less carbon atom than the starting material.

\[
\begin{align*}
\text{CH}_3 & \text{C} \underset{\text{O}}{\text{C}} \text{C} \text{NH}_2 \\
\text{CH}_3 & \text{Br}_2 + \text{OH}^- (\text{aq}) \\
\text{CH}_3 & \text{C} \underset{\text{NH}_2}{\text{C}} \text{NH}_2 \\
\end{align*}
\]

1-phenylmethanamine (C₆H₅CH₂NH₂) can also be produced in a three-step sequence given below where the last step is a Hofmann reaction.
(i) Draw the structures of compounds Q and S.

Q: \[
\text{CH}_2\text{CONCl}
\]

S: \[
\text{CH}_2\text{CONH}_2
\]

(ii) Suggest reagents and conditions required for stages I and II.

**Stage I:** PCl₅, rt / SOCl₂, reflux / PCl₃ reflux

**Stage II:** NH₃, rt

(e) (i) Arrange the following compounds in order of decreasing basicity. Explain your answer.

\[
\begin{align*}
\text{CH}_2\text{NH}_2 \quad &> \quad \text{H}_2\text{NCH}_3
\end{align*}
\]

and NH₃.

\[
\begin{align*}
\text{CH}_2\text{NH}_2 \quad &> \quad \text{H}_2\text{NCH}_3
\end{align*}
\]

is the strongest base as the presence of electron-donating alkyl group increases availability of lone pairs of electrons on N and thus make it more available to accept a proton.

\[
\begin{align*}
\text{CH}_2\text{NH}_2
\end{align*}
\]

is the weakest base as the lone pair of electrons on N can be delocalised into the benzene ring and thus lone pair of electrons is less available to accept proton.

(ii) Calculate the pH of the resulting solution when 25 cm³ of 0.0200 mol dm⁻³ HCl is added to 25 cm³ of 0.0300 mol dm⁻³ 1-phenylmethanamine (C₆H₅CH₂NH₂).

(The Kₛ value of 1-phenylmethanamine is 2.19 x 10⁻⁵ mol dm⁻³.)
A weak base and the conjugate acid is present in the final solution (i.e. alkaline buffer present)

\[
pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} = - \log (2.19 \times 10^{-5}) + \log \frac{0.0005}{0.0025} = 4.961
\]

\[
pH = 14 - 4.961 = 9.04
\]

(iii) A 0.0200 mol dm^{-3} solution of 1-phenylmethanamine was mixed with an equal volume of 0.00100 mol dm^{-3} of aqueous magnesium sulfate. Determine whether a precipitate would be formed in this experiment.

(The numerical \(K_{sp}\) value of magnesium hydroxide is \(1.8 \times 10^{-12}\)).

\[
\text{mg(OH)}_2(s) \rightleftharpoons \text{mg}^{2+} + 2\text{OH}^{-}
\]

\[
[\text{OH}^{-}] = \sqrt{2.19 \times 10^{-5} \times 0.01} = 0.0004680 \text{ mol dm}^{-3}
\]

Ionic product of Mg(OH)_2 = \([\text{Mg}^{2+}] [\text{OH}^{-}]^2 = \frac{0.001}{2} \times (0.0004680)^2 = 1.10 \times 10^{-10} > \text{Ksp of Mg(OH)}_2
\]

Yes, a precipitate would be formed.
INSTRUCTIONS TO CANDIDATES

1. Write your name, index number and class on this question paper.
2. There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers A, B, C and D. Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Optical Mark Sheet.
3. Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
4. Any rough working should be done in this booklet.
5. You may use a calculator.
Section A

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

1 To determine the mass of arsenic present in a sample of pesticide, all the arsenic was first converted to arsenate ion, $\text{AsO}_4^{3-}$. $1.25 \times 10^{-3}$ mol of $\text{AgNO}_3$ was then added to precipitate $\text{AsO}_4^{3-}$ as $\text{Ag}_3\text{AsO}_4$. The excess $\text{Ag}^+$ ions needed 3.64 cm$^3$ of 0.054 mol dm$^{-3}$ KSCN to form silver thiocynate, $\text{AgSCN}$.

Calculate the mass of arsenic ($A_r = 74.9$) present in the sample of pesticide.

A 0.015 g  
B 0.026 g  
C 0.079 g  
D 0.488 g

2 In an experiment, a sample was vapourised, ionised and passed through an electric field. Analysis of the deflection occurring at the electric region revealed the following data for the sample. It was observed that a beam of $\text{Na}^+$ gives an angle of deflection of 4.3°.

![Diagram of electric field with deflection angles]

What are the possible identities of unknown particles, $q$ and $r$, and the value of $\alpha$?

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$q$</td>
<td>$r$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>A</td>
<td>Be$^{2+}$</td>
<td>Br$^-$</td>
</tr>
<tr>
<td>B</td>
<td>Be$^{2+}$</td>
<td>S$^{2-}$</td>
</tr>
<tr>
<td>C</td>
<td>Ba$^{2+}$</td>
<td>Br$^-$</td>
</tr>
<tr>
<td>D</td>
<td>Ba$^{2+}$</td>
<td>S$^{2-}$</td>
</tr>
</tbody>
</table>
3 How many moles of electrons must be removed from each mole of methylbenzene, C₆H₅CH₃, when it is oxidised to benzoic acid, C₆H₅COOH?

A 1  
B 2  
C 4  
D 6  

4 Which graph correctly describes the behaviour of fixed masses of the ideal gases I and J, where I has a higher Mᵣ than J?

A Constant T  

B Constant T  

C Constant P  

D Constant P
A student used the set-up below to heat a can containing 300 g of water.

The following data were recorded:

\[
\text{mass of propan-1-ol burnt} = m \text{ g} \\
\text{change in temperature of water} = \Delta T \text{ °C}
\]

Given that:

\[
\begin{align*}
\text{relative molecular mass of propan-1-ol} &= 60.0 \\
\text{enthalpy change of combustion of propan-1-ol} &= -2021 \text{ kJ mol}^{-1} \\
\text{specific heat capacity of water} &= c \text{ J g}^{-1} \text{ K}^{-1}
\end{align*}
\]

What is the efficiency of this heating process?

A \[ \frac{m \times 2021 \times 1000}{300 \times c \times \Delta T \times 60.0} \times 100\% \]

B \[ \frac{m \times c \times \Delta T \times 60.0}{300 \times 2021 \times 1000} \times 100\% \]

C \[ \frac{300 \times c \times \Delta T \times 60.0}{m \times 2021} \times 100\% \]

D \[ \frac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\% \]

Which of the following statements best explains why calcium and chlorine form CaCl\(_2\) rather than CaCl\(_3\)?

A Less energy is required to remove one electron from the calcium atom than to remove two electrons.

B More energy is released in forming chloride ions from chlorine molecules in the formation of CaCl\(_2\)(s) than in the formation of CaCl\(_3\)(s).

C The lattice energy of CaCl\(_3\)(s) is less exothermic than that of CaCl\(_2\)(s).

D When CaCl\(_3\)(s) is formed from its elements, more energy is released than when CaCl\(_2\)(s) is formed from its elements.
An exothermic chemical reaction proceeds by two stages.

\[ \text{reactants} \rightarrow \text{intermediate} \rightarrow \text{products} \]

The activation energy of stage 1 is 50 kJ mol\(^{-1}\). The overall enthalpy change of reaction is \(-100\) kJ mol\(^{-1}\).

Which diagram could represent the energy level diagram for the reaction?

A

\[
\begin{array}{c}
\text{progress of reaction} \\
\hline
\text{reactants} \\
\text{products}
\end{array}
\]

B

\[
\begin{array}{c}
\text{progress of reaction} \\
\hline
\text{reactants} \\
\text{products}
\end{array}
\]

C

\[
\begin{array}{c}
\text{progress of reaction} \\
\hline
\text{reactants} \\
\text{products}
\end{array}
\]

D

\[
\begin{array}{c}
\text{progress of reaction} \\
\hline
\text{reactants} \\
\text{products}
\end{array}
\]

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9647/01 [Turn over
A student set up the hydrogen electrode shown in the diagram below.

What would have to be changed to make this a standard hydrogen electrode?

A  the acid solution used  
B  the temperature of the gas and of the acid solution  
C  the pressure of the gas  
D  the metal comprising the electrode

The graph below shows how the fraction of a substance, $X$, represented by one of the following compounds in the equilibrium mixture shown below varies with temperature at pressures of $y$ Pa and $z$ Pa.

$$4\text{NH}_3(g) + 3\text{O}_2(g) \rightleftharpoons 2\text{N}_2(g) + 6\text{H}_2\text{O}(g) \quad \Delta H = -1267 \text{ kJ mol}^{-1}$$

Identify $X$ and the correct magnitudes of $y$ and $z$.

X  | Pressure  
---|---  
A  | $\text{NH}_3$  
B  | $\text{N}_2$  
C  | $\text{O}_2$  
D  | $\text{H}_2\text{O}$
10 The value of the ionic product of water, $K_w$, varies with temperature.

<table>
<thead>
<tr>
<th>temperature / °C</th>
<th>$K_w$ / mol² dm⁻⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$0.1 \times 10^{-14}$</td>
</tr>
<tr>
<td>10</td>
<td>$0.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>25</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

What can be deduced from this information?

A Molar concentration of $H^+$ ions decreases with temperature.
B The ionic dissociation of water decreases by a factor of 10 between 0 °C and 25 °C.
C The association of water molecules by hydrogen bonding increases as temperature increases.
D Water is no longer a neutral liquid at temperatures below 25 °C.

11 Ozone in the earth’s atmosphere decomposes according to the equation:

$$2O_3(g) \rightarrow 3O_2(g)$$

This reaction is thought occur via a two–step mechanism:

Step 1  $O_3(g) \rightleftharpoons O_2(g) + O(g)$ fast, reversible
Step 2  $O_3(g) + O(g) \rightarrow 2O_2(g)$ slow

What rate law is consistent with this mechanism?

A Rate = $k[O_3]^2 / [O_2]$  
B Rate = $k[O_3]^2 / [O_2]^3$
C Rate = $k[O_3]$  
D Rate = $k[O_3]^2$

12 S is a transition element. The 3d sub–shell of S in the compound $K[S(C_2O_4)_2(NH_3)_2]$ contains 3 electrons. How many unpaired electrons does S contain when it is in the elemental state?

A 2  
B 3  
C 4  
D 5
A reaction scheme starting from aqueous copper(II) sulphate solution is shown below. Both \( \text{G} \) and \( \text{H} \) are copper-containing species.

\[
\begin{align*}
\text{CuSO}_4(\text{aq}) & \xrightarrow{\text{NH}_3(\text{aq})} \text{G} & \text{excess} & \text{NH}_3(\text{aq}) & \xrightarrow{\text{Na}_4\text{edta}(\text{aq})} & \text{H} & \xrightarrow{\text{[Cu(edta)]}^2-} & \text{(aq)} \\
\text{I} & & \text{II} & & \text{III} & \\
\end{align*}
\]

Which of the following statements is correct?

A. \( \text{NH}_3 \) is a ligand in reaction I.

B. Reaction II is a redox reaction.

C. \( \text{H} \) is a deep blue solution containing \([\text{Cu(NH}_3)_3(\text{H}_2\text{O})_3]\text{SO}_4\).

D. The entropy of the system increases when reaction III occurs.

14 \( \text{W, X, Y} \) and \( \text{Z} \) are elements in Period 3.

\( \text{W} \) has greater electrical conductivity than \( \text{Y} \) but lower first ionisation energy than \( \text{X} \). \( \text{Y} \) has higher melting point than \( \text{W} \), and \( \text{Z} \) has a greater atomic radius than \( \text{W} \).

Based on this information, which of the following is a possible arrangement of these elements in increasing proton number?

A. \( \text{W, X, Y, Z} \)

B. \( \text{X, Y, W, Z} \)

C. \( \text{Y, X, Z, W} \)

D. \( \text{Z, W, Y, X} \)

15 An aqueous solution of sodium carbonate is added very slowly, till excess, to a solution containing 0.2 mol dm\(^{-3}\) of zinc nitrate and 0.1 mol dm\(^{-3}\) of silver nitrate at 25 °C.

The numerical value of the solubility product of zinc carbonate at 25 °C is \( 1.4 \times 10^{-11} \) and that of silver carbonate is \( 8.1 \times 10^{-12} \).

Which statement describes what happens in the solution?

A. Both zinc carbonate and silver carbonate are precipitated at the same time.

B. Zinc carbonate is precipitated first, followed by silver carbonate.

C. Silver carbonate is precipitated first, followed by zinc carbonate.

D. Only silver carbonate is precipitated.
16. Which of the following statements about the Group VII compounds is correct?

A. The halogens increase in oxidising power down the group.
B. The $K_{sp}$ values of the silver halides decrease down the group.
C. The lattice energy of the silver halides becomes more exothermic down the group.
D. The hydration energy of the gaseous halide ions becomes more negative down the group.

17. What is the total number of different chloroethanes, of formula $\text{C}_2\text{H}_6-n\text{Cl}_n$, where $n$ can be any integer from 1 to 6?

A. 6  B. 8  C. 9  D. 10

18. In which sequence is it correctly stated that the value of $pK_a$ decreases continuously?

A. $\text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H}$
B. $\text{C}_6\text{H}_5\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H}$
C. $\text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH}$
D. $\text{CCl}_3\text{CO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH}$

19. Oxidation of an alkene $X$ gives a diol; further oxidation gives a diketone. Which one of the following could be $X$?

A. ![Structure A]
B. ![Structure B]
C. ![Structure C]
D. ![Structure D]
20 Compound Z, which has an aromatic ring structure, is subjected to oxidative degradation under suitable conditions.

\[ Z \]

What are the most likely organic products from this reaction?

A. \( \text{CO}_2\text{H} \) and \( \text{CO}_2\text{H} \)

B. \( \text{CO}_2\text{H} \)

C. \( \text{CO}_2\text{H} \)

D. \( \text{CO}_2\text{H} \)

21 An account in a student’s notebook read:

‘An excess of aqueous bromine was added to aqueous phenol in a test–tube. 2,4,6–Tribromophenol was produced as a creamy–white precipitate suspended in a yellow alkaline solution.’

Which statement in this account must have been wrong?

A. The precipitate is 2,4,6–tribromophenol
B. The precipitate obtained is creamy–white.
C. The resultant solution is alkaline.
D. The resultant solution is yellow.
22  Citric acid, which causes the sharp taste of lemon juice, has the following formula.

\[
\text{C}_6\text{H}_8\text{O}_7
\]

Which of the following reacts completely with 1 mol of citric acid?

A  3 mol of PCl\(_5\)(s)
B  3 mol of Na\(_2\)CO\(_3\)(aq)
C  4 mol of NaOH(aq)
D  4 mol of Na(s)

23  CS has the structure shown below, is an active component of 'tear gas' and is readily hydrolysed.

Which of the following is a possible hydrolysis product of CS?

A  \[
\text{C}_6\text{H}_5\text{C} = \text{C} - \text{NH}_2\text{NH}_2
\]
B  \[
\text{C}_6\text{H}_5\text{C} = \text{C} - \text{CO}_2\text{CO}_2^-
\]
C  \[
\text{C}_6\text{H}_5\text{C} = \text{C} - \text{CONH}_2\text{CONH}_2
\]
D  \[
\text{C}_6\text{H}_5\text{CO}_2\text{H}
\]
Members of an ethyl ester homologous series have the general formula

$$R\text{O}C\text{H}_2\text{CH}_3$$

where $R = C_nH_{2n+1}$, and $n = 0, 1, 2 \ldots$

Each member undergoes Claisen condensation with either itself or another member of the series to form a β–keto ester. For example, the first member of the series, ethyl ethanoate, combines with itself in the presence of sodium ethanoate, followed by acidification, to form ethyl 3–oxobutanoate. Ethanol is eliminated in the process.

Which one of the following is a possible product of the Claisen condensation between ethyl ethanoate and the fourth member of the series?

A

B

C

D
At alkaline pH, Sanger’s reagent, also known as FDNB, reacts with the amine group in terminal amino acid residues of polypeptide chains. Upon hydrolysis, coloured dinitrophenyl compounds are produced. An example of such a reaction is as follows:

Which of the following terms or phrases best describes the type of reaction illustrated above?

A Nucleophilic substitution
B Elimination
C Electrophilic addition
D Electrophilic substitution

Which of the following mechanistic steps is least likely to occur?

A \( \text{H}_3\text{C} - \text{CO} + \text{CN}^- \rightarrow \text{H}_3\text{C} - \text{C} - \text{H} \)
B \( \text{C}_6\text{H}_6 + \text{Br} \rightarrow \text{C}_6\text{H}_5\) + \text{HBr}
C \( \text{C}_6\text{H}_5\text{Br} + \text{Br}^- \rightarrow \text{C}_6\text{H}_5\text{Br} \)
D \( \text{C}_6\text{H}_5\text{CH}_2\text{I} \rightarrow \text{C}_6\text{H}_5\text{CH}_2^- + \text{I}^- \)
Questions 27 and 28 refer to amino acid, arginine, which has the structure below.

\[
\text{pK}_a = 2.01 \\
\text{pK}_a = 9.04 \\
\text{pK}_a = 12.48
\]

arginine

27 Which of the following is the zwitterion form of arginine?

A \[
\text{H}_2\text{N}^+\text{NH} - \text{NH}_2\text{COO}^- \\
\text{NH}_3^+
\]

B \[
\text{H}_2\text{N}^+\text{NH} - \text{NH}_2\text{COO}^- \\
\text{NH}_2
\]

C \[
\text{H}_2\text{N}^+\text{NH} - \text{NH}_2\text{COO}^- \\
\text{NH}_3^+
\]

D \[
\text{H}_2\text{N}^+\text{NH} - \text{NH}_2\text{COO}^- \\
\text{NH}_3^+
\]
An aqueous alkali is gradually added to a certain volume of an acidic solution of arginine. The concentration of each solution is similar. Which of the following graphs best represents the change of pH during the reaction?

(pi represents the isoelectric point of arginine, and equivalents of OH– represent the number of moles of OH– that reacts with one mole of H+ in an acid–base reaction.)
Partial hydrolysis of insulin, the hormone essential for carbohydrate metabolism, gives the following tripeptide.

\[
\text{CH}_2\text{CH}_2\text{CO}_2\text{H} \\
(\text{CH}_3)_2\text{CH}\text{CH(NH}_2\text{)CONHCHCONHCH(CH}_3\text{)CO}_2\text{H}
\]

Which compound could be obtained by further hydrolysis of this tripeptide?

A \( \text{CH}_3\text{CH(CO}_2\text{H)}_2 \)

B \( (\text{CH}_3)_2\text{CHCH(NH}_2\text{)CONH}_2 \)

C \( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \)

D \( \text{H}_2\text{NCONHCHCO}_2\text{H} \)

A hexapeptide, \( \text{P} \), is hydrolysed to the following dipeptides:

- Ileu–Val
- Ala–Pro
- Lys–Leu

Carboxypeptidase, an enzyme which hydrolyses the peptide bond of an amino acid residue at the C–terminus, acts on \( \text{P} \) to liberate valine. 2,4–dinitrofluorobenzene, which reacts with an amino acid residue at the N–terminus to form dinitrophenyl–amino acid, reacts with \( \text{P} \) to yield, after hydrolysis, 2,4–dinitrophenylalanine. Which of the following is the amino acid sequence of polypeptide \( \text{P} \)?

A Ala–Pro–Lys–Leu–Ileu–Val

B Val–Ileu–Lys–Leu–Pro–Ala

C Ileu–Val–Ala–Pro–Lys–Leu

D Lys–Leu–Ala–Pro–Ileu–Val
Section B

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

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

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

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>1</td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 An amalgam is formed when mercury is used to dissolve another metal. The amalgam used in dental filling is a mixture of mercury and tin, SnHg. The diagram below shows an electrochemical cell formed between an amalgam filling and a gold inlay.

Some standard electrode potentials are given below.

\[
\begin{align*}
\text{Sn}^{2+}/\text{Sn}_8\text{Hg} & \quad -0.13 \text{ V} \\
\text{Au}^{3+}/\text{Au} & \quad +1.50 \text{ V} \\
\text{Al}^{3+}/\text{Al} & \quad -1.66 \\
\text{O}_2/\text{H}_2\text{O} & \quad +1.23
\end{align*}
\]

Which of the following statement(s) about the amalgam is/are true?

1. Regular consumption of acidic beverages promotes the corrosion of the amalgam filling.
2. When a piece of aluminium foil is in contact with the amalgam filling, the amalgam filling becomes the cathode.
3. \(\text{Sn}^{2+}\) ions are momentarily discharged when the amalgam filling is in contact with the gold inlay.
The responses A to D should be selected on the basis of

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

32 Ammonia is manufactured industrially by the Haber Process as shown.

\[ \text{N}_2(g) + 3\text{H}_2(g) \xleftrightarrow{\text{\Delta H < 0}} 2\text{NH}_3(g) \]

The operating conditions are:
400 to 450 °C; a pressure of 200 atm; an iron catalyst

Which of the following statement(s) is/are true about the Haber process for the manufacture of ammonia?

1. At higher temperatures, the production of ammonia becomes thermodynamically less feasible.
2. At higher pressures, the yield goes down but the rate of production of ammonia is faster.
3. The presence of a catalyst shifts the equilibrium position to the right and increases the yield.

33 Three unsaturated compounds undergo hydrogenation to form cyclohexane as follows.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexene + ( \text{H}_2 )</td>
<td>Predicted: -120</td>
</tr>
<tr>
<td>cyclohexa-1,3-diene + ( 2\text{H}_2 )</td>
<td>-240 ( \rightarrow ) -232</td>
</tr>
<tr>
<td>benzene + ( 3\text{H}_2 )</td>
<td>-360 ( \rightarrow ) -208</td>
</tr>
</tbody>
</table>

Which of the following deduction(s) can be made from the data above?

1. The delocalisation of \( \pi \) electrons in benzene lowers the predicted energy content of benzene by 152 \( \text{kJ mol}^{-1} \).
2. Cyclohexane is the most stable amongst all four substances.
3. Cyclohexa-1,3-diene has a higher energy content than cyclohexene.
The responses A to D should be selected on the basis of

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

34 Sodium hydrogensulfide, NaSH, is used to remove hair from animal hides. Which statement(s) about the SH– ion is/are correct?

1. Three lone pairs of electrons surround the sulfur atom.
2. Its conjugate acid contains a total of 18 electrons.
3. Sulfur has an oxidation state of +2.

35 Zinc protoporphyrin (ZPP) is a compound found in red blood cells when heme production is inhibited by the presence of lead or by a lack of iron in blood.

A structure of a molecule of ZPP is shown as follows.

Zinc is situated in the centre of a planar arrangement of four nitrogen atoms.

What does this structure suggest about the bonding around zinc?

1. dative covalency
2. σ bonding
3. oxidation state of zinc is zero
The responses A to D should be selected on the basis of

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

36 In an experiment, \( r \) mol of chlorine gas was bubbled into excess hot aqueous potassium hydroxide. Which of the following statement(s) is/are incorrect regarding this reaction?

1 Oxidation number of chlorine changes from 0 to –1 and 0 to +5
2 \( 3r \) mol of potassium hydroxide was required and \( \frac{5}{3}r \) mol of potassium chloride was produced.
3 A disproportionation reaction occurred and the final products obtained included potassium chlorate(I) and potassium chlorate(V).

37 Which of the following statement(s) about Group II elements from Mg to Ba is/are correct?

1 The pH of the solution from the reaction of the metal oxides with water decreases down the group.
2 The reactivity of the elements with water increases down the group.
3 The decomposition temperature of the carbonates increases down the group.

38 Long–chain alkanes are converted on an industrial scale into alkylsulfates for use as detergents, e.g. sodium dodecyl benzene sulfonate (SDBS).

\[
\text{SDBS} \quad \text{ONa} \quad \text{O}
\]

What deduction(s) about the properties of SDBS can be made from this structure?

1 Part of the structure is polar and is water–attracting.
2 The alkyl chain is soluble in oil droplets.
3 The shape of the molecule is tetrahedral about the sulfur atom.
The responses A to D should be selected on the basis of

<table>
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</table>

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

39. A sun protection cream contains the following ester as its active ingredient.

What are the products of its partial or total hydrolysis by aqueous sodium hydroxide?

1. \( \text{H}_3\text{CO}-\overset{\text{CH}=\text{CH}_2}{\text{CH}_2}\text{CHO}_2^- \text{Na}^+ \)

2. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{O}^- \text{Na}^+ \)

3. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CO}_2^- \text{Na}^+ \)

40. The following diagram shows some laboratory apparatus.

Which preparation(s) could this apparatus be used for?

1. bromoethane, from ethanol, sodium bromide and concentrated sulfuric acid.

2. propanal, from propanol, sodium dichromate(VI) and sulfuric acid.

3. 1,2–dibromopropane, from bromine and propene.
### 2012 DHS Preliminary Examination
#### H2 Chemistry 9647/01 Answer Key

<table>
<thead>
<tr>
<th>Question Number</th>
<th>Key</th>
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<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
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<td>B</td>
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<td>C</td>
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<td>D</td>
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<td>A</td>
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<td>19</td>
<td>D</td>
<td>39</td>
<td>D</td>
</tr>
<tr>
<td>20</td>
<td>B</td>
<td>40</td>
<td>B</td>
</tr>
</tbody>
</table>
Section A

1 B

\[ \text{Ag}^{+}\text{unreacted} + \text{SCN}^- \rightarrow \text{AgSCN} \]

Moles of Ag\(^{+}\)\text{unreacted} = No. of moles of SCN\(^-\)
\[ = \frac{3.64 \times 0.054}{1000} = 1.9656 \times 10^{-4} \text{ mol} \]

3Ag\(^{+}\)\text{reacted} + AsO_4^{3-} \rightarrow Ag_3AsO_4

Moles of Ag\(^{+}\)\text{reacted} = (1.25 \times 10^{-3}) - 1.9656 \times 10^{-4}
\[ = 1.053 \times 10^{-3} \text{ mol} \]

Moles of As = Moles of AsO_4^{3-}
\[ = \frac{1}{3} \times 1.053 \times 10^{-3} \text{ mol} \]

Mass of As = Moles of As \times 74.9
\[ = 0.026 \text{ g} \]

2 D

Extent of deflection \( \propto \frac{q}{m} \)

(charge is denoted by \( q \); mass is denoted by \( m \))

Cations will be deflected towards the negative plate and anions towards the positive plate.

| \( \text{Na}^+ \) | \( 1/23.0 \times (23 \times 4.3) \) | 4.3° |
| \( \text{Be}^{2+} \) | \( 2/9.0 \times (23 \times 4.3) \) | 22.0° |
| \( \text{Ba}^{2+} \) | \( 2/137 \times (23 \times 4.3) \) | 1.4° |
| \( \text{S}^2\) | \( 2/32.1 \times (23 \times 4.3) \) | 6.2° |
| \( \text{Br}^- \) | \( 1/79.9 \times (23 \times 4.3) \) | 1.2° |

3 D

Construct a half-equation for the oxidation of methylbenzene:
\[ \text{C}_6\text{H}_5\text{CH}_3 + 2\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{6H}^+ + \text{6e}^- \]

Alternatively,

\[
\text{CH}_3\text{C}=[\text{O}]\text{O} \quad \text{[O]} \quad \text{HO-C}=[\text{O}]
\]

O.S. of *C before oxidation = 4 – 7 = –3
O.S. of *C after oxidation = 4 – 1 = +3
Change in O.S. = +3 – (–3) = +6
∴ 6 electrons are removed during oxidation of methylbenzene to benzoic acid.

4 C

For options A and B,
\[ pV = nRT \]
\[ pV = (m/M)RT = \text{constant} \]
\[ \Rightarrow \text{Graph of } P \text{ against } pV \text{ should be a vertical line at a particular value of } pV. \]

For options C and D,
\[ pV = nRT = (mR/M)T \Rightarrow pV \propto T \]
\[ \Rightarrow \text{Since the } M_r \text{ of I is higher, the gradient of the line is gentler.} \]

5 D

Heat absorbed by water
\[ = \frac{300 \times c \times \Delta T}{1000} \text{ kJ mol}^{-1} \]

Moles of propan-1-ol burnt = \( \frac{m}{60.0} \) mol

Heat released by burning \( m \) g of propan-1-ol = \[ \frac{m \times 2021}{60.0} \] kJ mol\(^{-1}\)
\[ \Rightarrow \text{Efficiency of heating process} \]
\[ = \frac{1000 \times \Delta T}{m \times 2021 \times 100} \times 100 \]
\[ = \frac{300 \times c \times \Delta T \times 60.0}{m \times 2021 \times 1000} \times 100\% \]
6 C

Calcium and chlorine form CaCl₂ rather than CaCl because $\Delta H$(CaCl₂) is more exothermic than $\Delta H$(CaCl).

$\Delta H$ is the sum of enthalpy changes involved in a series of processes leading from the elements to the compounds:
1. Forming separate atoms from elements ($\Delta H_{at}$)
2. Forming positive (from the metal atom) or negative (from the non-metal atom) ions. (Sum of I.E. or sum of E.A.)
3. Combining the ions together in an ionic lattice held together by the attraction between oppositely charged ions (LE).

For CaCl₂,
w less energy is required to ionise the Ca atom only once, to Ca²⁺
w only one Cl⁻ atom needs to be formed from Cl₂ and converted into a Cl⁻ ion
w lattice energy released by forming a 1:1 lattice of singly charged ions is less exothermic than that for CaCl₂, which involves Ca²⁺ ions.

Option C is the best answer.

7 C

![Diagram](image)

$E_a = +50 \text{ kJ mol}^{-1}$

formation of intermediate

reactants

$\Delta H = -100 \text{ kJ mol}^{-1}$

products

progress of reaction

8 A

In 1.0 mol dm⁻³ sulfuric acid, [H⁺] = 2.0 mol dm⁻³. To make the electrode a standard hydrogen electrode, either change the acid to a 1.0 mol dm⁻³ monoprotic acid (option A), or halve the concentration of sulfuric acid used.

9 B

Since forward reaction is exothermic, higher temperatures will favour the backward reaction. This increases [NH₃] and [O₂] and decreases [N₂] and [H₂O] at higher temperatures. Thus the two downward-sloping graphs apply to either N₂ or H₂O.

At a higher pressure, backward reaction is favoured, and [N₂] and [H₂O] decreases. Thus, $z > y$.

10 A

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}^+(aq) + \text{OH}^-(aq) \]

\[ K_w = [\text{H}^+][\text{OH}^-] \]

\[ [\text{H}^+] = \sqrt{K_w} \]

<table>
<thead>
<tr>
<th>Option</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>At 25 °C, [H⁺] = 1.0 × 10⁻⁷ mol dm⁻³ At 10 °C, [H⁺] = 0.5 × 10⁻⁷ mol dm⁻³ At 0 °C, [H⁺] = 0.3 × 10⁻⁷ mol dm⁻³</td>
</tr>
<tr>
<td>B</td>
<td>Ionic dissociation of water increases by a factor of 3.3 between 0 °C and 25 °C.</td>
</tr>
<tr>
<td>C</td>
<td>Extent of hydrogen bonding cannot be deduced from the given information.</td>
</tr>
<tr>
<td>D</td>
<td>[H⁺] = [OH⁻] at 0 °C, 10 °C and 25 °C. Thus water remains a neutral liquid at these temperatures. However pH of neutral water is no longer 7.0, but increases with decreasing temperature.</td>
</tr>
</tbody>
</table>
Rate law is determined by slow step in proposed mechanism, i.e. Rate = \( k'[\text{O}_3][\text{O}] \). This rate law cannot be compared directly with the experimental rate equation because it contains the concentration of an intermediate, \( \text{O} \). Thus we need to express rate law in a way that removes the intermediate \( \text{O} \).

From Step 1, \( K = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \Rightarrow [\text{O}] = K[\text{O}_3] \).

Assuming that Step 1 equilibrium is established quickly before \( \text{O} \) is reacted with \( \text{O}_3 \) in Step 2, Rate = \( k'[\text{O}_3][\text{O}] = k'[\text{O}_3][O] \).

where \( k = k'K \).

**Z** has a greater atomic radius than **W**

\( \Rightarrow Z \) is earlier on in the period (\( Z \ldots W \ldots \)).

**W** has greater electrical conductivity than **Y** and **Y** has higher boiling point than **W**

\( \Rightarrow Y \) is in Group 14 and hence **W** is a metal (not Si)

First trace of precipitate appears when ionic product = \( K_{sp} \).

\( \text{ZnCO}_3(s) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{CO}_3^{2-}(aq) \)

\( K_{sp} = [\text{Zn}^{2+}][\text{CO}_3^{2-}] = 1.4 \times 10^{-11} \)

\( \therefore [\text{CO}_3^{2-}] \) at which first trace of \( \text{ZnCO}_3 \) appears

\( = \frac{1.4 \times 10^{-11}}{0.2} = 7 \times 10^{-11} \text{ mol dm}^{-3} \)

\( \text{Ag}_2\text{CO}_3(s) \rightleftharpoons 2\text{Ag}^{2+}(aq) + \text{CO}_3^{2-}(aq) \)

\( K_{sp} = [\text{Ag}^{2+}][\text{CO}_3^{2-}] = 8.1 \times 10^{-12} \)

\( \therefore [\text{CO}_3^{2-}] \) at which first trace of \( \text{Ag}_2\text{CO}_3 \) appears

\( = \frac{8.1 \times 10^{-12}}{0.1^2} = 8 \times 10^{-10} \text{ mol dm}^{-3} \)

Thus \( \text{ZnCO}_3 \) will precipitate first when \( [\text{CO}_3^{2-}] \) reaches \( 7 \times 10^{-11} \text{ mol dm}^{-3} \). When \( [\text{CO}_3^{2-}] \) reaches \( 8 \times 10^{-10} \text{ mol dm}^{-3} \), \( \text{Ag}_2\text{CO}_3 \) will precipitate next.
17  C

<table>
<thead>
<tr>
<th>n</th>
<th>formula</th>
<th>distribution of C/ atoms</th>
<th>no. of chloroethanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₂H₅Cl</td>
<td>1 0</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>C₂H₄Cl₂</td>
<td>2 0</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>C₂H₃Cl₃</td>
<td>3 0</td>
<td>2</td>
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<td>4</td>
<td>C₂H₂Cl₄</td>
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<td>2</td>
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<td>C₂HCl₅</td>
<td>3 2</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>C₂Cl₆</td>
<td>3 3</td>
<td>1</td>
</tr>
</tbody>
</table>

Total no. of different chloroethanes = 9

18  A

The stronger an acid, the lower the $pK_a$ value. The following lists the four acids used in the options:
- w CH₃CO₂H
- w CCl₃CO₂H
- w C₂H₅OH
- w C₆H₅OH

Increasing acid strength:
C₂H₅OH < C₂H₅OH < CH₃CO₂H < CCl₃CO₂H

Decreasing $pK_a$ value:
C₂H₅OH > C₂H₅OH > CH₃CO₂H > CCl₃CO₂H

19  D

<table>
<thead>
<tr>
<th></th>
<th>product(s) of oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="imageA.png" alt="Image of A" /></td>
</tr>
<tr>
<td>B</td>
<td><img src="imageB.png" alt="Image of B" /></td>
</tr>
<tr>
<td>C</td>
<td><img src="imageC.png" alt="Image of C" /> + CO₂</td>
</tr>
<tr>
<td>D</td>
<td><img src="imageD.png" alt="Image of D" /></td>
</tr>
</tbody>
</table>

20  B

Alkyl side-chains on a benzene ring are susceptible to oxidative degradation if they possess at least one benzylic hydrogen atom.

![benzylic hydrogen](imageH.png)

Thus, side-chains on Z which can be oxidised are:

I : It is only possible to oxidise the carbon atom in –CH₂ to a lower oxidation state of +2 in –C=O, rather than +3 in –COOH. There is only 1 C atom connecting both benzene rings. If I is oxidised to –COOH, one of the benzene rings has to be reduced by replacing the oxidised carbon with a hydrogen atom.

II : II may be regarded as 2 separate alkyl groups, with each being oxidised to –COOH.
21 C

A (Account is correct) Electrophilic substitution of phenol by bromine in aqueous medium yields a tri-substituted product, rather than a mono-substituted one.

B (Account is correct) Ppt is 2,4,6-tribromophenol, which is white.

C (Account is wrong) Resultant solution contains 2,4,6-tribromophenol, which is acidic.

D (Account is correct) Resultant solution is yellow, due to the presence of excess dissolved bromine.

22 D

A O 1 mol –COOH reacts with 1 mol PCl₅, and 1 mol –OH group reacts with 1 mol PCl₅.
∴ 1 mol citric acid reacts with 4 mol PCl₅.

B O 3 mol tribasic acid reacts with 1 mol Na₂CO₃. (Alcohols are neutral, and do not react with Na₂CO₃.)
∴ 1 mol citric acid reacts with \( \frac{1}{3} \) mol Na₂CO₃.

C O 1 mol –COOH reacts with 1 mol NaOH. (Alcohols are neutral, and do not react with NaOH.)
∴ 1 mol citric acid reacts with 3 mol NaOH.

D P 1 mol –COOH reacts with 1 mol Na, and 1 mol –OH group reacts with 1 mol Na.
∴ 1 mol citric acid reacts with 4 mol Na.

23 B

Nitrile groups on CS are hydrolysed to either salts of carboxylic acids (alkaline hydrolysis) or carboxylic acids (acid hydrolysis).

24 A

Product of Claisen condensation of ethyl esters must be an ethyl \( \beta \)-keto ester:

\[
\begin{align*}
\text{CH}_3 \quad & \quad \text{O} \\
\text{O} \quad & \quad \text{CH}_3 \\
\end{align*}
\]

⇒ Options B and D are not possible.

4th member of series has 2 isomers:

\[
\begin{align*}
\text{I} & : \quad \text{H}_3\text{C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{CH}_3 \\
\text{II} & : \quad \text{H}_3\text{C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{CH}_3 \\
\end{align*}
\]

⇒ Option C is not possible, since it is derived from an isomer of the 5th member:

\[
\begin{align*}
\text{H}_3\text{C} \quad & \quad \text{O} \\
\text{O} \quad & \quad \text{O} \quad \text{O} \quad \text{CH}_3 \\
\end{align*}
\]

25 A

A substituent group (fluorine atom), and not a hydrogen, is substituted without disruption to the aromaticity of the benzene ring. This is therefore not an electrophilic substitution reaction.

F is highly electronegative. The C atom to which F atom is attached is \( \delta^+ \), and can attract a nucleophile.

This reaction is therefore a nucleophilic substitution reaction, with

\[
\begin{align*}
\text{H}_2\text{N} \quad & \quad \text{N} \quad \text{O} \\
\text{CH}_3 \quad & \quad \text{H} \quad \text{O} \\
\end{align*}
\]

being the nucleophile, and F atom being the leaving group.
26 C

Mechanism C involves the electrophilic addition of Br₂ to methylbenzene. This destroys the aromaticity of the benzene ring and is energetically not favourable.

27 B

In arginine, pKₐ of side-chain =NH₂⁺ group is higher than pKₐ of α–NH₃⁺ group. Thus α–NH₃⁺ group will be de-protonated first before zwitterion is formed.

28 C

Since an acidic solution of arginine is used, there are three groups, i.e. α-COOH, α-NH₂, and protonated basic side group, to be neutralised.

Thus this reaction may be regarded as a triprotic acid whose neutralisation takes place in three stages. This eliminates pH titration graphs for diprotic acids (options A and B). α-COOH is neutralised first, followed by α–NH₃⁺, and finally the protonated basic side group.

At half-equivalence point for each neutralisation stage, pH = pKₐ of each respective acidic group.

29 D

Hydrolysis of this tripeptide will break the amide linkage at X or Y.

30 A

Amino acid residue at N terminus: alanine (Ala)
Amino acid residue at C terminus: valine (Val)
Thus P is (N) Ala-Pro-Lys-Leu-Ileu-Val (C).
Section B

31 A

1 P Over time, the amalgam filling is oxidised by dissolved oxygen in the saliva.

\( (E^\circ)_{\text{cell}} = E^\circ (O_2/H_2O) - E^\circ (Sn_8Hg/Sn^{2+}) = +1.23 - (-0.13) = +1.36 \ V \)

An acidic medium results in \( (E^\circ)_{\text{cell}} \) becoming more positive. Corrosion becomes thermodynamically more feasible.

2 P Contact between aluminum foil and amalgam filling short-circuits the cell in Statement 1. Al reduces Sn\(^{2+}\) to Sn, and amalgam becomes the cathode.

3 P \( E^\circ (Sn_8Hg/Sn^{2+}) \) is more negative than \( E^\circ (Au^{3+}/Au) \). When Au is in contact with the amalgam, a galvanic cell is set up with the amalgam filling as the anode and gold inlay as the cathode. Tin in the amalgam is oxidised to Sn\(^{2+}\) and releases electrons to the gold cathode where oxygen is reduced preferentially.

\[ E^\circ (O_2/H_2O) \] is less positive than \( E^\circ (Au^{3+}/Au) \). Thus O\(_2\) is reduced.

32 D

\[ 2N_2(g) + 3H_2(g) \to 2NH_3(g) \quad \Delta H = -\text{ve} \]

1 P \( \Delta G = \Delta H - T \Delta S \)

\( \Delta S < 0 \Rightarrow -T \Delta S \) is always positive.

\( \Delta G < 0 \) only if |\( \Delta H \)| > |\( \Delta S \)|

At high temperatures, |\( \Delta H \)| < |\( \Delta S \)| and \( \Delta G \) > 0.

\( \therefore \) Reaction becomes less feasible as temperature increases.

2 O At higher pressures, by LCP, equilibrium position lies more to the right to favour the side of the reaction with fewer gas molecules, i.e. formation of NH\(_3\).

\( \therefore \) Yield of NH\(_3\) increases.

Higher pressures increase rate of reaction between gaseous reactants.

3 O Presence of a catalyst does not affect yield.

However a catalyst increases both the forward and backward reaction.

33 A

34 B

1 P No. of lone pairs around S atom = 3

2 P SH\(^-\) accepts an H\(^+\) ion to become its conjugate acid, H\(_2\)S.

\[
\text{H}^+ \cdot \text{S} \cdot \text{H}
\]

No. of electrons from S atom = 16

No. of electrons from H atoms = 2

Charge = 0

\( \therefore \) Total no. of electrons on H\(_2\)S = 16 + 2 = 18

3 O O.S. of S = 6 - 8 = -2
**35 B**

1. **P** Protoporphyrin molecule is a chelate. Each N atom / ion shares a lone pair with central Zn$^{2+}$ ion to form a dative bond.

2. **P** Each Zn–N bond is a σ-bond.

3. **O** Structure of ligand before bonding:

   ![Protoporphyrin molecule]

   Thus Zn has an oxidation state of +2.

**36 C**

1. **O** Oxidation number of chlorine changes from 0 in Cl$_2$ to –1 in Cl$^–$ and to +5 in ClO$_3$–.

2. **P** 6OH$^–$(aq) + 3X$^–$(aq) → 5 X$^–$(aq) + XO$_3$–(aq) + 3 H$_2$O(l)

   2$\pi$ mol of KOH was required and $\frac{5}{3}$ $\pi$ mol of KCl was produced.

3. **O** A disproportionation reaction occurred. However, the final products obtained included chloride and potassium chlorate (V).

**37 C**

1. **O** The pH of the solution from the reaction of the metal oxides with water increases down the group.

2. **P** The reactivity of the elements with water increases down the group.

3. **P** The decomposition temperature of the carbonates increases down the group due to the decrease in the polarising effect on the carbonate ion.

**38 A**

![Sodium dodecyl benzene sulphonate (SDBS)]

- hydrocarbon (hydrophobic part of molecule)
- polar (hydrophilic part of molecule)

**39 D**

The ester is hydrolysed by NaOH(aq) to form the following products:

**40 B**

1. **P** Bromoethane is more volatile than ethanol, and propanal is more volatile than propanol. Thus both products will distil over as they are being produced while the other substances remain in the flask.

2. **P** Propene is a gas at r.t.p.

3. **O** Ionic portion of SDBS is attracted to polar solvents like water – hydrophilic

   ![Sodium dodecyl benzene sulphonate (SDBS) structure]

2. **P** Hydrocarbon portion of SDBS is soluble in organic solvents – hydrophobic

3. **P** There are 4 bond pairs and 0 lone pair around S atom.
INSTRUCTIONS TO CANDIDATES

1. Write your name, index number and class on this cover page.
2. Answer all questions.
3. Write your answers in the spaces provided on the question paper.
4. A Data Booklet is provided.
5. The number of marks is given in brackets [ ] at the end of each question or part question.
6. You may use a calculator.

FOR EXAMINER’S USE

<table>
<thead>
<tr>
<th>Question No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Total</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marks</td>
<td>12</td>
<td>14</td>
<td>8</td>
<td>18</td>
<td>10</td>
<td>10</td>
<td>[72]</td>
<td></td>
</tr>
</tbody>
</table>
Answer all questions in the space provided.

1 Planning

This question is about the kinetics of urease–catalysed hydrolysis of urea in phosphate and citrate buffer solutions.

Urease is an enzyme that breaks down urea, \( \text{CO(NH}_2\text{)}_2 \), into carbon dioxide and ammonia. The production of ammonia raises the pH of the buffered solution mixture and can be detected using a suitable acid–base indicator.

\[
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{NH}_3
\]

Urease is active over a wide range of pH so a few indicators can be used provided that the original solution mixture is buffered at the right pH to start with.

The colour change of bromothymol blue and phenolphthalein in acid–base medium is shown in the table:

<table>
<thead>
<tr>
<th>Indicator</th>
<th>( pK_{\text{ind}} )</th>
<th>( \text{pH range} )</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td>bromothymol blue</td>
<td>7.0</td>
<td>5.9–7.6</td>
<td>Yellow(in acid)– blue (in alkali)</td>
</tr>
<tr>
<td>phenolphthalein</td>
<td>9.3</td>
<td>8.3–10.0</td>
<td>Colourless(in acid)–pink (in alkali)</td>
</tr>
</tbody>
</table>

Phosphate and citrate present in the buffer solutions do not react with urea or urease.

In order to study the effect of the enzyme concentration on the rate of hydrolysis of urea, you are provided with

- Choice of two indicators, bromothymol blue and phenolphthalein
- Choice of two buffered solutions, phosphate buffer at pH 7 and citrate buffer at pH 5
- 2% of urea solution
- 3% urease solution
- distilled water

In a preliminary experiment, a solution mixture containing 20 cm\(^3\) of urea solution, 8 cm\(^3\) of buffer solution, 6 cm\(^3\) of urease solution, 6 cm\(^3\) of water took 40 seconds for the indicator to show a colour change.

It is found that the time taken for the indicator in the reaction mixture to change colour doubled when urease used is diluted with an equal amount of water.

(a) (i) Suggest the appropriate choice of indicator and the buffer solution used in the preliminary experiment.

Choice of buffer solution: 

Choice of indicator: 

______________________________________________________________________________________

______________________________________________________________________________________
(ii) Using the results of the preliminary experiment predict the relationship between the rate of hydrolysis of urea and concentration of urease.

(b) (i) A student designed a series of experiments to investigate the prediction in the preliminary experiment by initial rate method.

Complete the table below to show

- all volumes to be used such that a simple comparison of the time taken for end-point of the indicator can be made with the preliminary experiment.
- how the measurements would be processed (that is, complete the heading for the last column) to enable the student to confirm or reject the preliminary prediction.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Volume of urea/ cm³</th>
<th>Volume of urease/ cm³</th>
<th>Volume of buffer/ cm³</th>
<th>Volume of water/ cm³</th>
<th>Time taken, t/ s</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>20</td>
<td>6</td>
<td>8</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

P: Preliminary experiment
(ii) Outline the procedural steps that the student would take to carry out the designed experiments in (b)(i), stating any assumption(s) made. Your plan should include:
- the apparatus used to measure the various volumes;
- the sequence that the various solutions are mixed;
- how the time for the colour change of indicator is measured; and
- other experimental details to ensure the consistency of the experiment.

You may also assume that standard laboratory apparatus are available.

(iii) Explain how the results of the experiments will confirm or reject the preliminary prediction.
(c) The rate of this reaction is also studied when the temperature is varied. Give a sketch of a graph to show how the rate will vary with temperature. Explain the shape of your sketch.

![Graph showing rate vs. temperature]

rate

20

T/ °C

Ethanoic acid, also commonly known as acetic acid, is an important chemical due to its varied uses in the industry.

(a) The preferred industrial method for its manufacture is by carbonylation of methanol, an exothermic reaction, accounting for 65% of the total world ethanoic acid manufacturing capacity.

\[
\text{CH}_3\text{OH(aq)} + \text{CO(g)} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H(aq)}
\]

The conditions employed are:

- 150 – 200 °C
- 30 – 60 atm
- rhodium–based catalyst

Using Le Chatelier’s Principle, explain why the above moderate pressure is chosen as the process condition.

[2]
(b) The graph below shows the changes in pH when a 25.0 cm$^3$ sample of vinegar, with ethanoic acid as its main component, is titrated against 0.45 mol dm$^{-3}$ aqueous sodium hydroxide.

(i) Using the information provided, show by calculations that the acid dissociation constant, $K_a$ of ethanoic acid has an approximate numerical value of $1.85 \times 10^{-5}$.

(ii) State a suitable indicator for this titration. Explain your choice.

Indicator: 

Reason for choice: 

[5]
(c)  The buffer produced at region A in (b) consists of a weak acid and its conjugate base.

(i)  Draw a diagram to illustrate the shape of the anion present. State the shape about each carbon atom and its respective bond angles.

(ii)  With clear reference to your drawing in c(i), state the type of hybridisation present for each carbon atom in the anion.

(iii)  The boiling points of both components of the buffer are given below.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>weak acid</td>
<td>118 °C</td>
</tr>
<tr>
<td>conjugate base</td>
<td>881 °C</td>
</tr>
</tbody>
</table>

With reference to the structures and interactions present, account for the large difference in the boiling points shown.

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

________________________________________________________________________

[7]

Total: 14
Sodium chlorate(I), NaC/O, found in household bleach produces chlorine upon addition of acidified dilute hydrochloric acid according to the equation below.

\[
\text{C/O}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + \text{Cl}^- (\text{aq}) \rightarrow \text{Cl}_2 (\text{aq}) + \text{H}_2\text{O(l)}
\]

A 10.0 cm\(^3\) sample of a household bleach is diluted to 100 cm\(^3\). 25.0 cm\(^3\) of this solution is then pipetted out into a conical flask containing dilute hydrochloric acid. Excess potassium iodide solution is added and the resultant solution turns brown. This resultant solution is then titrated against 0.100 mol dm\(^{-3}\) sodium thiosulfate solution and required 15.20 cm\(^3\) for complete reaction.

(i) Identify the specie that is responsible for the brown colouration and state the reaction that has taken place.

(ii) Calculate the concentration of the sodium chlorate(I) in the household bleach in g dm\(^{-3}\).

\[
\text{concentration} = \text{......................} \text{g dm}^{-3}
\]
(b) A small portion of three unlabelled samples of KCl, KBr and KI are reacted with concentrated phosphoric acid separately and each of the hydrogen halide gases produced are immediately passed through identical set-ups as shown.

(i) Suggest a hydrogen halide that can be identified using this set-up, clearly stating the equation of the reaction taking place and the expected observations for the organic layer.

Hydrogen halide: 
Equation: 
Expected observations: 

(ii) Describe a chemical test that can be carried out to distinguish between the two remaining potassium halide solutions and explain the expected observations.

Chemical Test: 

Observations: 

[Total: 8]
Magnesium oxide is one of the products formed when magnesium carbonate decomposes.

\[
\text{MgCO}_3(s) \rightarrow \text{MgO}(s) + \text{CO}_2(g) \quad \Delta H^\circ = +100 \text{ kJ mol}^{-1}
\]

(i) The decomposition of magnesium carbonate was studied at two different temperatures, to determine the ideal temperature for the industrial production of magnesium oxide. The products were bubbled into limewater and the observations are as follows:

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>Effect on limewater</th>
</tr>
</thead>
<tbody>
<tr>
<td>1050</td>
<td>White precipitate</td>
</tr>
<tr>
<td>400</td>
<td>No white precipitate</td>
</tr>
</tbody>
</table>

At a certain temperature, it was found that the reaction ceases to be feasible. Given the following entropy values, determine this temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Entropy / J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCO(_3)((s))</td>
<td>65.7</td>
</tr>
<tr>
<td>MgO((s))</td>
<td>26.9</td>
</tr>
<tr>
<td>CO(_2)((g))</td>
<td>213.6</td>
</tr>
</tbody>
</table>

\[
T = ............................................
\]

(ii) Hence, suggest why it is necessary to determine the unknown temperature instead of carrying out the industrial production of magnesium oxide at 1050K.
(iii) Using the data provided and relevant data from the *Data Booklet*, construct an appropriate fully-labelled energy cycle to calculate the lattice energy of magnesium carbonate.

<table>
<thead>
<tr>
<th>Enthalpy Term</th>
<th>ΔH / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy change of atomisation of magnesium</td>
<td>+148</td>
</tr>
<tr>
<td>Sum of 1ˢᵗ and 2ⁿᵈ electron affinities of oxygen</td>
<td>+657</td>
</tr>
<tr>
<td>Enthalpy change of formation of magnesium carbonate</td>
<td>−1096</td>
</tr>
<tr>
<td>Enthalpy change of formation of CO₂(g)</td>
<td>−393</td>
</tr>
<tr>
<td>O₂⁺(g) + CO₂(g) → CO₃²⁻(g)</td>
<td>−778</td>
</tr>
</tbody>
</table>
(b) The plots of $pV/RT$ against $p$ for one mole of an ideal gas and one mole of carbon dioxide gas from the decomposition of magnesium carbonate at 300K are given below.

(i) Show, on the same axes, how one mole of sulfur dioxide, $SO_2$ will behave at the same temperature of 300K. Label your graph clearly.

(ii) Explain the difference in behavior between carbon dioxide and sulfur dioxide at 300K.

(iii) Explain what happens when sulfur dioxide gas is cooled to 100K. Illustrate your answer clearly on the same axes in b(i).
(c) The temperatures for the thermal decomposition of carbonates of Group II elements magnesium to radium are as shown.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decomposition Temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCO$_3$</td>
<td>540</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>900</td>
</tr>
<tr>
<td>SrCO$_3$</td>
<td>1290</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>1350</td>
</tr>
<tr>
<td>RaCO$_3$</td>
<td>720</td>
</tr>
</tbody>
</table>

It was suggested that the decomposition temperature for radium carbonate to be $720^\circ$C. Comment on the accuracy of this suggestion.

(d) Write appropriate equations to illustrate the reactions of PC$_3$ and AlCl$_3$ with water. Hence, state the observations when they are separately added to test tubes containing aqueous magnesium carbonate.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_3$</td>
<td></td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td></td>
</tr>
</tbody>
</table>
The diagram below shows the synthetic pathway by which compound F may be prepared. The inorganic side product, which is produced together with compound F, is constantly removed from the reaction mixture.

(a) Give the structural formulae for compounds D and E.
(b) Suggest the reagents and conditions for steps 2 and 3.

Step 2: 

Step 3: 

[2]

(c) Draw the structures of the organic products formed when compound F is reacted with each of the following:

(i) Cl₂ in AlCl₃, room temperature

(ii) KOH(aq), reflux

(iii) cold dilute nitric acid

[4]
(d) Describe a chemical test that can be used to distinguish between compounds A and B.

Reagent(s) & conditions: ..............................................................

Observations: ...........................................................................

[2]

[Total: 10]

6 The reaction scheme below shows the final stages in the synthesis of compound S.

(a) Draw the displayed formulae of compounds R and Q.
(b) Give the synthetic route, involving *not more than three steps*, from P to Q. In your answer, suggest the reagent(s) and conditions involved in each step and draw the structural formulae of the intermediate organic products. Name the type of reaction occurring at each step.

(c) In the reaction of R and Q, another organic compound can also possibly be formed. Draw the structural formula of the organic compound and explain how its formation may arise.

[6]

[2]

[Total: 10]
INSTRUCTIONS TO CANDIDATES

Write your name, register number and class on this question paper and on the Cover Sheet provided.

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.

Start each question on a fresh sheet of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

At the end of the examination:

• Fasten all work securely together with the Cover Sheet on top.
• Hand in the question paper separately.

The total marks for this paper is 80 marks.
Answer any four questions.

1. The study of organic compounds includes the collection of kinetic data and thermodynamic data of the compounds.

(a) The kinetics of the hydrolysis of the ester, \( \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 \), may be investigated by the following method.

\[
\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{OH}
\]

In a 1 dm\(^3\) mixture, 0.350 mol of the ester was hydrolysed by heating with water and using hydrochloric acid as catalyst. The following results were obtained.

<table>
<thead>
<tr>
<th>Time/s</th>
<th>Concentration of ( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} )/mol dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>340</td>
<td>0.105</td>
</tr>
<tr>
<td>680</td>
<td>0.185</td>
</tr>
<tr>
<td>1080</td>
<td>0.243</td>
</tr>
<tr>
<td>1440</td>
<td>0.278</td>
</tr>
</tbody>
</table>

(i) Suggest how the progress of this reaction may be followed in order to obtain the results as stated.

(ii) By drawing a suitable graph using the data given above, show that the reaction is first order with respect to the ester. It has been found that the hydrolysis reaction is first order with respect to the hydrochloric acid.

(iii) Deduce the units of the rate constant.

(iv) State and explain the effect of a catalyst on the rate constant.

(v) Using suitable bond energy values from the *Data Booklet*, calculate the \( \Delta H \) for the hydrolysis of the ester.

(vi) Given that the standard enthalpy change of reaction for the hydrolysis is +7.6 kJ mol\(^{-1}\), suggest a reason for the difference between this given value and the value that you have calculated in (a)(v).

[11]

(b) Hydrolysis of ester can be achieved in the biological system by enzymes known as esterase. Enzymes are proteins that catalyse a specific chemical transformation in the biological system. Such enzymes are generally quaternary proteins.

(i) Sketch and explain the graph showing how the rate of hydrolysis changes with increasing concentration of the ester.

(ii) Explain the meaning of quaternary structure of proteins.

(iii) List 2 other major functions of proteins in the body.

(iv) Suggest and explain a chemical method for distinguishing the following pair of esters. You should state the expected observations.

\( \text{HCO}_2\text{CH}_2\text{CH}_3 \) and \( \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 \)

[9]

[Total: 20]
2 This question is about the chemistry of the transition metal, nickel and its compound.

(a) Explain why the colour of \([\text{Ni(NH}_3\text{)_6}]^{2+}\) is blue. \[3\]

(b) Ni(CO)\(_4\) is a compound formed by the reaction between nickel and carbon monoxide. The Mond process was developed by Ludwig Mond to extract and purify nickel from its ores. One of the stages of this process involves the decomposition of Ni(CO)\(_4\) at 227 °C to give nickel as shown in this equation below:

\[
\text{Ni(CO)}_4(g) \rightleftharpoons \text{Ni(s)} + 4\text{CO(g)}
\]

The equilibrium constant, \(K_p\), for the equilibrium at 227 °C is 1.01 atm\(^3\). A sample of gaseous Ni(CO)\(_4\) was placed in a 2 dm\(^3\) evacuated container at 227 °C. At equilibrium, the partial pressure of CO was 2.00 atm.

\[1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}\]

(i) Sketch the shapes of the hybrid orbitals around the C atom in carbon monoxide.

(ii) Write an expression for \(K_p\).

(iii) Calculate the total pressure of the system at equilibrium.

(iv) Calculate the mass of Ni(CO)\(_4\) placed in the container initially. \[8\]

(c) Ni is commonly used in catalytic hydrogenation reactions. One such example is given below.

Compound \(\text{A, C}_{10}\text{H}_{12}\text{NOCl}\), has a chiral centre and dissolves in dilute sulfuric acid. It reacts with 2,4–dinitrophenylhydrazine to form an orange precipitate, but does not react with Tollens' reagent. \(\text{A}\) reacts with \(\text{H}_2\) in the presence of Ni catalyst followed by addition of aqueous bromine to form \(\text{B, C}_{10}\text{H}_{11}\text{NOClBr}_3\). When 1 mol of compound \(\text{B}\) is heated under reflux with aqueous iodine and excess alkali, followed by careful acidification, compound \(\text{C, C}_8\text{H}_4\text{NO}_4\text{Br}_3\) is formed together with 2 mol of yellow solid \(\text{CH}_3\text{I}_3\).

Deduce the structures of compounds \(\text{A, B and C}\), giving reasons for your answer. \[9\]

[Total: 20]
This question is about the varied chemical uses of HCl.

(a) (i) In the electrolysis of a solution of hydrochloric acid with inert platinum electrodes, an ammeter showed a reading of 0.450 A in the external circuit of the cell. 110 cm$^3$ of gas was evolved at the cathode after 30 minutes under room temperature and pressure. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.

(ii) A student carried out a reaction involving acidified potassium dichromate(VI), together with an unknown half-cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be $-324\text{ kJ mol}^{-1}$ and the procedure involved transferring 6 mol of electrons from the unknown solution to potassium dichromate(VI).

Using the expression of $\Delta G^0 = -nFE^{\circ}_{\text{cell}}$, where $n$ is the number of moles of electrons transferred, $F$ is the Faraday constant and $E^{\circ}_{\text{cell}}$ is the overall cell potential, determine the $E^{\circ}_{\text{cell}}$ value and hence deduce the identity of the unknown half-cell.

(b) A sample of sodium hypochlorite, NaOCl, was dissolved in 100 cm$^3$ of 0.123 mol dm$^{-3}$ HOCI ($pK_a = 7.50$) solution forming a buffer of pH 6.20. The buffer is then used to absorb HCl gas. Calculate the concentration of gaseous HCl (in mol dm$^{-3}$) that is required to be added to the buffer solution until it reaches pH 6.

(c) The decomposition temperature of hydrogen chloride is close to 3000 K. Predict, with reasoning, if the decomposition temperature of hydrogen astatide would be higher or lower than 3000 K.

(d) Concentrated hydrochloric acid is commonly used in the reduction of trinitrobenzene (2,4,6-trinitrobenzene).

(i) Suggest the complete set of reagents, together with concentrated HCl, to be used in this reduction process.

(ii) Suggest the structural formula of the product formed.

(iii) Explain the relative basicity between the product formed in (d)(ii) and the melamine molecule as shown below in terms of their structures. The melamine molecule contains a triazine ring with 3 nitrogen atoms present in the ring.

```
  N
  |    |
  H2N
  |    |
  N
  |    |
  H2N

Melamine
```
(e) 2,4,6–trinitrobenzene can also undergo Friedel–Crafts alkylation with CH₃Cl to form 2,4,6–trinitromethylbezene. The alkyl side chain can then be further reacted to form useful halogen derivatives. However, some side products like hydrogen chloride gas and compound D can also be formed in the process.

Using 2,4,6–trinitromethylbezene as the starting material, describe an appropriate mechanism that would result in the production of compound D.  

[Total: 20]
4 Chlorine and its compounds are used to manufacture many products such as pesticides, medicines, plastics, bleaches and solvents.

(a) 1 mol of the following compounds is added to 1 dm$^3$ of water.

$\text{CH}_3\text{COCl}$, C/CH$_2$COOH and SiCl$_4$

Arrange the compounds in order of increasing pH of the resultant mixture formed. Briefly explain your answers, giving equations where appropriate. [4]

(b) Both chloric(I) acid, HOCI and hydrogen chloride react with propene. In the reaction between chloric(I) acid and propene, chlorine is added to carbon–1 of propene in the major product. However, in the reaction between hydrogen chloride and propene, chlorine is added to carbon–2 of propene in the major product.

(i) Draw the displayed formula of the major product formed between propene and chloric(I) acid.

(ii) Explain briefly why chlorine from chloric(I) acid and from hydrogen chloride add to different carbon atoms in their reactions with propene. [4]

(c) Despite health and environmental concerns, the chlorinated compound MCPA, is widely used as a weed killer.

![MCPA](image.png)

Using **not** more than 3 steps, draw a reaction scheme to show how MCPA can be synthesised from 2–methylphenol. [3]

(d) Compound E is a derivative of MCPA which may be a potential insecticide. The synthesis of Compound E is given below.

![Compound E](image.png)

Describe the mechanism for the synthesis of Compound E. [3]
(e) Describe the variation in melting points of the chlorides of the elements from sodium to phosphorus and explain the variation in terms of structure and bonding. [4]

(f) Describe a reaction, without the use of bromide solution, which shows that chlorine is a stronger oxidising agent than iodine. [2]

[Total: 20]
Phosphorus is an element in Period 3 of the Periodic Table with wide ranging application in inorganic and organic synthesis.

(a) Explain why the first ionisation energy of phosphorus is higher than that of sulfur, S, and arsenic, As, respectively. [2]

(b) Define the second ionisation energy of phosphorus with an appropriate equation. [2]

(c) When heated in air, phosphorus and sodium forms oxides which can react with acids, bases or water.

(i) Write balanced equations for the reaction between oxides for the two elements and an appropriate acid or base.

(ii) Describe the reactions, if any, of the two oxides with water containing universal indicator. Chemical equations are not required. [5]

(d) Phosphoric acid is used as a catalyst in the industrial preparation of \( \text{CH}_3\text{CH}_2\text{CH(OH)}\text{CH}_3 \) from compound \( F, \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \).

(i) State the reagent and any other conditions required in this industrial preparation.

(ii) Compound \( G \), which is an isomer of \( F \), exists as a pair of geometric isomers. Deduce the structure of \( G \).

(iii) Predict the carbon-containing products obtained when \( F \) and \( G \) are separately heated with acidified potassium manganate(VII). [3]

(e) \( \text{PCl}_5 \) is used for substitution reactions in organic chemistry.

An optically active compound \( P \), with molecular formula \( \text{C}_3\text{H}_7\text{O}_2\text{N} \), reacts with \( \text{PCl}_5 \) to give white fumes. When a solution containing \( P \) is warmed with aqueous sodium hydroxide, a pungent gas is evolved. Upon acidification of the resulting mixture, compound \( Q, \text{C}_3\text{H}_6\text{O}_3 \), can be isolated. When \( Q \) is warmed with concentrated sulphuric acid, a cyclic compound \( R, \text{C}_6\text{H}_8\text{O}_4 \), is formed. Compound \( S \) is a structural isomer of \( Q \) and is not optically active. When \( S \) is warmed with concentrated sulphuric acid, a non-cyclic compound \( T, \text{C}_3\text{H}_4\text{O}_2 \), is produced.

Deduce the structures of compounds \( P, Q, R, S \) and \( T \). Explain the chemistry of the reactions described. [8]
INSTRUCTIONS TO CANDIDATES

Write your name, register number and class on this question paper and on the Cover Sheet provided.
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.
Start each question on a fresh sheet of paper.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

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

- Fasten all work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

The total marks for this paper is 80 marks.
The study of organic compounds includes the collection of kinetic data and thermodynamic data of the compounds.

(a) The kinetics of the hydrolysis of the ester, \( \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 \), may be investigated by the following method.

\[
\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{OH}
\]

In a 1 dm³ mixture, 0.350 mol of the ester was hydrolysed by heating with water and using hydrochloric acid as catalyst. The following results were obtained.

<table>
<thead>
<tr>
<th>Time/s</th>
<th>Concentration of ( \text{CH}_3\text{CH}_2\text{CO}_2\text{H} )/mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>340</td>
<td>0.105</td>
</tr>
<tr>
<td>680</td>
<td>0.185</td>
</tr>
<tr>
<td>1080</td>
<td>0.243</td>
</tr>
<tr>
<td>1440</td>
<td>0.278</td>
</tr>
</tbody>
</table>

(i) Suggest how the progress of this reaction may be followed in order to obtain the results as stated.

**Taking samples of reaction at the stated intervals** (i.e. at 340 s, 680 s, 1080 s and 1440 s) and **quenching** it with large amount of cold water. **Titrate sample** with dilute NaOH and suitable indicator.

(ii) By drawing a suitable graph using the data given above, show that the reaction is first order with respect to the ester. It has been found that the hydrolysis reaction is first order with respect to the hydrochloric acid.

The half life of the ester is approximately 640 seconds based on the data. Hence, the order of reaction with respect to the ester is 1 since a constant half life is established.
(iii) Deduce the units of the rate constant.

\[
\text{Rate} = k[\text{ester}][\text{HC}]/
\]

Units for \( k \) is \( \text{mol}^{-1} \text{dm}^3 \text{ s}^{-1} \)

(iv) State and explain the effect of a catalyst on the rate constant.

The catalyst **increases the rate constant** by **decreasing the activation energy** of the reaction and offers an **alternative pathway** for reaction.

(v) Using suitable bond energy values from the *Data Booklet*, calculate the \( \Delta H \) for the hydrolysis of the ester.

\[
\Delta H = \left[ 8 \times 410 + 2 \times 350 + 2 \times 360 + 740 + 2 \times 460 \right] - \left[ 8 \times 410 + 2 \times 350 + 2 \times 360 + 740 + 2 \times 460 \right] \\
= 0 \text{ kJ mol}^{-1}
\]

(vi) Given that the standard enthalpy change of reaction for the hydrolysis is +7.6 kJ mol\(^{-1}\), suggest a reason for the difference between this given value and the value that you have calculated in (a)(v).

The **ester is not in gaseous phase** which would make the calculation by bond energy inaccurate.

(b) Hydrolysis of ester can be achieved in the biological system by enzymes known as esterase. Enzymes are proteins that catalyse a specific chemical transformation in the biological system. Such enzymes are generally quaternary proteins.

(i) Sketch and explain the graph showing how the rate of hydrolysis changes with increasing concentration of the ester.

![Graph](image)

At **low concentration** of ester, the rate of hydrolysis is roughly proportional to the concentration of ester and therefore the **order of reaction with respect to ester is about 1**.

At **moderate concentration** of ester, the rate of hydrolysis is no longer proportional to the concentration of ester and therefore the **order of reaction with respect to ester is mixed order**.
At high concentration of ester, the rate of hydrolysis is independent of the concentration of ester and therefore the order of reaction with respect to ester is about 0.

(ii) Explain the meaning of quaternary structure of proteins.

The quaternary structure of a protein refers to the spatial arrangement of two or more polypeptide chains, held together into a specific geometry by bonding interactions like van der Waals’ forces, hydrogen bonding, ionic bonds and disulfide bridges.

(iii) List 2 other major functions of proteins in the body.

- As enzymatic catalysts (e.g. amylase breaks down starch in the digestive system)
- As transport molecules (e.g. haemoglobin transports oxygen)
- As storage molecules (e.g. iron is stored in the liver as a complex with protein ferritin)
- In movement (e.g. proteins are the major component of muscles)
- For mechanical support (e.g. skin and bone contain collagen – a fibrous protein)
- Mediate cell responses (e.g. rhodopsin is a protein in the eye used for vision)
- For immunity / protection against diseases (antibody proteins)
- For control of growth and cell differentiation (hormones)

(iv) Suggest and explain a chemical method for distinguishing the following pair of esters. You should state the expected observations.

HCO₂CH₂CH₃ and CH₃CH₂CO₂CH₃

**Method 1:**
Add aqueous NaOH separately to the 2 compounds and heat. Then, add aqueous iodine to both compounds.

**Observations:**
- Yellow ppt. observed for HCO₂CH₂CH₃.
- No yellow ppt. observed for CH₃CH₂CO₂CH₃.

**OR**

**Method 2:**
Add acidified KMnO₄ separately to the 2 compounds and heat.

**Observations:**
- For HCO₂CH₂CH₃, purple colour is decolourised. Effervescence observed. Gas evolved gives white precipitate with limewater. (Gas is CO₂.)
- For CH₃CH₂CO₂CH₃, purple colour is decolourised. No effervescence observed.

[9]

[Total: 20]
This question is about the chemistry of the transition metal, nickel and its compound.

(a) Explain why the colour of \([\text{Ni(NH}_3)_6]^{2+}(\text{aq})\) is blue.

The d orbitals of Ni\(^{2+}\) are split into two groups of different energy levels by NH\(_3\) ligands. When white light shines on the complex, a d electron undergoes d–d transition and is promoted to a higher energy d orbital. During the transition, the d electron absorbs in the orange region of the visible spectrum. The blue colour observed is the colour of transmitted light, which is a mixture of remaining wavelengths that are not absorbed.

(b) Ni(CO)\(_4\) is a compound formed by the reaction between nickel and carbon monoxide. The Mond process was developed by Ludwig Mond to extract and purify nickel from its ores. One of the stages of this process involves the decomposition of Ni(CO)\(_4\) at 227 °C to give nickel as shown in this equation below:

\[
\text{Ni(CO)}_4(\text{g}) \rightleftharpoons \text{Ni(s)} + 4\text{CO(}g\)
\]

The equilibrium constant, \(K_p\), for the equilibrium at 227 °C is 1.01 atm\(^3\). A sample of gaseous Ni(CO)\(_4\) was placed in a 2 dm\(^3\) evacuated container at 227 °C. At equilibrium, the partial pressure of CO was 2.00 atm.

\[1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}\]

(i) Sketch the shapes of the hybrid orbitals around the C atom in carbon monoxide.

Show 2 sp hybrid orbitals

(ii) Write an expression for \(K_p\).

\[
K_p = \frac{[\text{Ni(s)}][\text{CO}_x(\text{g})]^4}{[\text{Ni(CO)}_4(\text{g})]} = 1.01
\]

(iii) Calculate the total pressure of the system at equilibrium.

\[
(2.00)^4 / p_{\text{Ni(CO)}_4} = 1.01 \\
p_{\text{Ni(CO)}_4} = 15.842 = 15.8 \text{ atm} \\
total \text{ pressure of system} = 15.842 + 2.00 = 17.8 \text{ atm}
\]

(iv) Calculate the mass of Ni(CO)\(_4\) placed in the container initially.

\[
\begin{array}{c|c|c}
\text{Ni(CO)}_4(\text{g}) & \rightleftharpoons & \text{Ni(s)} + 4\text{CO(}g)
\end{array}
\]

Initial p/atm 
15.8 + (2.00/4) = 16.3
Eqm p/atm 
15.8 – 2.00
Let mass of Ni(CO)$_4$ be m.

\[ pV = nRT = (m/M)RT \]

\[ 16.3 \times 1.01 \times 10^5 \times 2 \times 10^{-3} = \{m / [58.7 + 4 \times (12.0 + 16.0)]\} \times 8.31 \times (227 + 273) \]

\[ m = 135.27 = 135 \text{ g} \]

(c) Ni is commonly used in catalytic hydrogenation reactions. One such example is given below.

Compound A, C$_{10}$H$_{12}$NOC$l$, has a chiral centre and dissolves in dilute sulfuric acid. It reacts with 2,4–dinitrophenylhydrazine to form an orange precipitate, but does not react with Tollens’ reagent. A reacts with H$_2$ in the presence of Ni catalyst followed by addition of aqueous bromine to form B, C$_{10}$H$_{11}$NOC/lBr$_3$. When 1 mol of compound B is heated under reflux with aqueous iodine and excess alkali, followed by careful acidification, compound C, C$_8$H$_4$NO$_4$Br$_3$ is formed together with 2 mol of yellow solid CH$I$_3.

Deduce the structures of compounds A, B and C, giving reasons for your answer.

- A has comparable number of carbon and hydrogen atoms and more than 6 carbon atoms
  \[ \Rightarrow \text{A contains a benzene ring} \]

- A dissolves in dilute acid
  \[ \Rightarrow \text{A undergoes neutralisation and is likely to contain an amine group} \]

- A undergoes condensation with 2,4–DNPH to form an orange precipitate, but does not undergo oxidation with Tollens’ reagent
  \[ \Rightarrow \text{A contains a ketone} \]

- A undergoes reduction with H$_2$/Ni to give B
  \[ \Rightarrow \text{Ketone in A is reduced to a secondary alcohol} \]

- A undergoes electrophilic substitution with aqueous Br$_2$ to give B, which contains 3 bromine atoms.
  \[ \Rightarrow \text{A contains phenylamine group} \]

- B undergoes oxidation with aq alkaline I$_2$
  \[ \Rightarrow \text{B likely to contain CH$_2$CH(OH)–} \]
  \[ \Rightarrow \text{C contains carboxylic acid groups} \]

- B also undergoes nucleophilic substitution with excess alkali due to loss of Cl in the molecular formula of compound C
  \[ \Rightarrow \text{B is a chloroalkane} \]

- 2 moles of CH$I$_3 is formed per mole of compound B
  \[ \Rightarrow \text{3rd and 5th position of the benzene ring must be substituted} \]
A

B

C

[9]
[Total: 20]
3 This question is about the varied chemical uses of HCl.

(a) (i) In the electrolysis of a solution of hydrochloric acid with inert platinum electrodes, an ammeter showed a reading of 0.450 A in the external circuit of the cell. 110 cm$^3$ of gas was evolved at the cathode after 30 minutes under room temperature and pressure. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.

At the cathode, $2H^+ + 2e \rightarrow H_2$

Amount of hydrogen gas evolved = $110 / 24000 = 0.004583$ mol

Amount of hydrogen gas evolved =

\[ Q = 0.004583 \times 2 \times 96500 = 884.583 \text{ C} \]

\[ I = \frac{Q}{t} = \frac{884.583}{30 \times 60} = 0.4914 \text{ A} \]

\[ % \text{ error} = \left(\frac{0.450 - 0.4914}{0.4914}\right) \times 100\% = 8.42\% \]

(ii) A student carried out a reaction involving acidified potassium dichromate(VI), together with an unknown half–cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be $-324 \text{ kJ mol}^{-1}$ and the procedure involved transferring 6 mol of electrons from the unknown solution to potassium dichromate(VI).

Using the expression of $\Delta G^\circ = -nF E^\circ_{\text{cell}}$, where $n$ is the number of moles of electrons transferred, $F$ is the Faraday constant and $E^\circ_{\text{cell}}$ is the overall cell potential, determine the $E^\circ_{\text{cell}}$ value and hence deduce the identity of the unknown half cell.

Using $\Delta G = -nF E^\circ_{\text{cell}}$

$-324 \times 10^3 = - 6 (96500) E^\circ_{\text{cell}}$

\[ E^\circ_{\text{cell}} = + 0.560 \text{ V} \]

Since procedure involved transfer of 6 mol of electrons from potassium dichromate (VI) to the unknown solution,

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O \quad (+1.33)$

$E_{\text{red}} = +1.33 \text{ V}$

Using $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{oxd}}$

$0.560 = +1.33 - E^\circ_{\text{oxd}}$

$E^\circ_{\text{oxd}} = -(0.560 - 1.33) = +0.77 \text{ V}$

The $E^\circ_{\text{oxd}}$ tally with the Fe$^{3+}$/Fe$^{2+}$ half cell
(b) A sample of sodium hypochlorite, NaOCl, was dissolved in 100 cm$^3$ of 0.123 mol dm$^{-3}$ HOCI ($pK_a = 7.50$) solution forming a buffer of pH 6.20. The buffer is then used to absorb HCl gas. Calculate the concentration of gaseous HCl (in mol dm$^{-3}$) that is required to be added to the buffer solution until it reaches pH 6.

\[
pH = pK_a + \log \text{Error! Objects cannot be created from editing field codes.}
\]

\[
6.20 = 7.50 + \log \text{Error! Objects cannot be created from editing field codes.}
\]

\[\log \text{Error! Objects cannot be created from editing field codes.} = -1.30\]

\[\text{Error! Objects cannot be created from editing field codes.} = 0.0501\]

\[\text{Error! Objects cannot be created from editing field codes.} = 0.0501 \times 0.123\]

\[= 0.006162 \text{ mol dm}^{-3}\]

On addition of HCl, let $x$ be the concentration of $H^+$

\[\text{[HOCI]}_{\text{new}} = 0.123 + x\]

\[\text{[OCl]}_{\text{new}} = 0.006162 - x\]

\[6.00 = 7.50 + \log \text{Error! Objects cannot be created from editing field codes.}\]

\[-1.50 = \log \text{Error! Objects cannot be created from editing field codes.}\]

\[0.03162 = \text{Error! Objects cannot be created from editing field codes.}\]

\[0.03162(0.123) + 0.03162x = 0.006162 - x\]

\[1.03162x = 0.00227\]

\[x = 0.00220 \text{ mol dm}^{-3}\]

(c) The decomposition temperature of hydrogen chloride is close to 3000 K. Predict, with reasoning, if the decomposition temperature of hydrogen astatide would be higher or lower than 3000 K.

The decomposition temperature of hydrogen astatide would be lower than 3000 K because down the group, covalent bond length of $H$–X increases. bond dissociation energy decreases. thermal stability decreases.

(d) Concentrated hydrochloric acid is commonly used in the reduction of trinitrobenzene (2,4,6–trinitrobenzene).

(i) Suggest the complete set of reagents, together with concentrated HCl, to be used in this reduction process.

Tin with (excess) concentrated HCl, followed by aqueous NaOH

(ii) Suggest the structural formula of the product formed.
(iii) Explain the relative basicity between the product formed in (d)(ii) and the melamine molecule as shown below in terms of their structures. The melamine molecule contains a triazine ring with 3 nitrogen atoms present in the ring.

\[ \begin{array}{c}
\text{NH}_2 \\
\text{H}_2\text{N} \\
\text{N} \\
\text{N} \\
\text{NH}_2 \\
\end{array} \]

Melamine

Melamine is less basic. The lone pair of electrons on the N atom from the amine group in melamine is more delocalised into the \( \pi \) electron cloud in triazine ring because of the electronegative N atoms present in the ring. The availability of the lone pair of electrons to accept a proton for dative bonding is reduced.

(e) 2,4,6–trinitrobenzene can also undergo Friedel–Crafts alkylation with \( \text{CH}_3\text{Cl} \) to form 2,4,6–trinitromethylbezene. The alkyl side chain can then be further reacted to form useful halogen derivatives. However, some side products like hydrogen chloride gas and compound D can also be formed in the process.

\[ \begin{array}{c}
\text{NO}_2 \\
\text{CH}_2\text{CH}_2\text{O}_2\text{N} \\
\text{NO}_2 \\
\text{O}_2\text{N} \\
\text{NO}_2 \\
\end{array} \]

Compound D

Using 2,4,6–trinitromethylbezene as the starting material, describe an appropriate mechanism that would result in the production of compound D.

\[ \begin{array}{c}
\text{Cl} \cdot \text{Cl} \rightarrow \text{UV} \rightarrow \text{2 Cl} \cdot
d\end{array} \]

(Note: must use chlorine radicals so that hydrogen chloride will be produced as the side product in the propagation step)

**Initiation**

\[ \text{Cl} \cdot \text{Cl} \rightarrow \text{UV} \rightarrow \text{2 Cl} \cdot \]

**Propagation**

\[ \begin{array}{c}
\text{O}_2\text{N} \end{array} \text{CH}_3 + \text{Cl} \cdot \rightarrow \begin{array}{c}
\text{O}_2\text{N} \end{array} \text{CH}_2 \cdot + \text{HCl} \]

**Termination**
4 Chlorine and its compounds are used to manufacture many products such as pesticides, medicines, plastics, bleaches and solvents.

(a) 1 mol of the following compounds is added to 1 dm$^3$ of water.

\[ \text{CH}_3\text{COCI, C/CH}_2\text{COOH and SiCl}_4 \]

Arrange the compounds in order of increasing pH of the resultant mixture formed. Briefly explain your answers, giving equations where appropriate. \[4\]

Resultant mixture formed when 1 mole of C/CH$_2$COOH is added to 1 dm$^3$ of water is the least acidic as C/CH$_2$COOH ionises only partially in water:

\[ \text{C/CH}_2\text{COOH} + \text{H}_2\text{O} \Leftrightarrow \text{C/CH}_2\text{COO}^- + \text{H}_3\text{O}^+ \]
Resultant mixture formed when 1 mol of CH₃COCl is added to 1 dm³ of water is fairly acidic as CH₃COCl hydrolyses, forming HCl which is a strong acid:

\[ \text{CH}_3\text{COCl} (l) + \text{H}_2\text{O} (l) \rightarrow \text{CH}_3\text{COOH} (aq) + \text{H}^+ (aq) + \text{Cl}^- (aq) \]

Resultant mixture formed when 1 mole of SiCl₄ is added to 1 dm³ of water is the most acidic as 1 mole of SiCl₄ hydrolyses to form 4 mole of HCl:

\[ \text{SiCl}_4 \text{ (aq)} + 2\text{H}_2\text{O} (l) \rightarrow \text{SiO}_2 \text{ (s)} + 4\text{H}^+ (aq) + 4\text{Cl}^- (aq) \]

Hence, in order of increasing pH of the resultant mixture formed on reaction with water:

\[ \text{SiCl}_4, \text{CH}_3\text{COCl}, \text{C}/\text{CH}_2\text{COOH} \]

(b) Both chloric(I) acid, HOCl and hydrogen chloride react with propene. In the reaction between chloric(I) acid and propene, chlorine is added to carbon–1 of propene in the major product. However, in the reaction between hydrogen chloride and propene, chlorine is added to carbon–2 of propene in the major product.

(i) Draw the displayed formula of the major product formed between propene and chloric(I) acid.

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{O} \\
\text{Cl} \\
\text{H} \\
\end{array}
\]

(ii) Explain briefly why chlorine from chloric(I) acid and from hydrogen chloride add to different carbon atoms in their reactions with propene.

[4]

In HOCl, Cl is partially positive so that Cl⁺ is the electrophile and Cl⁺ adds to carbon–1 to form the more stable carbocation.

Subsequent addition of OH⁻ results in the formation of the major product with chlorine added to carbon–1.

In HCl, chlorine is partially negative so that the electrophile is H⁺ rather than Cl⁺. Hence H⁺ adds to carbon–1 to form the more stable carbocation.

(c) Despite health and environmental concerns, the chlorinated compound MCPA, is widely used as a weed killer.

\[
\begin{array}{c}
\text{OCH}_2\text{COOH} \\
\text{C}_\text{H}_3 \\
\text{Cl} \\
\end{array}
\]

MCPA

Using not more than 3 steps, draw a reaction scheme to show how MCPA can be
synthesised from 2-methylphenol. [3]

\[
\begin{align*}
\text{OH} & \quad \text{Cl}_2 \text{ in CCl}_4 \\
\text{OH} & \quad \text{Cl} \quad \text{NaOH} \\
\text{O}^\prime & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{H}^+ \\
\text{OCH}_2\text{COOH} & \quad \text{Cl} \quad \text{Cl} 
\end{align*}
\]

(d) Compound \(E\) is a derivative of MCPA which may be a potential insecticide. The synthesis of Compound \(E\) is given below.

\[
\begin{align*}
\text{OH} & \quad \text{Cl} \quad \text{CH}_3 \\
\text{Cl} & \quad \text{NaOH} \\
\text{O}^\prime & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{H}^+ \\
\text{OCH}_2\text{COOH} & \quad \text{Cl} \quad \text{Cl} 
\end{align*}
\]

Compound \(E\)

Describe the mechanism for the synthesis of Compound \(E\).

\[
\begin{align*}
\text{CH}_3 & \quad \text{S}^+ \quad \text{S}^- \\
\text{H}_2\text{C} & \quad \text{Cl} \\
\text{CH}_3 & \quad \text{slow} \\
\text{O}^- & \quad \text{Cl}^+ \\
\text{Cl}^+ & \quad \text{fast} \\
\text{OC} \quad \text{Cl}^- \\
\text{Cl} & \quad \text{OC} \quad \text{Cl}^- 
\end{align*}
\]

(e) Describe the variation in melting points of the chlorides of the elements from sodium to phosphorus and explain the variation in terms of structure and bonding. [4]

Melting points of sodium chloride and magnesium chloride are higher than that of aluminium chloride, silicon tetrachloride and phosphorus pentachloride.

This is because NaCl and MgCl\(_2\) have giant ionic lattice structures and a large amount of energy is required to overcome strong electrostatic forces of attractions between the ions so that their melting points are high.

Al\(_2\)Cl\(_6\), SiCl\(_4\) and PC\(_5\) have simple molecular structure with weak van der Waals forces between the molecules so their melting points are lower than the ionic NaCl and MgCl\(_2\).
The order of increasing melting point is SiCl₄, PCl₅ and Al₂Cl₆ since van der Waals forces increases also in that order due to greater ease of distortion of electron cloud as the number of electrons increases from SiCl₄ to PCl₅ to Al₂Cl₆.

(f) Describe a reaction, without the use of bromide solution, which shows that chlorine is a stronger oxidising agent than iodine. [2]

React aqueous sodium thiosulfate separately with chlorine and iodine. Chlorine is strong enough an oxidising agent to oxidise S₂O₃²⁻ to SO₄²⁻ but iodine is too weak an oxidising agent to oxidise S₂O₃²⁻ to SO₄²⁻. Instead, iodine oxidises S₂O₃²⁻ only to S₄O₆²⁻.

OR

React aqueous iron(II) sulphate separately with chlorine and iodine. Chlorine is strong enough an oxidising agent to oxidise Fe²⁺ to Fe³⁺ but iodine is too weak an oxidising agent to oxidise Fe²⁺ to Fe³⁺.

[Total: 20]

5 Phosphorus is an element in Period 3 of the Periodic Table with wide ranging application in inorganic and organic synthesis.

(a) Explain why the first ionisation energy of phosphorus is higher than that of sulfur, S, and arsenic, As, respectively. [2]

Inter–electronic repulsion between paired 3p electrons in S makes it easier to remove one of the paired 3p electron compared to the unpaired 3p electron of P. Therefore the first ionisation energy of P is higher than that of S. As has a larger atomic radius and outermost electron of As experiences larger shielding effect by inner shell of electrons. Therefore the first ionisation energy of P is higher than that of As.

(b) Define the second ionisation energy of phosphorus with an appropriate equation. [2]

The second I.E is the energy required to remove one mole of electron from one mole of singly positively charged gaseous phosphorus ions to form one mole of doubly positively charged gaseous phosphorus ions.

\[ P^+ (g) \rightarrow P^{2+} (g) + e^- \]

(c) When heated in air, phosphorus and sodium forms oxides which can react with acids, bases or water.

(i) Write balanced equations for the reaction between oxides for the two elements and an appropriate acid or base.

\[ Na_2O (s) + 2HCl (aq) \rightarrow 2NaCl (aq) + H_2O (l) \]
P₄O₆ (s) + 12NaOH (aq) → 4Na₃PO₃(aq) + 6H₂O (l)
P₄O₁₀ (s) + 12NaOH(aq) → 4Na₃PO₄(aq) +6H₂O (l)

(ii) Describe the reactions, if any, of the two oxides with water containing universal indicator. Chemical equations are not required.

Na₂O reacts **vigorously** with water to form **basic** solution
UI colour in solution: **blue/purple**

P₄O₆ or P₄O₁₀ reacts **readily** with water to form **acidic** solution.
UI colour in solution: **red**

(d) Phosphoric acid is used as a catalyst in the industrial preparation of CH₃CH₂CH(OH)CH₃ from compound F, CH₃CH₂CH=CH₂.

(i) State the reagent and any other conditions required in this industrial preparation.

Steam, 65 atm, 300°C

(ii) Compound G, which is an isomer of F, exists as a pair of geometric isomers. Deduce the structure of G.

CH₃CH=CHCH₃

(iii) Predict the carbon–containing products obtained when F and G are separately heated with acidified potassium manganate(VII).

F: CH₃CH₂COOH and CO₂
G: CH₃COOH

(e) PCl₅ is used for substitution reactions in organic chemistry.

An optically active compound P, with molecular formula C₃H₇O₂N, reacts with PCl₅ to give white fumes. When a solution containing P is warmed with aqueous sodium hydroxide, a pungent gas is evolved. Upon acidification of the resulting mixture, compound Q, C₃H₄O₃, can be isolated. When Q is warmed with concentrated sulphuric acid, a cyclic compound R, C₆H₈O₄, is formed. Compound S is a structural isomer of Q and is not optically active. When S is warmed with concentrated sulphuric acid, a non–cyclic compound T, C₃H₄O₂, is produced.

Deduce the structures of compounds P, Q, R, S and T. Explain the chemistry of the reactions described.

- P is optically active
  \[\Rightarrow P \text{ is chiral}\]
- P undergoes **substitution** reaction with PCl₅
酒精（alcohol）存在于P中

- P在加热与NaOH条件下进行碱性水解（alkaline hydrolysis），生成NH₃
- P中主要含胺基（primary amide）

- Q进行酯化/缩合/亲核酰基置换（esterification/condensation/nucleophilic acyl substitution）
- R含酯基（ester group）

- S非手性（not chiral）

- S进行消除反应（elimination）与浓H₂SO₄反应生成T
- T含烯烃（alkene）

结构图：

- P: CH₃
  H – C – CONH₂
  OH

- Q: CH₃
  H – C – COOH
  OH

- R: H₃C
  O
  O
  C – O – O – C – H
  H – C – CH₂COOH
  OH

- S: H
  H – C – CH₂COOH
  OH

- T: H
  H – C – C
  H
  COOH

[Total: 20]
READ THESE INSTRUCTIONS FIRST

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

There are forty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D.
Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
Section A

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

1 Methane was burned in an incorrectly adjusted burner. The methane was converted into a mixture of carbon dioxide and carbon monoxide in the ratio of 98:2, together with water vapour.

What will be the volume of oxygen consumed when $y$ dm$^3$ of methane is burned?

A 1.99$y$ dm$^3$  
B 1.995$y$ dm$^3$  
C 0.995$y$ dm$^3$  
D 0.99$y$ dm$^3$

2 To identify an oxide of nitrogen, 0.10 mol of the oxide was mixed with 10 dm$^3$ of hydrogen gas and passed over a heated catalyst. At the end of the reaction, 0.4 dm$^3$ of hydrogen gas remained. The ammonia produced required 125 cm$^3$ of 1.6 mol dm$^{-3}$ HCl for neutralisation. All gasoues volumes were measured at room temperature and pressure.

What is the formula of the oxide of nitrogen?

A NO  
B N$_2$O  
C NO$_2$  
D N$_2$O$_4$

3 A 2 g sample of hydrogen at temperature $T$ and of volume $V$ exerts a pressure of $p$. Deuterium, $^2$H is an isotope of hydrogen.

Which of the following would also exert a pressure $p$ at the same temperature?

A 2 g of deuterium of volume $V$  
B 4 g of deuterium of volume $\frac{1}{2}V$  
C a mixture of 1 g of hydrogen and 2 g of deuterium of total volume $V$  
D a mixture of 2 g of hydrogen and 1 g of deuterium of total volume $2V$

4 Which atom has the highest ratio of unpaired electrons to paired electrons in its ground state?

A boron  
B carbon  
C nitrogen  
D oxygen

5 Which one of the following pairs consist of a planar molecule and a polar molecule?

A C$_6$H$_5$CH$_3$ and CO$_2$  
B C$_6$H$_5$ and H$_3$PO$_4$  
C CH$_2$=CHCHO and CH$_3$OCH$_3$  
D C$_6$H$_6$ and CCl$_4$
6 Which of the following statements describe a phenomenon which can be explained by intermolecular hydrogen bonding?

A The melting points of the Group I hydroxides increase with increasing relative molecular mass.
B CH$_3$OCH$_3$ ($M_r = 46$) as a higher boiling point than CH$_3$CH$_2$CH$_3$ ($M_r = 44$)
C Ice has a lower density than water at 0°C.
D Glycine, NH$_2$CH$_2$COOH has a higher solubility in water than butane.

7 The kinetics of the reaction between H$^+$ (aq) and S$_2$O$_3^{2-}$ can be investigated experimentally by varying the volumes of HCl(aq) and Na$_2$S$_2$O$_3$(aq) used and determining the time taken, $t$, for the formation of sulfur to completely obscure the cross as shown in the diagram.

$$\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{S(s)} + \text{SO}_2(\text{g}) + \text{H}_2\text{O(l)}$$

The table below shows the experimental results obtained.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Volume used / cm$^3$</th>
<th>$t$ / s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 mol dm$^{-3}$ HCl(aq)</td>
<td>0.040 mol dm$^{-3}$ Na$_2$S$_2$O$_3$(aq)</td>
</tr>
<tr>
<td>1</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>15.0</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>15.0</td>
<td>10.0</td>
</tr>
<tr>
<td>4</td>
<td>20.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

What is the value of $x$ in Experiment 4?

A 21  C 85
B 43  D 170
A simple decomposition reaction is shown below.

\[ \text{AB(g)} \rightarrow \text{A(g)} + \text{B(g)} \]

The rate equation was found to be as follows.

\[ \text{Rate} = k[\text{AB}] \text{ where rate constant, } k = 0.2 \text{ s}^{-1} \]

Estimate the time taken for AB(g) to reach one eighth of its initial concentration of 1.5 mol dm\(^{-3}\). 

<table>
<thead>
<tr>
<th>Option</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.0 s</td>
</tr>
<tr>
<td>B</td>
<td>7.5 s</td>
</tr>
<tr>
<td>C</td>
<td>10.4 s</td>
</tr>
<tr>
<td>D</td>
<td>13.9 s</td>
</tr>
</tbody>
</table>

Hydrogen iodide dissociates into its elements according to the following equation.

\[ 2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)} \quad \Delta H = +9 \text{ kJ mol}^{-1} \]

A mixture of H\(_2\) (g), I\(_2\) (g) and HI (g) rapidly comes to equilibrium in a 2.0 L container. After the reaction has been at equilibrium for 10 minutes, the volume of the container is suddenly reduced to 1.3 L at constant temperature.

Which one of the following graphs best represents the effect of this decrease in volume on the concentration of the gases in the mixture?
10 Phosphorus(V) chloride, $\text{PCl}_5$, decomposes to form phosphorus(III) chloride, $\text{PCl}_3$, and chlorine, $\text{Cl}_2$ according to the equation

$$\text{PCl}_5(g) \leftrightharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$$

Four different flasks, 1, 2, 3 and 4, at the same temperature, contain a mixture of $\text{PCl}_5$, $\text{PCl}_3$ and $\text{Cl}_2$. The concentration, in mol dm$^{-3}$, of these components in each of the flasks is shown below. In three of the four flasks, the mixture of gases is at equilibrium.

In which one is the mixture of gases not at equilibrium?

<table>
<thead>
<tr>
<th>Flask</th>
<th>[PCl$_5$(g)]</th>
<th>[PCl$_3$(g)]</th>
<th>[Cl$_2$(g)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.15</td>
<td>0.20</td>
<td>0.30</td>
</tr>
<tr>
<td>B</td>
<td>0.20</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>C</td>
<td>0.10</td>
<td>0.10</td>
<td>0.40</td>
</tr>
<tr>
<td>D</td>
<td>0.30</td>
<td>0.80</td>
<td>0.15</td>
</tr>
</tbody>
</table>

11 Two titrations were performed as shown below

Which of the following statements is true?

A The weak acid will require a greater volume of NaOH solution than the strong acid to reach the equivalence point.

B The weak acid will require a smaller volume of NaOH solution than the strong acid to reach the equivalence point.

C The weak acid will require the same amount of NaOH as the strong acid to reach the equivalence point.

D The equivalence point in a titration of a weak monoprotic acid with NaOH solution cannot be determined.
12. Strontium hydride is an ionic compound. The standard enthalpy changes, $\Delta H_1$ and $\Delta H_2$ are known.

$$\text{Sr(s)} \rightarrow \text{Sr}^{2+}(g) + 2e^- \quad \Delta H_1$$

$$\text{H}_2(g) + 2e^- \rightarrow 2\text{H}^-(g) \quad \Delta H_2$$

What additional data is needed to determine the lattice energy of strontium hydride?

A. The first ionisation energy of hydrogen.
B. The standard enthalpy change of atomisation of hydrogen.
C. The standard enthalpy change of atomisation of strontium.
D. The standard enthalpy change of formation of strontium hydride.

13. Four half cells are constructed as follows.

- **Half cell I**: an electrode of metal $P$ in a 1.0 M solution of $P^+(aq)$ ions
- **Half cell II**: an electrode of metal $Q$ in a 1.0 M solution of $Q^+(aq)$ ions
- **Half cell III**: an electrode of metal $R$ in a 1.0 M solution of $R^+(aq)$ ions
- **Half cell IV**: an electrode of Cu(s) metal in a 1.0 M solution of $\text{Cu}^{2+}(aq)$ ions

The half cells are connected in pairs, as shown below, to form a series of galvanic cells. For each cell, the polarity of the electrodes and the voltage generated are recorded.

<table>
<thead>
<tr>
<th>Half cells used</th>
<th>Positive electrode</th>
<th>Negative electrode</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I and IV</td>
<td>$P$</td>
<td>$Cu$</td>
<td>0.46</td>
</tr>
<tr>
<td>II and IV</td>
<td>$Cu$</td>
<td>$Q$</td>
<td>0.57</td>
</tr>
<tr>
<td>III and IV</td>
<td>$Cu$</td>
<td>$R$</td>
<td>1.10</td>
</tr>
<tr>
<td>II and III</td>
<td>$Q$</td>
<td>$R$</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Which one of the following alternatives lists the metals in order of increasing strength as reducing agents?

A. $R$, $Q$, $Cu$, $P$  
B. $Cu$, $P$, $Q$, $R$  
C. $P$, $Cu$, $R$, $Q$  
D. $P$, $Cu$, $Q$, $R$  

14. Aqueous sodium chloride (brine) is electrolysed by using inert electrodes in a cell which is stirred so that the products of electrolysis are able to react. The cell is kept cold.

Which one of the following pairs of substances is among the major products?

A. Hydrogen and sodium chlorate(I)  
B. Hydrogen and sodium chlorate(V)  
C. Hydrogen and chlorine only  
D. Sodium hydroxide and chlorine only
15 The structure of compound $X$ is given below.

![Compound X](image)

How many chiral centres are there in the product when compound $X$ is hydrogenated with sodium boron hydride?

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>C</td>
<td>6</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>D</td>
<td>8</td>
</tr>
</tbody>
</table>

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

Based on bond energies listed in the *Data Booklet*, what are the possible products of the following reaction?

\[
\cdot \text{CH}_3 + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow
\]

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH$_4$ + CH$_3$CHCl</td>
<td>C</td>
<td>CH$_3$CH$_2$CH$_3$ + Cl$^*$</td>
</tr>
<tr>
<td>B</td>
<td>CH$_3$CH$_2$CH$_2^*$ + HCl</td>
<td>D</td>
<td>CH$_3$CH$_2$CH$_2$Cl + H$^*$</td>
</tr>
</tbody>
</table>

17 An organic compound $Y$ undergoes the following reactions:

(i) It decolourises a solution of bromine in tetrachloromethane.
(ii) It reacts with sodium bromide in concentrated sulfuric acid.
(iii) It reacts with hot alkali to produce a compound with two alcohol functional groups.

Which compound could be $Y$?

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HOH$_2$CCH=CHCH=CHCH$_2$Cl</td>
<td>B</td>
<td>Cl$_2$CHCH=CHCH$_3$COOH</td>
</tr>
<tr>
<td>C</td>
<td>BrCH$_2$CH$_2$CHCl/CH$_2$COCl</td>
<td>D</td>
<td>Cl/CH$_2$CH$_2$CH=CHCH(Cl)/CH$_2$OH</td>
</tr>
</tbody>
</table>
18 Ibuprofen is an anti-inflammatory agent.

![Ibuprofen](image)

Which of the following could be part of a sequence for synthesizing ibuprofen?

[In the sequence below, R = ]

A: 

B: 

C: 

D: 

19 In which of the following sequences does the value of \( pK_a \) decrease continuously?

A: \( \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H} > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} \)

B: \( \text{CCl}_3\text{CO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H} > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} \)

C: \( \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H} \)

D: \( \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H} \)
The production of 4-chloro-3-nitrobenzoic acid from methylbenzene is as follows:

Which of the following shows the correct intermediates for 1 and 2 with the highest yield of the final product?

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>![Intermediate A 1]</td>
<td>![Intermediate A 2]</td>
</tr>
<tr>
<td>C</td>
<td>![Intermediate C 1]</td>
<td>![Intermediate C 2]</td>
</tr>
<tr>
<td>D</td>
<td>![Intermediate D 1]</td>
<td>![Intermediate D 2]</td>
</tr>
</tbody>
</table>
21 An account in a student’s notebook read:
‘An excess of aqueous bromine was added to aqueous phenol in a test tube, 2,4,6-tribromophenol was produced as a creamy-white precipitate suspended in a yellow alkaline solution.’

Which statement in this account must have been **incorrect**?

A The precipitate is not 2,4,6-tribromophenol, but a mixture of 2- and 4-bromophenol.
B The precipitate obtained is not creamy-white, but yellow.
C The resultant solution is not alkaline, but acidic.
D The resultant solution is not yellow, but purple.

22 Ethanoic acid can be made by direct carbonylation of methanol, in presence of a rhodium catalyst.

\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{rhodium catalyst}} \text{CH}_3\text{COOH}
\]

Using a similar method, which of the following could be expected to produce compound **W**?

![Compound W](image)

A

B

C

D
The amino acids glutamine and glutamic acid can react with each other to form amide linkages.

![Glutamine and Glutamic acid](image)

What is the maximum number of different compounds, each containing one amide linkage, that can be formed from one molecule of glutamine and one molecule of glutamic acid?

A 2  
B 3  
C 4  
D 5

B is synthetic nonapeptide that is resynthesised from the amino acids found in honey bee venom. To investigate the sequence of amino acids in B, the nonapeptide was first hydrolysed by two enzymes. The protein fragments were then separated and their sequence determined.

The following protein fragments were obtained from the first enzyme which hydrolysed the peptide chain at the carboxylic end of the amino acid isoleucine, Ile.

\[
\text{Arg-Ile} \\
\text{Ser-Lys-Trp-Ile} \\
\text{Lys-Leu-Arg}
\]

The second enzyme, which hydrolysed the peptide chain at the carboxylic end of the amino acid lysine, Lys, yielded the following fragments

\[
\text{Arg-Ile-Ser-Lys-Trp-Ile-Lys-Leu-Arg}
\]

Which of the following is the correct primary structure of the nonapeptide B?

A Lys-Leu-Arg-Ile-Ser-Lys-Trp-Ile-Lys  
B Trp-Ile-Lys-Leu-Arg-Ile-Ser-Lys-Trp  
C Arg-Ile-Ser-Lys-Trp-Ile-Lys-Leu-Arg  
D Ser-Lys-Trp-Ile-Lys-Leu-Arg-Ile-Ser

Haemoglobin is the oxygen carrying pigment in red blood cells. It contains two α-sub-units and two β-sub-units. What are the main forces responsible for holding the four subunits together?

A van der Waals' forces  
B electrostatic forces  
C peptide bonds  
D hydrogen bonds
26 Two properties of non-metallic elements and their atoms are as follows.

property 1 has an oxide that can form a strong acid in water
property 2 has no paired 3p electrons

Which properties do phosphorus and sulfur have?

<table>
<thead>
<tr>
<th></th>
<th>phosphorus</th>
<th>sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 and 2</td>
<td>1 only</td>
</tr>
<tr>
<td>B</td>
<td>1 only</td>
<td>1 and 2</td>
</tr>
<tr>
<td>C</td>
<td>1 and 2</td>
<td>1 and 2</td>
</tr>
<tr>
<td>D</td>
<td>2 only</td>
<td>1 only</td>
</tr>
</tbody>
</table>

27 At 900 °C, CaCO₃ decomposes producing CO₂ and the metal oxide. At 1100 °C, CaSO₄ decomposes producing SO₃ and the metal oxide.

Which statement explains the greater stability of CaSO₄?

A CaCO₃ has a higher lattice energy than CaSO₄.
B The CO₂ molecule is smaller than SO₃.
C The charge density of CO₃²⁻ is greater than that of SO₄²⁻.
D CO₃²⁻ ions are more easily polarised than SO₄²⁻.

28 X is a salt of one of the halogens chlorine, bromine, iodine, or astatine (proton number 85). The reaction scheme shows a series of reactions using a solution of X as the starting reagent.

What could X be?

A sodium chloride
B sodium bromide
C potassium iodide
D potassium astatide
29. How does concentrated sulfuric acid behave when it reacts with sodium chloride?
   A. as an acid only
   B. as an acid and oxidising agent
   C. as an oxidising agent only
   D. as a reducing agent only

30. The diagram shows some reactions of salt Q.

   What is the identity of Q?
   A. Al₂(SO₄)₃
   B. PbSO₄
   C. ZnSO₃
   D. ZnSO₄
Section B

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

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

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

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
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</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 are correct</td>
<td>2 and 3 are correct</td>
<td>1 only is correct.</td>
</tr>
</tbody>
</table>

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

31 Which of the following quantities is equal to the Avogadro constant?

1. The number of oxygen atoms in 49.9 g of allactite, Mn₇(AsO₄)₂(OH)₁₈, of molar mass 798 g mol⁻¹
2. The number of aqueous chloride ions in a solution containing 0.5 mol of the complex, [Cr(H₂O)₅Cl]Cl₂
3. The number of ions in 168 g of Reinecke’s salt, NH₄[Cr(NH₃)₂(SCN)₄], of molar mass 336 g mol⁻¹

32 Which of the following is hydrogen bonded in the liquid state?

1. CH₃NH₂
2. CH₃CHO
3. CH₂F₂

33 Which suggested mechanisms are consistent with the experimentally obtained rate equations?

1. Rate = k(NO)[H₂]  
   2NO + H₂  →  N₂O + H₂O  (slow)  
   N₂O + H₂  →  N₂ + H₂O  (fast)
2. Rate = k[A]²[B]  
   2A ↔ A₂  (fast)  
   A₂ + B  →  A₃B  (slow)  
   A₃B + A  →  A₄B  (fast)
3. Rate = k[HBr][O₂]  
   2HBr + O₂  →  2HBrO  (slow)  
   HBrO + HBr  →  H₂O + Br₂  (fast)
34 The use of the Data Booklet is relevant to this question.
An example of a reaction catalysed by transition metal ions is given below:

$$\text{S}_2\text{O}_8^{2-}(aq) + 2\text{I}^- (aq) \rightarrow 2\text{SO}_4^{2-}(aq) + \text{I}_2(aq)$$

The $E^\circ$, values for the half-reactions are:

$E^\circ, (\text{I}_2 / \text{I}^-) = +0.54 \text{ V}$

$E^\circ, (\text{S}_2\text{O}_8^{2-} / \text{SO}_4^{2-}) = +2.01 \text{ V}$

Which of the following transition metal ions can be used to catalyse this reaction?

1. Fe$^{3+}$
2. Co$^{3+}$
3. V$^{3+}$

35 Which compounds could undergo elimination reaction when treated with hot ethanolic potassium hydroxide?

1. \[
\begin{align*}
\text{H} \\
\text{H}_3\text{C} & \text{-} \text{C} & \text{-} \text{CH}_3 \\
\text{Br} & & \\
\end{align*}
\]

2. \[
\begin{align*}
\text{Br} & \text{-} \text{C} & \text{-} \text{Br} \\
\text{Br} & & \text{CH}_3 \\
\end{align*}
\]

3. \[
\begin{align*}
\text{CH}_3 \\
\text{H}_3\text{C} & \text{-} \text{C} & \text{-} \text{CH}_2\text{Br} \\
\text{CH}_3 & & \\
\end{align*}
\]
The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th></th>
<th>A</th>
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</tr>
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</table>

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

36. Which of the following statements is true for the compound below?

1. It is a non-planar compound.
2. When boiled with aqueous sodium hydroxide, it is converted to
3. It will react with 2,4-dinitrophenylhydrazine at room temperature.

37. Esters can be synthesized by reaction of a carboxylate anion with an alkyl halide.

$$
\text{RCO}_2^- + \text{R'}X \rightarrow \text{RCO}_2\text{R'} + X^- \quad \text{where} \ X = \text{Cl, Br or I}
$$

Which of the following esters can be prepared using this method?

1. 
2. 
3. 
38 Which of the following mixture produce ND₃ gas upon heating?  
[D = ²H, an isotope of hydrogen]

1. CaO (s) and ND₂Cl (s)  
2. CH₃CN and NaOD in D₂O  
3. CH₃CONH₂ and NaOD in D₂O

39 Which properties in the sequence hydrogen chloride, hydrogen bromide and hydrogen iodide steadily increase?

1. thermal stability  
2. bond length  
3. ease of oxidation

40 The rock dolomite is a double carbonate of magnesium and calcium, CaCO₃·MgCO₃. When heated strongly, a product called calcined dolomite is formed which is used to line some furnaces for the production of metals.

Why is calcined dolomite used for this purpose?

1. It is a refractory material.  
2. It will absorb acidic impurities in metallurgical processes.  
3. It will reduce metallic oxides to metals.
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INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION 2
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS INDEX NUMBER

CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper

Additional Materials: Data Booklet

11 September 2012
2 hours

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer all questions in the space provided.
A Data Booklet is provided.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

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

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

For Examiner’s Use

<table>
<thead>
<tr>
<th>Section A</th>
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<tbody>
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Significant figures

Handwriting

Total 72

This document consists of 18 printed pages.
1 Planning (P)

A student was given 50 cm$^3$ of three acidic solutions labelled X, Y and Z. She was asked to provide the identities of them by conducting a simple experiment.

The identities of the three solutions are:

1 mol dm$^{-3}$ ethanoic acid, CH$_3$COOH
1 mol dm$^{-3}$ hydrochloric acid, HC/$\text{I}$
2 mol dm$^{-3}$ hydrochloric acid, HC/$\text{I}$

Her teacher advised her to measure the temperature change of the reactions and calculate the enthalpy change of neutralisation of an acid and base reaction. The student is also provided with 200 cm$^3$ of 1 mol dm$^{-3}$ sodium hydroxide, NaOH.

The student let the volume ratio of each of the three solutions to sodium hydroxide be 1:1. She tested the experiment and realised that with this volume ratio, she is unable to differentiate the different concentrations of hydrochloric acid.

(a) Construct balanced equations for the reactions between the given acids and base. [1]

(b) The following table shows the volumes used by the student. Explain, with the aid of calculation, why the student’s experiments will not aid the differentiation of the different concentrations of hydrochloric acid.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Volume of 1 mol dm$^{-3}$ NaOH / cm$^3$</th>
<th>Volume of 1 mol dm$^{-3}$ HC/$\text{I}$ / cm$^3$</th>
<th>Volume of 2 mol dm$^{-3}$ HC/$\text{I}$ / cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
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<tr>
<td>2</td>
<td>50</td>
<td>50</td>
<td>50</td>
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</table>
(c) Write a plan which will allow an identification of the three solutions to be made. You may use the reagents and apparatus normally found in a school or college laboratory. However, you are not provided with an indicator.

In your plan you should give essential details, including quantities, of the identification procedure.

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..............................................................................................[6]
(d) Explain how you can make use of your experimental data to identify the three solutions.

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(e) Discuss one possible source of error in conducting your experiment and suggest improvement to produce a more reliable result.

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

[Total: 12]
2 (a) Iodine is not very soluble in water but in the presence of iodide ions, it can dissolve to form a tri-iodide complex as follows:

\[ \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^- \]

(i) Draw a dot and cross diagram for the tri-iodide ion and hence state its shape and bond angle.

Shape: ........................................

Bond angle: .................................

(ii) Explain why fluorine does not form the corresponding F$_3$ ion.

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

.................................................................................................................................  [3]

(b) IF$_7$ is a colourless gas prepared by the direct combination of iodine and fluorine. The I–F bond energy can be obtained from thermochemical data.

Standard enthalpy change of formation of IF$_7$(g) = –944 kJ mol$^{-1}$
Standard enthalpy change of atomisation of iodine = +107 kJ mol$^{-1}$

(i) Define what is meant by the standard enthalpy change of formation of IF$_7$.

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

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(ii) Draw an energy cycle diagram to determine the I–F bond energy. Incorporate values from the data above and any other relevant data from the Data Booklet into the diagram.
(iii) Explain why the I–F bond energy is not the mean of the I–I and F–F bond values.

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

[6]

(c) The typical daily food requirement of a person can be considered to be 1.2 kg of carbohydrate. The person obtains energy by oxidation of the carbohydrate, which can be represented by the formula \((\text{CH}_2\text{O})_n\).

(i) Construct an equation for the complete oxidation (combustion) of the carbohydrate \((\text{CH}_2\text{O})_n\).

…………………………………………………………………………………………..

(ii) The empirical relative formula mass of the carbohydrate is 30. Use your equation in (i) to calculate the number of moles of oxygen required by the person each day.

(iii) Calculate the volume of oxygen at room temperature and pressure for a human with a lifetime of 70 years.

[3]

[Total: 12]
3 (a) Panadol is the trade name for paracetamol or acetaminophen which is an over the counter analgesic (pain reliever) and antipyretic (fever reducer).

It can be synthesised in the lab from phenol via a series of steps.

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{dil HNO}_3} A \xrightarrow{\text{I}} B \xrightarrow{\text{II}} \text{paracetamol} \\
\end{align*}
\]

(i) State the reagents and conditions for step I and step II.

Step I:
Reagent(s): \[\text{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots}\]
Condition(s): \[\text{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots}\]

Step II:
Reagent(s): \[\text{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots}\]
Condition(s): \[\text{\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots}\]

(ii) Draw the structures of compound A and B in the boxes below.

A:  

B:
Paracetamol can be easily hydrolysed by aqueous NaOH to produce compound C and D. In the spaces below, write the formulae of the two products.

(iii) C: __________________________ D: __________________________

(b) One of the causes of fever is bacterial infection. Alcohol solutions are used as disinfectants on the skin as it can penetrate the bacterial cell wall and denature the proteins inside the cell.

(i) What do you understand by the term denaturation of proteins?

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

(ii) The part of the protein molecule which is affected by the ethanol added is as follows:

\[ \text{CH}_2\text{C} - \text{O} - \text{O} - \text{H} - \text{O} - \text{H} - \text{CH}_2\]

\[\text{spatial structure represents R group interaction}\]

Suggest what R group interaction was disrupted by ethanol.

...........................................................................................................................................................................................................................................................................................................................................................................................................................................
(iii) Another application of denaturation is found in the making of cheese. Casein is the predominant protein found in milk. When Lactobacillus bacterium is added to milk, lactic acid (2-hydroxypropanoic acid) is produced.

\[
\text{2-hydroxypropanoic acid}
\]

Besides hydrogen bonding, suggest and write an equation to explain what R group interaction is disrupted when lactic acid is produced.

Explanation

\[
\text{Equation}
\]

[4]

(c) The following table compares the \( pK_a \) values of ethanol, 2-hydroxypropanoic acid with that of ethanoic acid.

<table>
<thead>
<tr>
<th>compound</th>
<th>formula</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>( \text{CH}_3\text{CH}_2\text{OH} )</td>
<td>15.9</td>
</tr>
<tr>
<td>Ethanoic acid</td>
<td>( \text{CH}_3\text{COOH} )</td>
<td>4.76</td>
</tr>
<tr>
<td>2-hydroxypropanoic acid</td>
<td>( \text{CH}_3\text{CH(OH)COOH} )</td>
<td>3.86</td>
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</table>

(i) Suggest a reason why \( pK_a \) value of ethanoic acid is so much less than ethanol.

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(ii) Suggest a reason why 2-hydroxypropanoic acid is more acidic than ethanoic acid.

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[3]

(d) The degree of dissociation (ionisation) of ethylamine, CH₃CH₂NH₂, in 0.010 mol dm⁻³ aqueous solution is 0.17.

(i) Calculate the hydroxide ion concentration of this solution.

(ii) Calculate a value for the base dissociation constant, $K_b$, for ethylamine, stating the units.

[2]

[Total: 15]
4 (a) Nucleophiles are electron-rich species that can donate electrons and attack regions of low electron density. Reactions 1 and 2 show how the nucleophile, \( \text{Nu}^- \), reacts with two different carbonyl groups.

\[
\begin{align*}
\text{R–C–R}_1 & \quad + \quad \text{Nu}^- \quad \rightarrow \quad \text{R–C–R}_1 & \quad \text{Reaction 1} \\
\text{R–C–X} & \quad + \quad \text{Nu}^- \quad \rightarrow \quad \text{R–C–\text{Nu}} & \quad \text{Reaction 2}
\end{align*}
\]

where \( X: Cl, Br, I \)

The intermediates, \( X \) and \( Y \), shown below are formed by nucleophilic attack on two different compounds containing a carbonyl group of low electron density.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C–CH}_3 & \quad \text{CN} & \quad \text{X} \\
\text{CH}_3\text{CH}_2\text{C–C}^{\prime} & \quad \text{NH}_3^+ & \quad \text{Y}
\end{align*}
\]

(i) State the nucleophile required to form intermediate \( X \) and \( Y \) respectively.

Nucleophile for intermediate \( X \): ........................................

Nucleophile for intermediate \( Y \): ........................................

(ii) Identify the organic starting material to form intermediate \( X \).

(iii) State the type of reaction that gives intermediate \( Y \).

..........................................................
(iv) Suggest a mechanism for the complete reaction in which Y is an intermediate.

(b) In a reaction discovered just over 100 years ago by the German chemist Karl Fries, compound G is converted into compound K when it is heated with AlCl₃.

Compound K is a structural isomer of G.

\[
\begin{align*}
\text{Compound G} & \quad \xrightarrow{\text{AlCl}_3} \quad \text{K (C}_8\text{H}_8\text{O}_2) \\
\end{align*}
\]

Compound K is a 1,4-disubstituted benzene derivative. It is insoluble in water, but dissolves in NaOH(aq). It gives a white precipitate with Br₂(aq), and a yellow precipitate with alkaline aqueous iodine.
(i) Use the information given, name the functional groups in compound K.

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

(ii) Deduce the structural formula of K.

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

(iii) Draw the structural formulae for the aromatic products when compound K undergoes the following reactions.

\[ \text{compound } K \]

\[ \text{I}_2 + \text{NaOH}(\text{aq}) \]

\[ \text{Br}_2 (\text{aq}) \]

\[ \text{NaOH}(\text{aq}) \]
5 (a) An element $M$ forms an oxide which is a powerful oxidising agent. An acidified solution of the oxide of $M$, $MO_x$ ($x = 1, 2$ or $3$) will oxidise $Mn^{2+}$ (aq) to $MnO_4^-$ (aq), itself reduced to the element $M$. When $10.0 \ cm^3$ of $0.5 \ mol \ dm^{-3}$ of $MO_x$ was reacted with $0.40 \ mol dm^{-3}$ $Mn^{2+}$ (aq) in the presence of $H^+$ (aq), $15.0 \ cm^3$ of $Mn^{2+}$ (aq) was needed for complete reaction.

(i) Calculate the number of moles of electrons donated by $Mn^{2+}$.

(ii) Calculate the mole ratio of $MO_x$ and electrons accepted by $MO_x$.

(iii) Determine the original oxidation number of $M$ and the value of $x$.

(iv) Construct an equation for the reaction between $MO_x$(aq) and acidified $Mn^{2+}$(aq).
(b) Water, \( H_2O \), covers 70.9% of the Earth’s surface and is vital for all known forms of life. About 0.005% of water molecules consist of an oxygen atom bonded to two atoms of the hydrogen isotope, deuterium, \( ^2D \).

Deuterium oxide, \( D_2O \), is known as ‘heavy water’ and is used for research in chemical reactions because deuterium atoms react less quickly than normal hydrogen atoms, \( ^1H \).

Like \( H_2O \), pure \( D_2O \) is weakly ionised.

\[
2D_2O \rightleftharpoons D_3O^+ + OD^-
\]

For \( D_2O \), we can use the term \( K_D \) instead of \( K_W \) and \( pD \) instead of \( pH \).

(i) Explain what is meant by \textit{dynamic equilibrium}.

(ii) For pure \( D_2O \), \( K_D = 1.35 \times 10^{-15} \). Calculate the values of the following.

I. \( [D_3O^+] \)

II. \( pD \)

(iii) For this system, \( K_D \) increases when temperature increases. Suggest and explain whether the ionic dissociation of ‘heavy water’ is an exothermic or endothermic process.
(iv) When pure H₂O and pure D₂O are mixed, exchange of H and D atoms takes place and the following equilibrium is established.

\[ \text{D}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons 2\text{HD}_2\text{O}(l) \]

A mixture of 30 g of D₂O and 27 g of H₂O was placed in a vessel at 298 K. At equilibrium, it was found that the degree of dissociation of D₂O is 0.49. Calculate the \( K_c \) for this system.

[7]

[Total: 11]
Many copper minerals are found in hydrothermal deposits where they were formed by crystallization from very hot solutions which were trapped underground at high pressures. One such copper mineral is chalcopyrite, CuFeS₂.

Copper is extracted from the ore chalcopyrite, CuFeS₂, in a three-stage process. In the first stage of this extraction, the chalcopyrite is heated with silicon dioxide and oxygen.

(a) Balance the following equation for this first stage in which copper sulfide is formed.

\[
\text{CuFeS}_2 + \text{SiO}_2 + \text{O}_2 \rightarrow \text{Cu}_2\text{S} + \text{FeSiO}_3 + \text{SO}_2
\]

(b) Write the electronic configuration for Cu⁺ in Cu₂S:

\[
\text{Cu}^+ \text{...} \text{...} \text{...} \text{...} \text{...}
\]

(c) When water is added to white anhydrous CuSO₄, the solid dissolves to give a blue solution. On addition of concentrated NH₄Cl (aq), the solution changes to a yellow-green due to formation of copper containing species D. Concentrating the solution produces green crystals E of an ammonium salt with empirical formula CuN₂H₈Cl₄.

(i) Suggest the formulae of cation present in E.

Cation present in E ........................................

(ii) Suggest the formulae of anion D.

Anion D........................................

(iii) Suggest a balanced equation for the formation of anion D from aqueous CuSO₄.

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

When excess of NH₃ (aq) is added to species D, the yellow green solution turns to a deep blue solution.

(iv) Use this information and the information above to suggest the strength of NH₃, H₂O and Cl⁻ ligands in decreasing order.

......................................... > ................................ > ................................
(d) When a dilute aqueous solution containing a bidendate ligand, ethanedioate ion, C_2O_4^{2-}, is added to a solution containing aqueous copper(II) ions, a ligand exchange reaction occurs. In this reaction, four water molecules in the hydrated copper ion are replaced and a new complex \( F \) is formed.

(i) Explain what is meant by a bidendate ligand.

……………………………………………………………………………………………
……………………………………………………………………………………………

(ii) Suggest the formulae of complex \( F \) formed.

Identity of \( F \) ……………………………………………………………………………

(iii) In the complex \( F \) formed, the two water molecules are opposite each other. Draw a diagram to show how the ethanedioate ions are bonded to a copper ion and give a value for one of the O-Cu-O bond angles. You are not required to show the water molecules.

O-Cu-O bond angle: ………………………………………………………………

[4]

[Total: 10]
Answer **ALL** questions on the spaces provided.

1 **Planning (P)**

A student was given 50 cm³ of three acidic solutions labelled X, Y and Z. She was asked to provide the identities of them by conducting a simple experiment.

The identities of the three solutions are:

- 1 mol dm⁻³ ethanoic acid, \( \text{CH}_3\text{COOH} \)
- 1 mol dm⁻³ hydrochloric acid, \( \text{HCl} \)
- 2 mol dm⁻³ hydrochloric acid, \( \text{HCl} \)

Her teacher advised her to measure the temperature change of the reactions and calculate the enthalpy change of neutralisation of an acid and base reaction. The student is also provided with 200 cm³ of 1 mol dm⁻³ sodium hydroxide, \( \text{NaOH} \).

The student let the volume ratio of each of the three solutions to sodium hydroxide be 1:1. She tested the experiment and realised that with this volume ratio, she is unable to differentiate the different concentrations of hydrochloric acid.

(a) Construct balanced equations for the reactions between the given acids and base. [1]

\[
\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \quad \left(\frac{1}{2} \text{ m}\right) \\
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O} \quad \left(\frac{1}{2} \text{ m}\right)
\]

(b) The following table shows the volumes used by the student. Explain, with the aid of calculation, why the student’s experiments will **not** aid the differentiation of the different concentrations of hydrochloric acid.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Volume of 1 mol dm⁻³ ( \text{NaOH} ) / cm³</th>
<th>Volume of 1 mol dm⁻³ ( \text{HCl} ) / cm³</th>
<th>Volume of 2 mol dm⁻³ ( \text{HCl} ) / cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

No. of moles of 1 mol dm⁻³ \( \text{NaOH} \) = 1 x \( \frac{50}{1000} \) = 0.05 moles

No. of moles of 1 mol dm⁻³ \( \text{HCl} \) = 1 x \( \frac{50}{1000} \) = 0.05 moles

No. of moles of 2 mol dm⁻³ \( \text{HCl} \) = 2 x \( \frac{50}{1000} \) = 0.10 moles

**NaOH is the limiting reagent** [\( \frac{1}{2} \text{ m} \)]

No. of moles of water formed (for the acids) = 0.05 moles

Thus, the **amount of water produced is the same throughout**. Thus, the heat evolved / temperature change measured will be the same for the different concentrations of \( \text{HCl} \), **unable to differentiate the different concentration of \( \text{HCl} \)**.

**Note:** The enthalpy change of neutralisation of different \( [\text{HCl}] \) will be the same.
(c) Write a plan which will allow an identification of the three solutions to be made. You may use the reagents and apparatus normally found in a school or college laboratory. However, you are **not** provided with an indicator.

In your plan you should give essential details, including quantities, of the identification procedure.

To insert lines…………………………………………………………………………………………[6]

**Procedure**

1. By using a 50cm³/100cm³ measuring cylinder, place 50cm³ of NaOH, into the dry polystyrene cup provided supported with a glass beaker.
2. Measure and note the initial temperature of NaOH solution using a 1.0 °C interval thermometer.
3. By using a **second** 50cm³/100cm³ measuring cylinder (otherwise must mention washing & drying of the previous m.cylinder), measure 25 cm³ of acidic solution X.
4. Note the initial temperature of solution X.
   (both initial temp taken to find the average initial temp)
5. Add solution X to the cup in step 1.
6. Stir gently with a thermometer and note the highest temperature reached
7. Repeat the experiment (steps 1 to 6) with solutions Y and Z, using different measuring cylinders or mentioned in procedure measuring cylinder must be dry.

Record all your readings (temperature) in an appropriate table. or a sample table is drawn.

(d) Explain how you can make use of your experimental data to identify the three solutions.

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...........................................................................................................................[2]

Feasibility of the identification depends on volume used in the experiment.

Must use results obtained (either \( \Delta H_{\text{neu}} \) calculated or \( \Delta T \))

When \( V_{\text{NaOH}} \) **should be greater than** \( V_{\text{HCl}} \).
-using enthalpy change of neutralisation calculated:
Due to partial dissociation of CH₃COOH, some heat is absorbed to dissociate the weak acid. Thus, the $\Delta H_{\text{neu}}$ is less exothermic/smaller $\Delta T$ than HCl of same concentration.

In this experiment, more no. of moles of water produced with 2.0 mol dm⁻³ HCl used is than when 1.0 mol dm⁻³ HCl used. Thus, the one with a larger/twice the $\Delta T$ is the one using solution 2.0 mol dm⁻³ HCl.
(Although different concentration of HCl used in the experiment, they will have same $\Delta H_{\text{neu}}$ calculated.)

(e) Discuss one possible source of error in conducting your experiment and suggest improvement to produce a more reliable result.

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

- Heat loss to the surrounding is not taken into account, the enthalpy change of neutralisation is less exothermic than expected. Use a lid to cover the cup to reduce heat loss.
- (dependent on thermometer used) There is a percentage error in the enthalpy change calculated as the 1°C interval thermometer is used. Use a thermometer with higher precision (0.2°C interval) to reduce the percentage error.
- Slow response of thermometer. Use a data logger with temperature sensor instead.

[Total: 12]

2 (a) Iodine is not very soluble in water but in the presence of iodide ions, it can dissolve to form a tri-iodide complex as follows:

$$I_2 + I^- \rightarrow I_3^-$$

(i) Draw a dot and cross diagram for the tri-iodide ion and hence state its shape and bond angle.

*Bond angle of 180°.*

Thus the complex is **linear** in shape.
(ii) Explain why fluorine does not form the corresponding \( F_3^- \) ion.

Fluorine, being in Period 2, is not able to expand its outermost shell to accommodate 10 electrons.

(b) \( IF_7 \) is a colourless gas prepared by the direct combination of iodine and fluorine. The \( I-F \) bond energy can be obtained from thermochemical data.

- Standard enthalpy change of formation of \( IF_7(g) = -944 \) kJ mol\(^{-1}\)
- Standard enthalpy change of atomisation of iodine = +107 kJ mol\(^{-1}\)

(i) Define what is meant by the *standard enthalpy change of formation* of \( IF_7 \).

It is the enthalpy change when 1 mole of \( IF_7 \) is formed from its constituent elements, iodine and fluorine in their standard states under standard conditions of 1 atm and 298 K.

(ii) Draw an energy cycle diagram to determine the \( I-F \) bond energy. Incorporate values from the data above and any other relevant data from the *Data Booklet* into the diagram.

\[
7\text{BE}(I-F) -944.0 = +107 + \frac{7}{2}(+158)
\]

\[
\text{BE}(I-F) = +229 \text{ kJ mol}^{-1}
\]

(iii) Explain why the \( I-F \) bond energy is not the mean of the \( I-I \) and \( F-F \) bond values.

Fluorine is more electronegative than iodine. The covalent bond between the atoms is polarised, giving rise to a stronger bond.

(c) The typical daily food requirement of a person can be considered to be 1.2 kg of carbohydrate. The person obtains energy by oxidation of the carbohydrate, which can be represented by the formula \((CH_2O)_n\).
(i) Construct an equation for the complete oxidation (combustion) of the carbohydrate \((\text{CH}_2\text{O})_n\).
\[
(\text{CH}_2\text{O})_n + n\text{O}_2 \rightarrow n\text{CO}_2 + n\text{H}_2\text{O}
\]

(ii) The empirical relative formula mass of the carbohydrate is 30. Use your equation in (i) to calculate the number of moles of oxygen required by the person each day.

- Moles of carbohydrate = \(\frac{1200}{30n} = \frac{40}{n}\) mol
- Moles of oxygen = \(n \times \frac{40}{n} = 40\) mol

(iii) Calculate the volume of oxygen at room temperature and pressure for a human with a lifetime of 70 years.

- Moles of oxygen in 70 years = \(40 \times 70 \times 365 = 1.02 \times 10^6\) mol
- Volume at rtp = \(1.02 \times 10^6 \times 24 = 2.45 \times 10^7\) dm³

3 (a) Panadol is the trade name for paracetamol or acetaminophen which is an over the counter analgesic (pain reliever) and antipyretic (fever reducer).

It can be synthesised in the lab from phenol via a series of steps.

\[
\begin{align*}
\text{OH} & \quad \text{dil HNO}_3 \quad \text{A} \quad \text{I} \quad \text{B} \quad \text{II} \quad \text{OH} \\
\text{paracetamol} & \quad \text{C} \quad \text{N} \quad \text{CH}_3 \\
\end{align*}
\]

(i) State the reagents and conditions for step I and step II.

Step I:
- Reagent(s): ……………………………………………………………………………………………………..
- Condition(s): …………………………………………………………………………………………………..

Step II:
Step 1: Sn, concentrated HCl; heat with reflux
Then NaOH (aq); room temperature
Step 2: CH₃COCl, r.t.

(ii) Draw the structures of compound A and B in the boxes below.

A: \[
\begin{array}{c}
\text{OH} \\
\text{NO}_2 \ [1]
\end{array}
\]

B: \[
\begin{array}{c}
\text{OH} \\
\text{NH}_2 \ [1]
\end{array}
\]

Paracetamol can be easily hydrolysed by aqueous NaOH. In the spaces below, write the formulae of the two products.

(iii)

C: 

D:

CH₃COO⁻Na⁺

Ans
(b) One of the causes of fever is bacterial infection. Alcohol (ethanol) solutions are used as disinfectants on the skin as it can penetrate the bacterial cell wall and denature the proteins inside the cell.

(i) What do you understand by the term *denaturation* of proteins?

Denaturation of proteins refer to the disruption of the shape of the protein molecule without altering its primary structure but resulting in the loss of biological activity.

(ii) The part of the protein molecule which is affected by the ethanol added is as follows:

\[
\begin{align*}
\text{CH}_2\text{C}
\end{align*}
\]

represents R group interaction

Suggest what R group interaction was disrupted by ethanol.

**Ethanol disrupts the intermolecular hydrogen bonds**

(iii) Another application of denaturation is found in the making of cheese. Casein is the predominant protein found in milk. When Lactobacillus bacterium is added to milk, lactic acid (2-hydroxypropanoic acid) is produced.
2-hydroxypropanoic acid

Besides hydrogen bonding, suggest and write an equation to explain what R group interaction is disrupted in this case.

Explanation ...........................................................................................................................................
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Equation ...........................................................................................................................................
......................................................................................................................................................
**Lactic acid produced disrupts the ionic bonds in the protein**

-\( \text{COO}^- + \text{H}^+ \rightarrow \text{COOH} \)

---

(c) The following table compares the pK\(_a\) values of ethanol, 2-hydroxypropanoic acid with that of ethanoic acid.

<table>
<thead>
<tr>
<th>compound</th>
<th>formula</th>
<th>pK(_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>CH(_3)CH(_2)OH</td>
<td>15.9</td>
</tr>
<tr>
<td>2-hydroxypropanoic acid</td>
<td>CH(_3)CHOHCOOOH</td>
<td>3.86</td>
</tr>
<tr>
<td>Ethanoic acid</td>
<td>CH(_3)COOH</td>
<td>4.76</td>
</tr>
</tbody>
</table>

(i) Suggest a reason why pK\(_a\) value of ethanoic acid is so much less than ethanol.

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Comparing the pK\(_a\) values, ethanoic acid is more acidic than alcohol because

\( \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_3\text{O}^+ \)

For the ethoxide ion, CH\(_3\)CH\(_2\)O\(^-\), the electron donating ethyl group intensifies the negative charge on the oxygen atom of the anion (ethoxide ion).
Thus, the anion is not stable, hence less acidic than ethanoic acid.

\[ \text{CH}_3\text{COOH} + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \]

For the ethanoate ion, there is a delocalisation of the negative charge over the two oxygen atoms. This disperses the negative charge and stabilises the anion. Thus \( \text{CH}_3\text{COO}^- \) is more stable than \( \text{CH}_3\text{CH}_2\text{O}^- \).

(ii) Suggest a reason why 2-hydroxypropanoic acid is more acidic than ethanoic acid.

The higher acidity is due to the stabilisation of the carboxylate ion by intramolecular hydrogen bonding with the hydroxy group.

(d) The degree of dissociation (ionisation) of ethylamine (\( \text{CH}_3\text{CH}_2\text{NH}_2 \)) in 0.010 m\( \text{d}m^3 \) aqueous solution is 0.17.

(i) Calculate the hydroxide ion concentration of this solution.

Ans:

\[ [\text{OH}^-] = \text{concentration} \times \text{degree of dissociation} = c\alpha \]

\[ = 0.010 \times 0.17 = 0.0017 = 1.7 \times 10^{-3} \]

(ii) Calculate a value for the base dissociation constant, \( K_b \), for ethylamine (\( \text{CH}_3\text{CH}_2\text{NH}_2 \)), stating the units.

\[ K_b = \frac{[\text{OH}^-][\text{CH}_3\text{CH}_2\text{NH}_3^+]}{[\text{CH}_3\text{CH}_2\text{NH}_2]} = \frac{(1.7 \times 10^{-3})^2}{0.01} = 2.89 \times 10^{-4} \text{ mol dm}^{-3} \]

[Total: 15]
4 (a) Nucleophiles are electron-rich species that can donate electrons and attack regions of low electron density.

\[
\begin{align*}
\text{R} \quad &\text{C} \quad \text{R}_1 \quad + \text{Nu}^- \quad \rightarrow \quad \text{R} \quad &\text{C} \quad \text{R}_1 \quad \text{Nu} \quad \text{Reaction 1} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} \quad &\text{C} \quad \text{C} \quad \text{X} \quad + \text{Nu}^- \quad \rightarrow \quad \text{R} \quad &\text{C} \quad \text{C} \quad \text{Nu} \quad \text{Reaction 2} \\
\end{align*}
\]

where X: Cl, Br, I

The intermediates, X and Y, shown below are formed by nucleophilic attack on the above two different compounds containing a carbonyl group of low electron density.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C} \quad &\text{CH}_3 \quad \text{CN} \\
\text{CH}_3\text{CH}_2\text{C} \quad &\text{Cl} \quad \text{NH}_3^+ \\
\text{X} \quad &\text{Y} \\
\end{align*}
\]

(i) State the nucleophile to form intermediate X and Y respectively.

Nucleophile for intermediate X: ..............................................

Nucleophile for intermediate Y: ..............................................
(ii) Identify the organic starting material to form intermediate X.

[1]

Butan-2-one or CH₃CH₂COCH₃

(iii) State the type of reaction that gives intermediate Y.

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

Nucleophilic addition

(iv) Describe a mechanism for the complete reaction in which Y is an intermediate.

[3]

(b) In a reaction discovered just over 100 years ago by the German chemist Karl Fries, compound G is converted into compound K when it is heated with A/CI₃.
Compound K is a structural isomer of G.

![Chemical Structure](image)

Compound K is a 1,4-disubstituted benzene derivative. It is insoluble in water, but dissolves in NaOH(aq). It gives a white precipitate with Br₂(aq), and a yellow precipitate with alkaline aqueous iodine.

(i) Use the information given above to name the functional groups in compound K.

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

**Phenol & ketone**

(ii) Suggest the structural formula of K.

![Chemical Structure](image)

(iii) Suggest structures for the aromatic products of the following reactions.
5  (a)  An element M forms an oxide which is a powerful oxidising agent. An acidified solution of the oxide of M, MOₓ (x = 1, 2 or 3) will oxidise Mn²⁺(aq) to MnO₄⁻(aq), itself reduced to the element M. When 10.0 cm³ of 0.5 mol dm⁻³ of MOₓ was reacted with 0.40 moldm⁻³ Mn²⁺(aq) in
the presence of H\(^+(aq)\), 15.0cm\(^3\) of Mn\(^{2+}(aq)\) was needed for complete reaction.

(i) Calculate the number of moles of electrons donated by Mn\(^{2+}\).

\[ \text{Mn}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \]

Mol of Mn\(^{2+}\) = \( \frac{15}{1000} \times 0.40 = 6.00 \times 10^{-3} \text{ mol} \)

Mol of e donated by Mn\(^{2+}\) = 5 \times 6.00 \times 10^{-3} = 0.03 \text{ mol} = \text{mol of e accepted by MO}_x

(ii) Calculate the mole ratio of MO\(_x\) and electrons accepted by MO\(_x\).

\[ \text{Mol of MO}_x = \frac{10}{1000} \times 0.5 = 5.00 \times 10^{-3} \text{ mol} \]

\[ \text{MO}_x : \text{mol of e accepted by MO}_x \]

5 \times 10^{-3} : 0.03

1: 6

(iii) Determine the original oxidation number of M and the value of x.

\[ \text{MO}_x + 6\text{e} \rightarrow \text{M} \]

Original oxidation number of M = + 6

x = 3

(iv) Construct an equation for the reaction between MO\(_x\)(aq) and acidified Mn\(^{2+}\)(aq).

\[ \text{[O]}: \text{Mn}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \]

\[ \text{[R]}: \text{MO}_3 + 6\text{e} + 6\text{H}^+ \rightarrow \text{M} + 3\text{H}_2\text{O} \]

Overall: 6Mn\(^{2+}\) + 9H\(_2\)O + 5MO\(_3\) \rightarrow 6MnO\(_4^-\) + 18H\(^+\) + 5M

(b) Water, H\(_2\)O, covers 70.9% of the Earth’s surface and is vital for all known forms of life. About 0.005% of water molecules consist of an oxygen atom bonded to two atoms of the hydrogen isotope, deuterium, \(^2\text{H}\).

Deuterium oxide, D\(_2\)O, is known as ‘heavy water’ and is used for research in chemical reactions because deuterium atoms react less quickly than normal hydrogen atoms, \(^1\text{H}\).

Like H\(_2\)O, pure D\(_2\)O is weakly ionised.

\[ 2\text{D}_2\text{O} \rightleftharpoons \text{D}_3\text{O}^+ + \text{OD}^- \]

For D\(_2\)O, we can use the term \( K_D \) instead of \( K_W \) and pD instead of pH.

(i) Explain what is meant by dynamic equilibrium.

Dynamic equilibrium is a system in which the forward and the backward reactions are taking place at the same rate and thus the concentrations of reactants and products remain constant.
(ii) For pure D₂O, K_D = 1.35 x 10^{-15}. Calculate the values of the following.

I. [D₃O⁺]
II. pD
   (I) [D₃O⁺] = (1.35 x 10^{-15})^{1/2} = 3.67 x 10^{-8} mol dm⁻³
   (II) pD = – lg(3.67 x 10^{-8}) = 7.43

(iii) For this system, K_D increases when temperature increases. Suggest and explain whether the ionic dissociation of ‘heavy water’ is an exothermic or endothermic process.

As temperature increases, position of equilibrium shifts to the right since K_D increases. By LCP, increase in temperature favours endothermic reaction by absorbing additional heat. Thus ionic dissociation of ‘heavy water’ is endothermic.

(iv) When pure H₂O and pure D₂O are mixed, exchange of H and D atoms takes place and the following equilibrium is established.

D₂O(l) + H₂O(l) ⇌ 2HDO(l)

A mixture of 30 g of D₂O and 27 g of H₂O was placed in a vessel at 298 K. At equilibrium, it was found that the degree of dissociation of D₂O is 0.49. Calculate the K_c for this system.

\[ \text{Mol of D}_2\text{O} = \frac{30}{20} = 1.5 \text{ mol} \]
\[ \text{Mol of H}_2\text{O} = \frac{27}{18} = 1.5 \text{ mol} \]

\[ \begin{array}{c|ccc}
\text{n}_{\text{initial}} / \text{mol} & \text{D}_2\text{O}(l) & + & \text{H}_2\text{O}(l) & \rightleftharpoons & 2\text{HDO}(l) \\
1.5 & 1.5 & 0 \\
\text{change} / \text{mol} & -1.5 \times 0.49 & = & -0.735 & -0.735 & +1.47 \\
\text{n}_{\text{final}} / \text{mol} & 0.765 & 0.765 & 1.47 \\
\end{array} \]

\[ K_c = \frac{[\text{HDO}]^2}{[\text{H}_2\text{O}][\text{D}_2\text{O}]} = \frac{(0.765)^2}{(0.765)^2} = \frac{1.47}{0.765} = 3.69 \]

[Total: 11]

6 Many copper minerals are found in hydrothermal deposits where they were formed by crystallization from very hot solutions which were trapped underground at high pressures. One such copper mineral is chalcopyrite, CuFeS₂.
Copper is extracted from the ore chalcopyrite (CuFeS₂) in a three-stage process. In the first stage of this extraction, the chalcopyrite is heated with silicon dioxide and oxygen.

(a) Balance the following equation for this first stage in which copper sulfide is formed.

\[ 2\text{CuFeS}_2 + 2\text{SiO}_2 + 4\text{O}_2 \rightarrow \text{Cu}_2\text{S} + 2\text{FeSiO}_3 + 3\text{SO}_2 \]  

(b) Write the electronic configuration for Cu⁺ in Cu₂S:

\[ \text{Cu}^+ \quad 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} \]  

(c) When water is added to white anhydrous CuSO₄, the solid dissolves to give a blue solution. On addition of concentrated NH₄Cl (aq), the solution changes to a yellow-green due to formation of copper containing species D. Concentrating the solution produces green crystals E of an ammonium salt with empirical formula CuN₂H₈Cl₄.

(i) Suggest the formulae of cation present in E.

Cation present in E ..........................

NH₄⁺

(ii) Suggest the formulae of anion present in D

Identify of D ..........................................

CuCl₄²⁻

(iii) Suggest a balanced equation for the formation of D from aqueous CuSO₄.

\[ \text{Cu(H}_2\text{O)}_6^{2+} (\text{aq}) + 4\text{Cl}^- (\text{aq}) \rightarrow \text{CuCl}_4^{2-} + 6\text{H}_2\text{O} \]

When excess of NH₃ (aq) is added to species D, the yellow green solution turns to a deep blue solution. (iii) Use this information and the information above to suggest the strength of NH₃, H₂O and Cl⁻ ligands in decreasing order.

........................ > ..................... > .....................

...NH₃...>...Cl⁻...>......H₂O...

(d) When a dilute aqueous solution containing a bidentate ligand, ethanedioate ion \((\text{C}_2\text{O}_4^{2-})\) is added to a solution containing aqueous copper(II) ions, a ligand exchange reaction occurs. In this reaction, four water molecules in the hydrated copper ion are
replaced and a new complex \( \mathbf{F} \) is formed.

(i) Explain what is meant by a bidendate ligand.

Ligands which contains two groups that have a lone pair of electrons each which can be donated to the central metal ion, forming two dative bonds.

(ii) Identity of \( \mathbf{F} \) …………………………………………………………………………………………………

\[ \text{[Cu(C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^2^- \]

In the complex \( \mathbf{F} \) formed, the two water molecules are opposite each other. Draw a diagram to show how the ethanedioate ions are bonded to a copper ion and give a value for one of the O-Cu-O bond angles. You are not required to show the water molecules.

(iii) \[
\begin{array}{c}
\text{Diagram of Complex } \mathbf{F} \\
\end{array}
\]

(iv) O-Cu-O bond angle: ………………………………………………………………………………

90°

[4]
INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION 2
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS INDEX NUMBER

CHEMISTRY 9647/03
Paper 3 Free Response 14 September 2012
2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data booklet
Cover Page

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 4 out of 5 questions.
Begin each answer on a fresh sheet of paper.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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 question.

This document consists of 13 printed pages and 1 blank page.
Answer 4 out of 5 questions.

1 (a) N,N-dimethyltryptamine is a psychoactive drug whose primary action is to alter cognition and perception. Depending on the dose and method of administration, its subjective effects can range from short-lived milder psychedelic states to powerful immersive experiences.

\[
\text{N,N-dimethyltryptamine}
\]

(i) Suggest a reason why N,N-dimethyltryptamine is soluble in acidic solutions.

(ii) Would you expect N,N-dimethyltryptamine to have a high or low melting point? Explain your answer in terms of structure and bonding. [4]

(b) \textit{para}-Methoxyamphetamine first came into circulation in the early 1970s and went by the street names of "Chicken Powder" and "Chicken Yellow" and was found to be the cause of a number of drug overdose deaths in the United States and Canada at that time. It can be synthesised by the following route.

\[
\text{J} \xrightarrow{\text{I}} \text{K} \xrightarrow{\text{II}} \xrightarrow{\text{III}} \text{para-Methoxyamphetamine}
\]

(i) Suggest reagents and conditions for steps II and III.

(ii) What type of reaction is step II?

(iii) Suggest why compound J is converted into K before step II is carried out.

(c) Propene is an important starting product in the petrochemical industry and is often used as the raw material for a wide variety of products.

(i) Name and describe the mechanism of the reaction between propene and hydrogen bromide.

(ii) The bromine atom in the product from (i) is very reactive towards nucleophilic reagents. The bromine atom in 1–bromopropene is unreactive towards nucleophilic reagents. Suggest an explanation for the unreactivity of the bromine atom in 1–bromopropene.

[5]

(d) Compound P is a neutral, sweet-smelling liquid with molecular formula C₅H₈O₂. It reacts with hot sulfuric acid to give a single compound Q, C₅H₁₀O₃. Q has two stereoisomers and gives a pale yellow precipitate with alkaline iodine and compound R. Deduce the structures of P, Q and R.

[5]

[Total:20]
2 (a) When a precipitate is formed, $\Delta G^{\theta}_{\text{ppt}}$, in kJ mol$^{-1}$, is given by the following expression.

$$\Delta G^{\theta}_{\text{ppt}} = \frac{2.303RT \log K_{\text{sp}}}{1000}$$

(i) Given that the $K_{\text{sp}}$ value of BaF$_2$ is $1.70 \times 10^{-6}$ at 298 K, calculate $\Delta G^{\theta}_{\text{ppt}}$, in kJ mol$^{-1}$, for BaF$_2$.

(ii) The standard enthalpy change of formation of BaF$_2$ is $-858$ kJ mol$^{-1}$. Use your answer in (a)(i) to calculate $\Delta S^{\theta}_{\text{ppt}}$, in J mol$^{-1}$ K$^{-1}$ for the formation of the precipitate at 298 K.

(iii) Explain the significance of the sign of your answer in (ii).

(iv) Predict and explain whether the precipitation will be feasible at high or low temperature.

(v) Suggest how the magnitude of the lattice energy of BaF$_2$ might compare to that of BaCl$_2$. Explain your answer.

[7]

(b) In the past, chemical analysis was carried out by chemists using traditional laboratory apparatus. Many qualitative tests used depended on an application of the principles of solubility product.

(i) Write an expression for the $K_{\text{sp}}$ of barium fluoride.

(ii) Predict whether precipitation occurs if 50.0 cm$^3$ of 0.150 mol dm$^{-3}$ of Ba(OH)$_2$ solution is mixed with 50.0 cm$^3$ of 0.100 mol dm$^{-3}$ of KF solution in the laboratory.

The $K_{\text{sp}}$ of BaF$_2$ is $1.70 \times 10^{-6}$ mol$^3$ dm$^{-9}$.

[3]

(c) Myrcene is a naturally occurring compound found in the leaves of bay trees. It is known to be a polyunsaturated hydrocarbon. It can react with hydrogen to produce a saturated hydrocarbon.

In a laboratory investigation, a 1.00 g sample of pure myrcene fully reacted with exactly 510 cm$^3$ of hydrogen gas measured at 20.0°C and 105.0 kPa. In this reaction, myrcene was converted to a saturated alkane with a molecular formula C$_{10}$H$_{22}$.

(i) What type of reaction has occurred between the myrcene and hydrogen?

(ii) Calculate the amount, in moles, of hydrogen reacting.

(iii) Calculate the mass of C$_{10}$H$_{22}$ produced in the reaction.

(iv) Determine the number of double bonds in each molecule of myrcene.

[6]
(d) In September 2009, the wholesale of weedkiller containing chlorate(V) ions was banned in various European countries.

Chlorate(V) ions can act as a strong oxidising agent in acid solution according to the following half equation:

$$\text{ClO}_3^- (aq) + 6\text{H}^+ (aq) + 6e^- \rightarrow \text{Cl}^- (aq) + 3\text{H}_2\text{O}(l)$$

In an experiment, 25.0 cm$^3$ of a sample of sodium chlorate(V) solution reacted with an excess of sodium iodide, NaI. The iodine produced required 25.00 cm$^3$ of 1 mol dm$^{-3}$ of sodium thiosulfate, Na$_2$S$_2$O$_3$, for complete reaction.

(i) Write a balanced equation between chlorate(V) ions and iodide ions in acidic medium.

(ii) Calculate the number of moles of iodine liberated by the chlorate(V) solution.

(iii) Calculate the concentration of sodium chlorate(V) in the solution.

[4]

[Total: 20]
3 (a) A sample of aspirin was prepared by reacting 2.20 g of salicylic acid with 4.20 cm³ of ethanoic anhydride in a conical flask. After heating for 20 minutes the reaction mixture was cooled and white crystals precipitated. The crystals were then collected, dried to constant mass and weighed.

The equation for the reaction is:

![Chemical structure of salicylic acid, ethanoic anhydride, and aspirin](image)

The following results were obtained.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>mass of salicylic acid</td>
<td>2.20 g</td>
</tr>
<tr>
<td>volume ethanoic anhydride</td>
<td>4.20 cm³</td>
</tr>
<tr>
<td>mass of product</td>
<td>2.25 g</td>
</tr>
</tbody>
</table>

Use the following data to answer the questions below.

<table>
<thead>
<tr>
<th></th>
<th>molar mass (g mol⁻¹)</th>
<th>density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aspirin</td>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>ethanoic anhydride</td>
<td>102</td>
<td>1.08</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>138</td>
<td>-</td>
</tr>
</tbody>
</table>

(i) Calculate the initial amount, in moles, of salicylic acid used in this preparation.

(ii) What initial amount, in moles, of ethanoic anhydride was used?

(iii) What is the maximum mass of aspirin that can theoretically be produced from these reagents?

(iv) Determine the percentage yield in this preparation.

(v) To check whether the aspirin obtained is contaminated with salicylic acid, a simple chemical test can be carried out. Suggest what reagent can be used and state the observation.

(vi) In carrying out the above preparation, the acid anhydride used must not contain moisture. Write an equation for the reaction between ethanoic anhydride with water.

(vii) Acid chlorides closely resemble the acid anhydrides in chemical reactions. They also react with nucleophilic reagents but at a faster rate and therefore more difficult to handle. Suggest another reason why ethanoyl chloride is not used in the above preparation of aspirin.
(b) A company wish to manufacture solid oxide fuel cell for use in the home. These fuel cells uses natural gas to produce electricity through an electrochemical process summarised in the diagram below.

(i) Write an equation for the reaction at the cathode where atmospheric oxygen is converted to oxide ions.

(ii) A complex series of reactions takes place at the anode. These may be summarised by the half-equation:

$$4O_2^\text{-}(g) + CH_4(g) \rightarrow CO_2(g) + 2H_2O(g) + 8e$$

Write an equation that represents the overall reaction that takes place in this fuel cell.

(iii) Suggest one way in which a fuel cell differs from other galvanic cells.

[3]

(c) The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.

Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution. When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

Calculate the following, using appropriate data from the Data Booklet,

(i) number of moles of copper produced at the cathode

(ii) number of moles of electrons needed to produce this copper
(iii) number of moles of electrons that passed through the cell

(iv) Hence calculate the percentage of the current through the cell that has been ‘wasted’ in dissolving the impurities at the anode. [4]

(d) (i) State what is meant by an *acidic buffer solution*.

(ii) Explain, using relevant equations, how a mixture of HC/O and NaC/O can regulate pH when relatively small amount of acid or base is added to the solution.

(iii) Explain why NaC/O exists as a solid whereas HC/O exists as a liquid under standard condition. [6]

[Total: 20]
4 (a) By considering the likely mechanism of each reaction, suggest reasons why reaction I below must be heated for some time for it to occur, whereas reaction II takes place almost instantaneously at room temperature.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Br(l)} + \text{NaOH(aq)} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH(aq)} + \text{NaBr(aq)} \quad \text{reaction I} \]
\[ \text{HBr(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O} + \text{NaBr(aq)} \quad \text{reaction II} \]

(b) How would the rate of reaction between CH₃CH₂CH₂Cl(l) and NaOH(aq) compare to that of reaction I? Use appropriate data from the *Data Booklet* to explain your answer.

(c) In the presence of ethanolic potassium hydroxide, there is a competition between substitution and elimination of the bromoalkane. The data below shows some examples.

<table>
<thead>
<tr>
<th>Formula of bromoalkane</th>
<th>Type of bromoalkane</th>
<th>Conditions</th>
<th>elimination/substitution ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₂CHBr</td>
<td>Secondary</td>
<td>2 mol dm⁻³ OH⁻ in 60 % ethanol*</td>
<td>1.5</td>
</tr>
<tr>
<td>(CH₃)₂CHBr</td>
<td>Secondary</td>
<td>2 mol dm⁻³ OH⁻ in 80 % ethanol*</td>
<td>2.2</td>
</tr>
<tr>
<td>(CH₃)₃CBr</td>
<td>Tertiary</td>
<td>2 mol dm⁻³ OH⁻ in 100 % ethanol</td>
<td>13.0</td>
</tr>
</tbody>
</table>

* the remainder is water

Using the data given above, draw the structural formula of the major product of each of the following reactions:

(i) Heating (CH₃)₂CHCH₂Br with NaOH(aq)
(ii) Heating CH₃CH₂CHBrCH₂CH₃ with NaOH in 100 % ethanol
(iii) Heating (CH₃)₃CBr with NaOH in 100 % ethanol

(d) The rate constant for the reaction of CH₃CH₂CHBrCH₃ and KCN was measured at various temperatures and the results are shown below.

<table>
<thead>
<tr>
<th>T/ K</th>
<th>( \text{k} )/ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( 3.7 \times 10^{-5} )</td>
</tr>
<tr>
<td>310</td>
<td>( 9.4 \times 10^{-5} )</td>
</tr>
<tr>
<td>320</td>
<td>( 5.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>330</td>
<td>( 2.0 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

(i) Deduce the overall order of this reaction.

(ii) From the plotted graph given and by using the modified Arrhenius equation,

\[ \ln k = \text{constant} - \frac{E_a}{RT} \]

determine the activation energy, \( E_a \), of the reaction.
(ii) Estimate the rate constant of the reaction at 340 K and hence calculate the half-life of the reaction at the same temperature.

(e) Caffeine is a stimulant found in coffee and tea. It is also added to cola drinks. The structure of caffeine is given below.

(i) Copy the above structure and label (with a *) all the carbon atoms with bond angles of 109°.

(ii) On the structure that you have drawn, draw a circle round an amide group.
(iii) Decaffeinated coffee and tea are made by extracting the caffeine from solid coffee or tea using a solvent.

Suggest, with two reasons, which of the following industrial solvents would be the most suitable.

- Benzene
- A hydrocarbon, such as cyclohexane
- Liquid carbon dioxide

(f) Iron is an extremely important metal used in haemoglobin to transport oxygen molecules from the lungs to muscle cells and to carry carbon dioxide in the reverse direction.

One haemoglobin molecule contains four haem groups, each of which contains one iron atom. In the haem group four nitrogen atoms are in the same plane as the iron atom. The oxygen molecule is attached above this plane, and the iron atom is joined to a protein chain below this plane.

(i) How many oxygen \textbf{atoms} could one haemoglobin molecule transport?

(ii) By what type of bonding is the oxygen molecule likely to be held to the iron atom in haem?

(iii) What is the geometry of bonding around the iron atom?
5 (a) Bromine containing products, such as sodium bromate is frequently used in hair straightener and conditioning products.

(i) Write a balanced equation for the reaction that can make a solution that contains sodium bromate(I) under suitable condition in the laboratory.

(ii) Bromine can be obtained from the sodium bromide dissolved in sea water by the following step:

Blowing out the bromine with air and absorbing it in aqueous sodium carbonate.

This step produces a mixture of solution \( Z \) and sodium bromide in the molar ratio of 1:5. \( Z \) has the following composition by mass:

\[
\text{Na, 15.2%; Br, 52.9%; O, 31.8%}
\]

I. Calculate the empirical formula of \( Z \).

II. Construct an equation for the formation of \( Z \) in the above step mentioned.

(iii) An acidified aqueous solution of \( Z \) reacts with hydrogen sulfide, \( \text{H}_2\text{S} \), to give a precipitate of sulfur and an orange red solution. On shaking with trichloroethane, the colour is transferred to the organic layer.

I. State the role of \( \text{H}_2\text{S} \) and suggest an identity for the orange red solution.

II. Construct a balanced equation for the reaction.

(iv) When solid calcium fluoride reacts with concentrated sulfuric acid, gaseous hydrogen fluoride is produced. A similar reaction occurs with solid calcium chloride but with solid calcium bromide, bromine is formed.

I. Write an equation for the reaction of solid calcium fluoride with concentrated sulfuric acid.

II. Explain why when reacted with concentrated sulfuric acid, solid calcium bromide form bromine whereas solid calcium chloride forms hydrogen chloride? Suggest a possible reaction product of the concentrated sulfuric acid in the reaction.

[9]
(b) Acyl chlorides are useful intermediates for making various acid derivatives. The following reaction shows two reactions of acyl chlorides.

**Reaction scheme 1**

\[
\text{Acyl chloride } B + \text{ethyl diamine} \rightarrow \text{D}
\]

**Reaction scheme 2**

\[
\text{Acyl chloride } C + \text{NaOH} + \text{E}
\]

(i) Suggest the structures of acyl chlorides B and C used in reaction scheme 1 and 2.

(ii) Suggest the type of polymer E.

(iii) Both compound B and compound D are soluble in water.

I. Write a balanced equation when compound B dissolves in water and describe the effect of the resulting solution on Universal Indicator solution.

II. Explain why compound D is soluble in water.

(iv) Suggest an observation for reaction scheme 2.

(c) “Ca\(^{2+}\) and Cl\(^{-}\) are isoelectronic but the radii of the ions are different”.

(i) Explain the term 'isoelectronic'.

(ii) With the aid of the Data Booklet, explain the above observation as fully as you can.

(iii) State two ways in which the behaviour of Ca\(^{2+}\) ions in an electric field differs from that of Cl\(^{-}\) ions.
1 (a) N,N-dimethyltryptamine is a psychoactive drug whose primary action is to alter cognition and perception. Depending on the dose and method of administration, its subjective effects can range from short-lived milder psychedelic states to powerful immersive experiences.

![N,N-dimethyltryptamine](image)

(i) Suggest a reason why N,N-dimethyltryptamine is soluble in acidic solutions.

It will react with acid to form a salt / cation which is able to form ion-dipole interactions with water molecules.

(ii) Would you expect N,N-dimethyltryptamine to have a high or low melting point? Explain your answer in terms of structure and bonding.

It is expected to have a low melting point. It has a simple molecular structure with weak van der Waals’ forces between molecules. Thus less energy is required to break the weak forces.

(b) Propene is an important starting product in the petrochemical industry and is often used as the raw material for a wide variety of products.

(i) Name and describe the mechanism of the reaction between propene and hydrogen bromide.

Electrophilic Addition

**Step 1**

\[
\begin{align*}
\text{H}_3\text{C} &= \text{C} & \text{H}_3\text{C} &= \text{CH}_3 \\
\text{H} &= \text{H} & \text{H} &= \text{Br} \\
\text{slow} & \quad \text{carbocation} \\
\end{align*}
\]
Step 2

(ii) The bromine atom in the product from b(i) is very reactive towards nucleophilic reagents. The bromine atom in 1–bromopropene is unreactive towards nucleophilic reagents. Suggest an explanation for the unreactivity of the bromine atom in 1–bromopropene.

[2]

In 1-bromopropene, the p orbital of Br overlaps with the π orbital of adjacent C atom, strengthening the C – Br bond. Thus, the C – Br bond is too strong to be broken and hence unreactive towards nucleophilic reagents.

OR

In 1-bromopropene, the C atom is adjacent to the double bond and hence less electron deficient and thus less susceptible to nucleophilic attacks.

(c) *para*-Methoxyamphetamine first came into circulation in the early 1970s and went by the street names of "Chicken Powder" and "Chicken Yellow" and was found to be the cause of a number of drug overdose deaths in the United States and Canada at that time. It can be synthesised by the following route.

(i) Suggest reagents and conditions for steps II and III.

II: CH₃Br / CH₃I / CH₃Cl, heat with reflux
III: NH₃ in ethanol, heat in a sealed tube

(ii) What type of reaction is step II?

Nucleophilic substitution

(iii) Suggest why compound J is converted into K before step II is carried out.

To generate a stronger nucleophile, phenoxide ion.

(iv) What type of stereoisomerism does para-methoxyamphetamine exhibits? Draw the structures of the stereoisomers of para-methoxyamphetamine.

Optical isomerism

(d) Compound P is a neutral, sweet-smelling liquid with molecular formula C₅H₈O₂. It reacts with hot sulfuric acid to give a single compound Q, C₅H₁₀O₃. Q has two stereoisomers and gives a pale yellow precipitate with alkaline iodine and compound R. Deduce the structures of P, Q and R.

P undergoes acidic hydrolysis with hot sulfuric acid to give Q. P is an ester.

Q contains CH₃CH(OH) since it undergoes mild oxidation with alkaline iodine.

Q only contains 1 chiral carbon since it has two stereoisomers.
The image contains chemical structures labeled as P, Q, and R. The legend indicates that the total score for the images is 20.
2 (a) When a precipitate is formed, $\Delta G^\theta_{ppt}$, in kJ mol$^{-1}$, is given by the following expression.

$$
\Delta G^\theta_{ppt} = \frac{2.303RT \log K_{sp}}{1000}
$$

(i) Given that the $K_{sp}$ value of BaF$_2$ is $1.70 \times 10^{-6}$ at 298K, calculate $\Delta G^\theta_{ppt}$, in kJ mol$^{-1}$, for BaF$_2$.

$$
\Delta G^\theta_{ppt} = \left[2.303 \times 8.31 \times 298 \times \log (1.70 \times 10^{-6})\right] \div 1000 = -32.9 \text{ kJ mol}^{-1}
$$

(ii) The standard enthalpy change of formation of BaF$_2$ is $-858 \text{ kJ mol}^{-1}$. Use your answer in (a)(i) to calculate $\Delta S^\theta_{ppt}$, in J mol$^{-1}$ K$^{-1}$ for the formation of the precipitate at 298K.

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

$$
-32.9 = -858 - (298) \Delta S
$$

$$
\Delta S = -2.77 \text{ kJ mol}^{-1}\text{K}^{-1}
$$

$$
= -2770 \text{ J mol}^{-1}\text{K}^{-1}
$$

(iii) Explain the significance of the sign of your answer in (ii).

The sign is negative which means that entropy decreases as the system is more ordered/less disordered when there is a phase change from aqueous to solid state.

(iv) Predict and explain whether the precipitation will be feasible at high or low temperature.

Since $\Delta S$ is negative, $(-T\Delta S)$ is always positive. At high temperature, the magnitude of $(-T\Delta S)$ would be greater than $\Delta H$. Hence $\Delta G$ would be positive and the reaction would not be feasible. Therefore the reaction is feasible at low temperature.

(v) Suggest how the magnitude of the lattice energy of BaF$_2$ might compare to that of BaCl$_2$. Explain your answer.

- Although fluoride ion and chloride ion have the same charge,
- fluoride ion is smaller than chloride ion.
- $|L.E| \propto \frac{q_+ q_-}{r_+ + r_-}$ or Since lattice energy is inversely proportional to the
(b) In the past, chemical analysis was carried out by chemists using traditional laboratory apparatus. Many qualitative tests used depended on an application of the principles of solubility product.

(i) Write an expression for the $K_{sp}$ of barium fluoride.

$$K_{sp} = [\text{Ba}^{2+}] [\text{F}^-]^2$$

(ii) Predict whether precipitation occurs if 50.0 cm$^3$ of 0.150 mol dm$^{-3}$ of Ba(OH)$_2$ solution is mixed with 50.0 cm$^3$ of 0.100 mol dm$^{-3}$ of KF solution in the laboratory.

The $K_{sp}$ of BaF$_2$ is $1.70 \times 10^{-6}$ mol$^3$ dm$^{-9}$.

$$[\text{Ba}^{2+}]_{\text{new}} = \frac{0.150}{2} = 0.075 \text{ mol dm}^{-3}$$

$$[\text{F}^-]_{\text{new}} = \frac{0.100}{2} = 0.05 \text{ mol dm}^{-3}$$

$$\text{IP} = [\text{Ba}^{2+}] [\text{F}^-]^2 = 0.075 \times (0.05)^2 = 1.875 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9}$$

$$1.875 \times 10^{-4} \text{ mol}^3 \text{ dm}^{-9} > K_{sp} \quad \text{Precipitation occurs.}$$

(c) Myrcene is a naturally occurring compound found in the leaves of bay trees. It is known to be a polyunsaturated hydrocarbon. It can react with hydrogen to produce a saturated hydrocarbon.

In a laboratory investigation, a 1.00 g sample of pure myrcene fully reacted with exactly 510 cm$^3$ of hydrogen gas measured at 20.0°C and 105.0 kPa. In this reaction, myrcene was converted to a saturated alkane with a molecular formula C$_{10}$H$_{22}$.

(i) What type of reaction has occurred between the myrcene and hydrogen?

Addition of hydrogen /hydrogenation/redox/reduction

(ii) Calculate the amount, in moles, of hydrogen reacting.

$$\text{no of moles of H}_2 = \frac{pV}{RT} = \frac{105 \times 10^3 \times 510 \times 10^{-6}}{(8.31 \times (20.0 + 273))} = 0.0220 \text{ mol}$$

(iii) Calculate the mass of C$_{10}$H$_{22}$ produced in the reaction.

$$\text{mass of C}_{10}\text{H}_{22} = \text{mass of myrcene} + \text{mass of H}_2$$
mass of H₂ = 0.0220 × 2.0 = 0.044 g
mass of C₁₀H₂₂ = 1.00 + 0.0440 = 1.04 g

(iv) Determine the number of double bonds in each molecule of myrcene.

no of moles of C₁₀H₂₂ = 1.044 / 142 = 7.35x10⁻³ mol = n(myrcene)
equation for reaction is myrcene + xH₂ → C₁₀H₂₂
n(H₂) / n(myrcene) = x / 1
0.0220 / 7.35x10⁻³  = x
3 = x
3 molecules of H₂ added to each myrcene molecule. Hence there are 3 C=C double bonds.

The following is an alternate approach.
no of moles of C₁₀H₂₂ = 7.35x10⁻³ mol
no of moles of myrcene = 7.35x10⁻³
Molar mass of myrcene = 1.0 / 7.35x10⁻³ = 136 g mol⁻¹
molar mass of myrcene is 6 less than molar mass C₁₀H₂₂.
→ 3 H₂ molecules added to each myrcene molecule
→ 3 C=C double bonds.
One mark was awarded if 3 double bonds was stated, but to obtain the second mark a logical explanation of how the number of double bonds was determined was required.

(d) In September 2009, the wholesale of weedkiller containing chlorate(V) ions was banned in various European countries.

Chlorate(V) ions can act as a strong oxidising agent in acid solution according to the following half equation:

\[ \text{ClO}_3^- (aq) + 6H^+ (aq) + 6e^- \rightarrow Cl^- (aq) + 3H_2O(l) \]

In an experiment, 25.0 cm³ of a sample of sodium chlorate(V) solution reacted with an excess of sodium iodide, NaI. The iodine produced required 25.00 cm³ of 1 mol dm⁻³ of sodium thiosulfate, Na₂S₂O₃, for complete reaction.

(i) Write a balanced equation between chlorate(V) ions and iodide ions in acidic medium.

\[
[R]: \text{ClO}_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O
\]

\[
[O]: 2I^- \rightarrow I_2 + 2e
\]

Overall: \[ \text{ClO}_3^- + 6H^+ + 6I^- \rightarrow Cl^- + 3H_2O + 3I_2 \]

(ii) Calculate the number of moles of iodine liberated by the chlorate(V) solution.

\[
[R]: \quad I_2 + 2e \rightarrow 2I^-
\]

\[
[O]: \quad 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e
\]
\[
\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}
\]

No of moles of thiosulfate = \( \frac{25}{1000} \times 1 = 0.025 \text{ mol} \)

No of moles of iodine = 0.025 + 2 = 0.0125 mol

(iii) Calculate the concentration of sodium chlorate(V) in the solution.

\[
\text{Mole Ratio} \\
\text{ClO}^- : \text{I}_2 \\
1:3
\]

No of moles of chlorate = 0.0125 \times 3 = 4.167 \times 10^{-3} \text{ mol}

Concentration of sodium chlorate(V) = \( \frac{4.167 \times 10^{-3}}{25} \times \frac{1000}{1} = 0.167 \text{ mol dm}^{-3} \)

[Total: 20]
3 (a) A sample of aspirin was prepared by reacting 2.20 g of salicylic acid with 4.20 cm$^3$ of ethanoic anhydride in a conical flask. After heating for 20 minutes the reaction mixture was cooled and white crystals precipitated. The crystals were then collected, dried to constant mass and weighed.

The equation for the reaction is:

\[
\text{salicylic acid(s)} + \text{ethanoic anhydride(l)} \rightarrow \text{aspirin(s)}
\]

The following results were obtained.

- Mass of salicylic acid: 2.20 g
- Volume ethanoic anhydride: 4.20 cm$^3$
- Mass of product: 2.25 g

Use the following data to answer the questions below.

<table>
<thead>
<tr>
<th></th>
<th>Molar mass (g mol$^{-1}$)</th>
<th>Density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aspirin</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>ethanoic anhydride</td>
<td>102</td>
<td>1.08</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>138</td>
<td></td>
</tr>
</tbody>
</table>

(i) Calculate the initial amount, in moles, of salicylic acid used in this preparation.

\[
\text{no of moles of salicylic acid} = \frac{2.20}{138} = 0.0159 \text{ mol}
\]

(ii) What initial amount, in moles, of ethanoic anhydride was used?

\[
\text{mass of ethanoic anhydride} = \text{Volume} \times \text{Density} \\
= 4.20 \times 1.08 \text{ g} \\
\text{no of moles of ethanoic anhydride} = 4.20 \times \frac{1.08}{102} = 0.0445 \text{ mol}
\]

(iii) What is the maximum mass of aspirin that can theoretically be produced from these reagents?

Salicylic acid is the limiting reagent
\[
\text{no of moles of aspirin} = \text{no of moles of salicylic acid} = 0.0159 \text{ mol} \\
\text{mass of aspirin} = 0.0159 \times 180 = 2.86 \text{ g}
\]

(iv) Determine the percentage yield in this preparation.
% yield = \( \frac{\text{mass of aspirin collected}}{\text{mass of aspirin theoretical}} \times 100 \)
\[
= \frac{2.25}{2.86} \times 100
= 78.4\%
\]

(v) To check whether the aspirin obtained is contaminated with salicylic acid, a simple chemical test can be carried out. Suggest what reagent can be used and state the observation.

Neutral FeC₅(aq)(reacts with phenol), forming purple coloration  
OR  
Br₂(aq), orange decolourise & white ppt formed.

(vi) In carrying out the above preparation, the acid anhydride used must not contain moisture. Write an equation for the reaction between ethanoic anhydride with water.

(vii) Acid chlorides closely resemble the acid anhydrides in chemical reactions. They also react with nucleophilic reagents but at a faster rate and therefore more difficult to handle.  
Suggest another reason why ethanoyl chloride is not used in the above preparation of aspirin.

HCl fumes will be produced which is a toxic gas

(b) A company wish to manufacture solid oxide fuel cell for use in the home. These fuel cells uses natural gas to produce electricity through an electrochemical process summarised in the diagram below.

(i) Write an equation for the reaction at the cathode where atmospheric oxygen is
converted to oxide ions.

\[
\begin{align*}
O_2(g) + 4e & \rightarrow 2O^-(g) \\
\frac{1}{2} O_2(g) + 2e & \rightarrow O^2-(g)
\end{align*}
\]

(ii) A complex series of reactions takes place at the anode. These may be summarised by the half-equation

\[
4O^2-(g) + CH_4(g) \rightarrow CO_2(g) + 2H_2O(g) + 8e
\]

Write an equation that represents the overall reaction that takes place in this fuel cell.

\[
CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)
\]

(iii) Suggest one way in which a fuel cell differs from other galvanic cells.

- fuel cells require a continuous supply of reactants, whereas in a galvanic cell they are stored in the cell
- or some products are removed from fuel cells
- or fuel cell electrodes are porous.

(c) The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.

Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is ‘wasted’ in dissolving the impurities at the anode which then remain in solution.

When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

Calculate the following, using appropriate data from the Data Booklet.

(i) number of moles of copper produced at the cathode

\[
\text{amount of copper} = \frac{225}{63.5} = 3.54 \text{ mol}
\]

(ii) number of moles of electrons needed to produce this copper

\[
\text{amount of electrons needed} = 2 \times 3.54 = 7.08/9 (7.087) \text{ mol}
\]
(iii) number of moles of electrons that passed through the cell

no. of coulombs = \(20 \times 10 \times 60 \times 60 = 7.2 \times 10^5\) C

\[
\text{no. of moles of electrons} = \frac{7.2 \times 10^5}{96500} = 7.46\text{ mol}
\]

(iv) Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode.

percentage “wasted” = \(100 \times \frac{7.087 - 7.461}{7.461} = 5.01\text{ (5.0)%}\)

(d) (i) State what is meant by an acidic buffer solution.

Acidic buffer solution is a mixture of a weak acid and its soluble salt and resist pH changes when little amount of acid or alkali is added.

(ii) Explain, using relevant equations, how a mixture of HC/O and NaC/O can regulate pH when relatively small amount of acid or base is added to the solution.

**Small additional H⁺ ions are removed by the large reservoir of NaC/O**

\[
\text{NaC/O} + \text{H}^+ \rightarrow \text{HC/O} + \text{Na}^+
\]

**Small additional OH⁻ ions are removed by large reservoir of HC/O**

\[
\text{HC/O} + \text{OH}^- \rightarrow \text{C/O}^- + \text{H}_2\text{O}
\]

(iii) Explain why NaC/O exists as a solid whereas HC/O exists as a liquid under standard condition.

NaClO has giant ionic structure which consists of strong electrostatic forces of attraction between oppositely charged ions whereas HClO has simple molecular structure which consists of weak van der Waals’ forces between molecules.

Less energy is needed to break the weak VDW. Hence NaC/O exists as a solid whereas HC/O exists as a liquid.

2 correct structures stated-
(a) By considering the likely mechanism of each reaction, suggest reasons why reaction I below must be heated for some time for it to occur, whereas reaction II takes place almost instantaneously at room temperature.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}(l) + \text{NaOH}(aq) & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(aq) + \text{NaBr}(aq) \quad \text{I} \\
\text{HBr}(aq) + \text{NaOH}(aq) & \rightarrow \text{H}_2\text{O} + \text{NaBr}(aq) \quad \text{II}
\end{align*}
\]

Reaction I involves breaking of strong covalent bonds, thus heat is required.

Reaction II involves reaction of opposite charge ions attracting one another, thus the reaction occurs instantaneously.

(b) How would the rate of reaction between \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l) \) and \( \text{NaOH}(aq) \) compare to that of reaction I? Use appropriate data from the Data Booklet to explain your answer.

This hydrolysis reaction involves breaking of C-X bond. Since \( \text{C-Cl bond (BE of 340 kJ mol}^{-1}) \) is stronger than that of \( \text{C-Br bond (BE of 280 kJ mol}^{-1}) \), the rate of hydrolysis to break C-Cl bond in \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l) \) is slower.

(c) In the presence of ethanolic potassium hydroxide, there is a competition between substitution and elimination of the bromoalkane. The data below shows some examples.

<table>
<thead>
<tr>
<th>Formula of bromoalkane</th>
<th>Type of bromoalkane</th>
<th>Conditions</th>
<th>elimination/substitution ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{(CH}_3\text{)}_2\text{CHBr} )</td>
<td>Secondary</td>
<td>2 mol dm(^{-3}) OH(^{-}) in 60 % ethanol*</td>
<td>1.5</td>
</tr>
<tr>
<td>( \text{(CH}_3\text{)}_2\text{CHBr} )</td>
<td>Secondary</td>
<td>2 mol dm(^{-3}) OH(^{-}) in 80 % ethanol*</td>
<td>2.2</td>
</tr>
<tr>
<td>( \text{(CH}_3\text{)}_3\text{CBr} )</td>
<td>Tertiary</td>
<td>2 mol dm(^{-3}) OH(^{-}) in 100 % ethanol</td>
<td>13.0</td>
</tr>
</tbody>
</table>

* the remainder is water

Using the data given above, draw the structural formula of the major product of each of the following reactions:
(i) Heating (CH₃)₂CHCH₂Br with NaOH(aq)

(\text{(CH₃)₂CHCH₂OH})

(ii) Heating CH₃CH₂CHBrCH₂CH₃ with NaOH in 100 % ethanol

(CH₂CH₂CH=CHCH₃)

(iii) Heating (CH₃)₃CBr with NaOH in 100 % ethanol

(\text{(CH₃)₂C=CH₂})

(d) The rate constant for the reaction of CH₃CH₂CHBrCH₃ and KCN was measured at various temperatures and the results are shown below.

<table>
<thead>
<tr>
<th>T/K</th>
<th>300</th>
<th>310</th>
<th>320</th>
<th>330</th>
</tr>
</thead>
<tbody>
<tr>
<td>k/s⁻¹</td>
<td>3.7 x 10⁻⁵</td>
<td>9.4 x 10⁻⁵</td>
<td>5.5 x 10⁻⁴</td>
<td>2.0 x 10⁻³</td>
</tr>
</tbody>
</table>

(i) Deduce the overall order of this reaction.

1ˢᵗ order because the unit of rate constant is s⁻¹.

(ii) From the plotted graph given and by using the modified Arrhenius equation,

\[
\ln k = \text{constant} - \frac{E_a}{RT}
\]
determine the activation energy, $E_a$, of the reaction.

\[ \text{plot of } \ln k \text{ ag } 1/T \]

The slope of the line is found to be $-\frac{E_a}{R}$.

Thus, slope = $\frac{-10 - (-4.6)}{(3.3 - 2.9) \times 10^{-3}}$ = $-13500$ = $-\frac{E_a}{R}$

$E_a = 112.2 \text{ kJ mol}^{-1}$

(ii) Estimate the rate constant of the reaction at 340 K and hence calculate the half-life of the reaction at the same temperature.

From the graph at 340 K,

$\ln k = -5.10$
\[
\text{thus, } k = 6.10 \times 10^{-3} \text{ s}^{-1}
\]

\[
\text{since } t_{1/2} = \ln 2 / k = 114 \text{ s}
\]

(e) Caffeine is a stimulant found in coffee and tea. It is also added to cola drinks. The structure of caffeine is given below.

![Caffeine structure](image)

(i) Copy the above structure and label (with a *) all the carbon atoms with bond angles of 109 °.

![Labelled structure](image)

(ii) On the structure that you have drawn, draw a circle round an amide group.

![Amide group](image)
(iii) Decaffeinated coffee and tea are made by extracting the caffeine from solid coffee or tea using a solvent.

Suggest, with two reasons, which of the following industrial solvents would be the most suitable.

- Benzene
- A hydrocarbon, such as cyclohexane
- Liquid carbon dioxide

Liquid carbon dioxide is the most suitable solvent

Reason 1: Liquid carbon dioxide is not toxic.

Reason 2: Liquid carbon dioxide has low boiling point & can be easily evaporated off without leaving any odour.

(f) Iron is an extremely important metal used in haemoglobin to transport oxygen molecules from the lungs to muscle cells and to carry carbon dioxide in the reverse direction.

One haemoglobin molecule contains four haem groups, each of which contains one iron atom. In the haem group four nitrogen atoms are in the same plane as the iron atom. The oxygen molecule is attached above this plane, and the iron atom is joined to a protein chain below this plane.
(i) How many oxygen **atoms** could one haemoglobin molecule transport?  

8 atoms (also allow 4 oxygen molecules)  

(ii) By what type of bonding is the oxygen molecule likely to be held to the iron atom in haem?  

Dative bond / co-ordinate bond  

(iii) What is the geometry of bonding around the iron atom?  

Octahedral / 6 co-ordinate  

[Total: 20]
5. (a) Bromine containing products, such as sodium bromate is frequently used in hair straightener and conditioning products.

(i) Write a balanced equation for the reaction that can make a solution that contains sodium bromate(I) under suitable condition in laboratory.

\[
\text{Br}_2 + 2 \text{ NaOH} \rightarrow \text{NaBr} + \text{NaBrO} + \text{H}_2\text{O}
\]

(ii) Bromine can be obtained from the sodium bromide dissolved in sea water by the following step:

Blowing out the bromine with air and absorbing it in aqueous sodium carbonate.

This step produces a mixture of solution Z and sodium bromide in the molar ratio of 1:5. Z has the following composition by mass:

\[
\text{Na}, 15.2\% ; \text{Br}, 52.9\% ; \text{O}, 31.8\%
\]

I. Calculate the empirical formula of Z.

II. Construct an equation for the formation of Z in the above step mentioned.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Br</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass in 100g</td>
<td>15.2</td>
<td>52.9</td>
<td>31.9</td>
</tr>
<tr>
<td>Mr</td>
<td>23.0</td>
<td>79.9</td>
<td>16.0</td>
</tr>
<tr>
<td>No. of moles</td>
<td>0.66</td>
<td>0.66</td>
<td>1.99</td>
</tr>
<tr>
<td>Simplest ratio</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

Empirical formula of Z : NaBrO$_3$

II: \[3 \text{ Br}_2 + 6 \text{ OH}^- \rightarrow \text{BrO}_3^- + 5 \text{ Br}^- + 3 \text{ H}_2\text{O}\]

(iii) An acidified aqueous solution of Z reacts with hydrogen sulphide, H$_2$S, to give a precipitate of sulphur and an orange red solution. On shaking with trichloroethane, the colour is transferred to the organic layer.
I) State the role of H₂S and suggest an identity for the orange red solution.

II) Construct a balanced equation for the reaction.

I) It is acting as a reducing agent.
Orange red solution is bromine.

II) Half equation:

\[
\begin{align*}
H_2S & \rightleftharpoons S + 2e^+ + 2H^+ \\
2BrO_3^- + 12H^+ + 10e^- & \rightleftharpoons Br_2 + 6H_2O
\end{align*}
\]

Overall equation: \(5H_2S + 2H^+ + 2BrO_3^- \rightarrow 5S + Br_2 + 6H_2O\)

(iv) When solid calcium fluoride reacts with concentrated sulfuric acid, gaseous hydrogen fluoride is produced. A similar reaction occurs with solid calcium chloride but with solid calcium bromide, bromine is formed.

I) Write an equation for the reaction of solid calcium fluoride with concentrated sulfuric acid.

II) Explain why when reacted with concentrated sulfuric acid, solid calcium bromide form bromine whereas solid calcium chloride forms hydrogen chloride? Suggest a possible reaction product of the concentrated sulfuric acid in the reaction.

I. \(CaF_2 + 2H_2SO_4 \rightarrow 2HF + Ca(HSO_4)_2\)

II. With conc. \(H_2SO_4\), \(CaBr_2\) produces \(\text{HBr which is readily oxidised}\) by conc. \(H_2SO_4\) to \(Br_2\).

\(CaCl_2\), however, produces \(\text{HCl which is not further oxidised}\) by conc. \(H_2SO_4\).

A possible reaction product is \(\text{SO}_2\).

\([2\text{HBr} + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O]\)
(b) Acyl chlorides are useful intermediates for making various acid derivatives. The following reaction shows two reactions of acyl chlorides.

Reaction scheme 1

\[
\text{Acyl chloride } B + \text{ethyl diamine} \rightarrow \text{D}
\]

Reaction scheme 2

\[
\text{Acyl chloride } C + \text{NaOH} + \text{phenol} \rightarrow \text{E}
\]

(i) Suggest the structures of acyl chlorides used in reaction scheme 1 and 2. [2]

(ii) Suggest the type of polymer E. [1]
(iii) Both compound B and compound D are soluble in water.

I. Write a balanced equation when compound B dissolves in water and describe the effect of the resulting solution on Universal Indicator solution.

II. Explain why compound D is soluble in water.

\[
\begin{align*}
\text{O} & \quad \text{Cl} \\
\text{Cl} & \quad + \text{H}_2\text{O} \\
\rightarrow & \quad \text{O} \quad \text{HO} \\
& \quad \text{OH} \\
& \quad + 2\text{HCl}
\end{align*}
\]

1m for equation

The solution turns red.

II. Compound D is an amide, it is able to form compatible interactions with water which is \text{hydrogen bonding between the compound D and water molecules}.

Thus, compound D is soluble in water.

(iv) Suggest an observation for reaction scheme 2.

Steamy white fumes of HCl

(c) “Ca^{2+} and Cl^{-} are isoelectronic but the radii of the ions are different”.

(i) Explain the term ‘isoelectronic’.

Ions that contain the same number of electrons.

(ii) With the aid of the Data Booklet, explain the above observation as fully as you can.

- Both Ca^{2+} and Cl^{-} are isoelectronic, hence same shielding effect.
- However, Ca^{2+} (20 protons) \text{ has higher nuclear charge than Cl}^{-} (17 protons) hence higher effective nuclear charge.
- Hence there is stronger \text{electrostatic attraction} between nucleus and valence electrons of Ca^{2+}.
- Thus, valence electrons of Ca^{2+} are pulled closer to the nucleus and Ca^{2+} is smaller.
- Ca^{2+} has smaller \text{ionic radii} than Cl^{-}. 

22
(iii) State **two** ways in which the behaviour of Ca\(^{2+}\) ions in an electric field differs from that of Cl\(^{-}\) ions.

- Ca\(^{2+}\) are deflected towards the **negative** potential. Cl\(^{-}\) ions are deflected towards the **positive** potential.
- Ca\(^{2+}\) will be deflected to a greater extend as it has higher charge/mass ratio compared to Cl\(^{-}\).
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, class and shade your exam index number on the Answer Sheet in the spaces provided.

There are forty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D. Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

A Data Booklet is provided. Do not write anything on the Data Booklet.
SECTION A

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

1. Use of the Data Booklet is relevant to this question.

When \( \text{x mol} \) of cobalt is added to a solution containing \( \text{y mol} \) of cobalt(III) ions, cobalt(II) ions are formed in the resultant solution.

In the resultant solution, the number of moles of cobalt(II) ions are three times that of cobalt(III) ions. Hence, which of the following are possible values of \( \text{x} \) and \( \text{y} \)?

\[
\begin{array}{cc}
\text{x} & \text{y} \\
\text{A} & 1 \hspace{1cm} 2 \\
\text{B} & 1 \hspace{1cm} 3 \\
\text{C} & 1 \hspace{1cm} 5 \\
\text{D} & 2 \hspace{1cm} 3 \\
\end{array}
\]

2. In an experiment, a sample of gadolinium element was vaporised, ionised and passed through an electric field. Analysis of the deflection occurring at the electric field region revealed the following data for a beam of \( ^{157}\text{Gd}^+ \).

![Diagram of deflection]

What would be the angle of deflection for a sample of doubly charged strontium ions?

\[
\begin{array}{cccc}
\text{A} & 0.6^\circ & \text{B} & 3.6^\circ \\
\text{C} & 7.2^\circ & \text{D} & 16.5^\circ \\
\end{array}
\]

3. In which pair of molecules is the strength of intermolecular forces of I greater than that of II?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{F} )</td>
<td>( \text{CH}_3\text{CH}_2\text{CHF}_2 )</td>
</tr>
<tr>
<td>B</td>
<td>trans ( \text{CH}_3\text{CC}═\text{CC}\text{CH}_3 )</td>
<td>cis ( \text{CH}_3\text{CC}═\text{CC}\text{CH}_3 )</td>
</tr>
<tr>
<td>C</td>
<td>( \text{CH}_4 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>D</td>
<td>( \text{CH}_3\text{CH}_2\text{COOH} )</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} )</td>
</tr>
</tbody>
</table>
4. The equation below represents the reaction of gaseous atoms of non-metal Y and of hydrogen to form gaseous Y$_2$H$_6$ molecules.

$$2Y(g) + 6H(g) \rightarrow Y_2H_6(g) \Delta H = -2775 \text{ kJ mol}^{-1}$$

The bond energy of an H–Y bond is 395 kJ mol$^{-1}$.
What is the bond energy of a Y–Y bond?

A $-405.0$ kJ mol$^{-1}$
B $-202.5$ kJ mol$^{-1}$
C $+202.5$ kJ mol$^{-1}$
D $+405.0$ kJ mol$^{-1}$

5. Hydrogen peroxide slowly decomposes into water and oxygen.

$$2\text{H}_2\text{O}_2(l) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$$

Given that the standard enthalpy change of formation of H$_2$O$_2$(l) is $-188$ kJ mol$^{-1}$ and standard enthalpy change of formation of H$_2$O(l) is $-286$ kJ mol$^{-1}$, calculate the enthalpy change of this decomposition.

A $-98$ kJ mol$^{-1}$
B $-196$ kJ mol$^{-1}$
C $+98$ kJ mol$^{-1}$
D $+300$ kJ mol$^{-1}$

6. Nitrosyl chloride, NOCl, decomposes on heating according to the equation below:

$$\text{NOC}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{Cl}_2(g)$$

When 100 cm$^3$ of nitrosyl chloride was placed in a closed container at constant pressure and heated to a constant temperature, it was found that nitrogen monoxide constitutes 40% of the equilibrium mixture.
What is the total volume of gases in the equilibrium mixture at the temperature of the reaction?

A 100 cm$^3$  B 125 cm$^3$  C 150 cm$^3$  D 167 cm$^3$
7. The equilibrium constant for the reaction represented by the following equation is smaller than 1.0. Which of the following gives the correct relative strengths of the acids and bases in the reaction?

\[ \text{HPO}_4^{2-}(aq) + \text{H}_2\text{BO}_3^- (aq) \rightleftharpoons \text{H}_2\text{PO}_4^- (aq) + \text{HBO}_3^{2-} (aq) \]

<table>
<thead>
<tr>
<th>Acids</th>
<th>Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. ( \text{H}_2\text{PO}_4^- &gt; \text{H}_2\text{BO}_3^- ) and ( \text{HBO}_3^{2-} &gt; \text{HPO}_4^{2-} )</td>
<td></td>
</tr>
<tr>
<td>B. ( \text{H}_2\text{BO}_3^- &gt; \text{H}_2\text{PO}_4^- ) and ( \text{HBO}_3^{2-} &gt; \text{HPO}_4^{2-} )</td>
<td></td>
</tr>
<tr>
<td>C. ( \text{H}_2\text{PO}_4^- &gt; \text{HBO}_3^{2-} ) and ( \text{H}_2\text{BO}_3^- &gt; \text{HPO}_4^{2-} )</td>
<td></td>
</tr>
<tr>
<td>D. ( \text{H}_2\text{BO}_3^- &gt; \text{HPO}_4^{2-} ) and ( \text{H}_2\text{PO}_4^- &gt; \text{HBO}_3^{2-} )</td>
<td></td>
</tr>
</tbody>
</table>

8. A sparingly soluble barium salt dissociates in solution according to the equation:

\[ \text{BaL}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{L}^-(aq) \]

If the solubility product of \( \text{BaL}_2 \) is \( q \) mol\(^3\) dm\(^{-9}\), what is the concentration of \( \text{L}^- \) at equilibrium in a saturated solution of \( \text{BaL}_2 \)?

| A. \( \frac{q}{3} \) | B. \( \frac{q^{\frac{1}{4}}}{4} \) | C. \( \frac{q^{\frac{1}{2}}}{4} \) | D. \( (2q)^{\frac{1}{3}} \) |

9. A commercial pharmaceutical drug \( X \) has a constant half-life of 2.0 hours. The drug will lose its effectiveness in the human body once its mass falls below 40 mg. Given that a patient was prescribed with 320 mg tablet form of drug \( X \), how often should he take his prescription in order to maintain the effectiveness of drug in his body?

| A. every 2.0 hours | C. every 6.0 hours |
| B. every 4.0 hours | D. every 8.0 hours |

---

Line of the Data Booklet is relevant to this question.

When a mol of cobalt is added to a solution containing \( y \) mol of cobalt(III) ions, and a solution that can be written as \( x \) and \( \text{Fe}^{3+} \) ions, the number of moles of cobalt(II) ions are three times that of cobalt(III) ions. Hence, which of the following are possible values of \( x \) and \( y \)?

| A. 0 and 1 | C. 1 and 0 |
| B. 1 and 1 | D. 2 and 2 |
A plasma is a gaseous mixture in which the atoms have been completely stripped of their electrons, leaving bare nuclei. Because of its possible use in controlled nuclear fusion reactions, plasma behavior has been intensively studied.

When $^1\text{H}$ and $^4\text{He}$ nuclei, each carrying a certain electric charge, are passed between two plates, carrying a certain electric charge, $^1\text{H}$ and $^4\text{He}$ nuclei are deflected differently. The deflection path of $^1\text{H}$ is shown in the diagram below.

Which of the following is correct?

In which pair of molecules is the intermolecular forces of molecule I greater than that in molecule II?

<table>
<thead>
<tr>
<th></th>
<th>CH₃CH₂F</th>
<th>CH₃CH₂F</th>
<th>CH₃CH₂CH₂F</th>
<th>CH₃CH₂CH₂F</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CH₃CH₂F</td>
<td>CH₃CH₂F</td>
<td>CH₃CH₂CH₂F</td>
<td>CH₃CH₂CH₂F</td>
</tr>
<tr>
<td>II</td>
<td>CH₃CH₂CH₂F</td>
<td>CH₃CH₂CH₂F</td>
<td>CH₃CH₂COOH</td>
<td>CH₃CH₂COOH</td>
</tr>
</tbody>
</table>

The equation below represents the combustion of gaseous atoms of non-metal X and hydrogen to form gaseous X₂H₆ molecules.

$$2\text{X}(g) + 6\text{H}(g) \rightarrow \text{X}_2\text{H}_6(g)$$

$\Delta H = -2775$ kJ mol$^{-1}$

The bond energy of an H–X bond is 395 kJ mol$^{-1}$.

What is the bond energy of an X–X bond?

<table>
<thead>
<tr>
<th></th>
<th>–405.0 kJ mol$^{-1}$</th>
<th>–202.5 kJ mol$^{-1}$</th>
<th>+202.5 kJ mol$^{-1}$</th>
<th>+405.0 kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+202.5 kJ mol$^{-1}$</td>
<td>+405.0 kJ mol$^{-1}$</td>
<td>+405.0 kJ mol$^{-1}$</td>
<td>+405.0 kJ mol$^{-1}$</td>
</tr>
</tbody>
</table>

The following energy cycle represents the enthalpy changes in the formation of carbon dioxide from its constituent elements in their standard states.

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6.

Which substances are present at level Y in this diagram?

- A
- B
- C
- D

7.

In an experiment, $7.75 \times 10^{-3}$ mol sample of $\text{AlCl}_3$ was allowed to dimerise in a 1.8 dm$^3$ container at 200°C. At the end of the reaction, the gases exerted a total pressure of $3.745 \times 10^3$ Pa. Assuming $\text{AlCl}_3$ behaves as an ideal gas, calculate the mole fraction of $\text{AlCl}_3$ that has dimerised.

- A
- B
- C
- D

8.

In a sparingly soluble barium salt dissociates in solution according to the equation:

$$\text{Ba}_2\text{L}_2(s) \rightarrow \text{Ba}^{2+}(aq) + 2\text{L}^- (aq)$$

If the solubility product of $\text{Ba}_2\text{L}_2$ is $q$ mol$^3$ dm$^{-6}$, what is the concentration of $\text{L}^-$ at equilibrium in a saturated solution of $\text{Ba}_2\text{L}_2$ (aq)?

- A
- B
- C
- D

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A commercial pharmaceutical drug X has a half-life of 2.0 hour. The drug will lose its effectiveness in the human body once the mass of drug falls below 40 mg. Given that a patient was prescribed with 320 mg tablet form of drug X, how often should he take his prescription in order to maintain the effectiveness of drug in his body?

A every 2.0 hours  
B every 4.0 hours  
C every 6.0 hours  
D every 8.0 hours
Pepsin is a digestive enzyme found in gastric juice that aids in the digestion of proteins. The graph below shows how the rate of reaction varies with the concentration of protein (protein concentration for pepsin enzyme).

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

A. The rate is first order at low protein concentration and zero order at high protein concentration.
B. The rate is second order at low protein concentration and zero order at high protein concentration.
C. Increasing the protein concentration will increase the rate of reaction.
D. The enzyme is unable to function at high protein concentrations.

10. The reaction of hydrogen peroxide with iodide ions in an acidic solution is first order with respect to hydrogen peroxide as well as iodide ions, and zero order with respect to hydrogen ions.

\[ \text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{I}_2(\text{aq}) \]

Two experiments were carried out. Which of the following pairs of diagrams represents the variation of [H₂O₂] and [H⁺] with time?

Experiment 1: In the presence of excess [I⁻]
Experiment 2: In the presence of excess [I⁻] and [H₂O₂]
11. The standard electrode potentials of Ag⁺|Ag(s), Zn²⁺|Zn(s) and Cu²⁺|Cu(s) are +0.80 V, −0.76 V and +0.34 V, respectively. Which of the following conclusions can be drawn from these data?

A Silver is less electropositive than copper.
B Silver displaces zinc from a solution containing zinc ions. Silver displaces zinc from a solution containing zinc ions.
C Zinc ion has a greater tendency to be reduced than copper ion. Silver is an oxidising agent.
D Zinc has a lower tendency than silver to form positively charged ions.

- [H₂O₂] time
- [H⁺] time
- [H₂O₂] time
- [H⁺] time
- [H₂O₂] time
- [H⁺] time
12 Four metals Pb, x, y and z, were connected in pairs as shown in the diagram below and the voltage was recorded.

The results obtained are set out recorded in the table below.

<table>
<thead>
<tr>
<th>Negative terminal</th>
<th>Positive terminal</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>x</td>
<td>0.35</td>
</tr>
<tr>
<td>y</td>
<td>Pb</td>
<td>1.10</td>
</tr>
<tr>
<td>z</td>
<td>Pb</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Which set shows an increase in the reducing power of the metals? Which is the order of increasing ease of oxidation of the metals?

A weakest Pb, x, y, z
B strongest Pb, x
C Pb, x, y, z
D Pb, y, z

13. Which property of Group II elements (beryllium to barium) decreases with increasing atomic number?

A reactivity with water
B solubility of hydroxides second ionisation energy
11. The element astatine lies below iodine in Group VII of the Periodic Table. Which one of the following properties is correct for astatine?

A. It forms diatomic molecules which dissociate less readily than chlorine molecules.
B. It reacts explosively with hydrogen.
C. It can oxidise iodide to iodine.
D. It exists as a crystalline solid.

153. The following graph shows the first ionisation energies of eight consecutive elements J to R, which have atomic numbers between 3 to 20 in the Periodic Table.
Which one of the following statements about the elements is **false**?

A. **R** has the highest melting point.
B. The ionic radius of **J** is larger than the ionic radius of **K**.
C. **Q** forms a insoluble hydroxide which dissolves in excess dilute NaOH(aq).
D. OxideCl<sub>2</sub> of **P** gives a higher pH than oxideCl<sub>2</sub> of **N** when reacted with water.

14. Which property of Group 1B elements (beryllium to barium) decreases with increasing atomic number?

A. reactivity with water
B. second ionisation energy
C. solubility of hydroxides
D. stability of the carbonates

15. The element astatine lies below iodine in Group VII of the Periodic Table. Which one of the following properties is correct for astatine?

A. It forms diatomic molecules which dissociates less readily than chlorine molecules.
B. It reacts explosively with hydrogen.
C. It can oxidise iodide to iodine.
D. It exists as a crystalline solid.
13. The following graph shows the first ionisation energies of eight consecutive elements J to R, which have atomic numbers between 3 to 20 in the Periodic Table.

Which one of the following statements about the elements is false?

A. Q forms a hydroxide which reacts with dilute NaOH(aq).
B. R has the highest melting point.
C. The ionic radius of J is larger than the ionic radius of K.
D. Chloride of P gives a higher pH than chloride of N when reacts with water.

14. Which one of the following is not true for radium, the last member of Group II in the Periodic Table?

A. Radium compounds tend to be covalent rather than ionic.
B. Radium compounds conduct electricity when molten.
C. Radium is the most reactive Group II element.
D. Radium reacts with water to release hydrogen gas.

15. Which one of the following statements about Group VII chemistry is false?

A. The colour intensity of the elements increases down the group.
B. The volatility of hydrogen iodide is smaller than that of hydrogen chloride.
D. The reaction between chlorine and sodium thiosulfate results in the oxidation state of sulfur increasing from +2 to +2.5.

16. A chromium compound dissolves in water to give a green solution which undergoes the
14. The following reactions.

\[
\begin{array}{c}
\text{E (green solution)} \xrightarrow{\text{NH}_3(aq)} \text{F (purple solution)} \\
\downarrow \quad \text{H}_2\text{O}_2(aq) \\
\text{G (yellow solution)} \xrightarrow{\text{H}^+(aq)} \text{H (orange solution)}
\end{array}
\]

Which of the following statements is incorrect?

A. The reaction of E to form F is a ligand displacement reaction.
B. The complex ion in F is more stable than that in complex E.
C. The chromium-containing ion in the yellow solution \( \text{G} \) contains \( \text{Cr}_2\text{O}_7^{2-} \) ions.
D. The reaction of \( \text{G} \) to \( \text{H} \) is an acid-base reaction.

17. Use of the Data Booklet is relevant to this question.

Which of the following is not true about the first row transition metals or its compounds?

A. \( \text{Fe(CN)}_3^- \) does not oxidise Br\(^{-}\) to Br₂.
B. \( \text{CrCl}_2(aq) \) is chemically unstable when left to stand in the atmosphere.
C. On addition of \( \text{H}_2\text{O}_2(aq) \) to acidified \( \text{KMnO}_4(aq) \), the purple solution remains.
D. On addition of \( \text{H}_2\text{O}_2(aq) \) to hot acidified \( \text{KMnO}_4(aq) \), the purple solution remains decolourised.

18. In black and white photographic film, light converts silver chloride into metallic silver. After the film has been developed, the unreacted silver chloride is removed by reaction with sodium thiosulfate to produce a 'fixed' negative.

\[
\text{AgCl}^- + 2\text{Na}_2\text{S}_2\text{O}_3^- \rightarrow 4\text{Na}^+ + \text{Cl}^- + [\text{Ag(S}_2\text{O}_3)_2]^2-
\]

What is the function of the thiosulfate ion?

A. To make the silver ions soluble
B. To oxidise the silver ions
C. To oxidise the silver metal
19. Species with the molecular formula CH₃ can act as an electrophile, a free radical or a nucleophile depending on the number of outer shell electrons on the central carbon atom.

How many outer shell electrons must be present on carbon atom for CH₃ to act as an electrophile, a free radical or a nucleophile in these different ways?

<table>
<thead>
<tr>
<th></th>
<th>CH₃ as an electrophile</th>
<th>CH₃ as a free radical</th>
<th>CH₃ as a nucleophile</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>D</td>
<td>8</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

D to reduce the silver ions
16

20. The diagram shows the structure of the naturally-occurring molecule cholesterol.

Cholesterol is separately treated with

- cold, dilute acidified KMnO$_4$
- hot, concentrated acidified KMnO$_4$

What is the change in the number of chiral carbon atoms in the molecule during each reaction?

<table>
<thead>
<tr>
<th></th>
<th>cold, dilute acidified KMnO$_4$</th>
<th>hot, concentrated acidified KMnO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>+1</td>
<td>0</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>+1</td>
<td>-1</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>+2</td>
<td>0</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>+2</td>
<td>-1</td>
</tr>
</tbody>
</table>
21. **When heated with chlorine, 2,2-dimethylbutane undergoes free radical substitution.**

The alkyl free radical $R^\cdot$ is formed in the propagation step as shown. The hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

In a propagation step the free radical $R^\cdot$ is formed.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{C} &-\text{CH}_3 + \text{Cl}^- \rightarrow R^\cdot + \text{HCl}
\end{align*}
\]

How many different forms of $R^\cdot$ are possible?

- **A** 2
- **B** 3
- **C** 4
- **D** 5

22. **Compound W** was used in the following synthesis route.

\[
\begin{align*}
\text{COCH} &-\text{CH}_2 \xrightarrow{\text{HCN, trace KCN}} \text{Compound X} \xrightarrow{\text{Br}_2(aq)} \text{Compound Y}
\end{align*}
\]

How many sp, sp$^2$ and sp$^3$ hybridised carbon atoms are there in compound Y?

- **A** 0 6 4
- **B** 0 6Z 3
- **C** 1 6 3
- **D** 1 6Z 2
18. Platinum(IV) chloride forms a compound with ammonia in which the co-ordination number of Pt is 6. The formula unit of one such compounds is found to contain a cation and only two chloride ions.

Which of the following correctly shows the formula of this compound?

A  \( \text{Pt(NH}_3\text{)}_2\text{Cl}_2 \)  
B  \( \text{Pt(NH}_3\text{)}_4\text{Cl}_4 \)  
C  \( \text{Pt(NH}_3\text{)}_6\text{Cl}_2 \)  
D  \( \text{Pt(NH}_3\text{)}_5\text{Cl}_4 \)

19. Which of the following cannot behave as a nucleophile?

A  \( \text{N(CH}_3\text{)}_3\text{CH}_3 \)  
B  \( \text{P(O}_2\text{C}_6\text{H}_5\text{)}_3 \)  
C  \( \text{CH}_3\text{CH}_2\text{OH} \)  
D  \( \text{CH}_3\text{CH}_2\text{Li} \)

20. Cholecalciferol (Vitamin D3) has the structure shown below. It is generated in the skin when light energy is absorbed. How many stereoisomers does the molecule have?

A  25  
B  26  
C  27  
D  28

21. Each of the following compounds is effective as a refrigerant.

Which one of these, when released into the atmosphere, will cause the greatest depletion of the ozone layer?

A  \( \text{CCl}_2\text{F}_2 \)  
B  \( \text{CH}_3\text{OCH}_3 \)  
C  \( \text{CH}_3\text{CH}_2\text{F}_2 \)  
D  \( \text{CH}_3\text{CH}_2\text{CH}_3 \)

22. Compound \( W \) was used in the following synthesis route.

What are the numbers of \( \text{sp}, \text{sp}^2 \), and \( \text{sp}^3 \)-hybridised carbon atoms in compound \( Y \)?

A  0, 6, 4  
B  0, 7, 3  
C  1, 6, 3  
D  1, 7, 2

23. In which reaction does the underlined carbon-containing ligand in the reactant have a bond angle that is larger than the corresponding carbon in the product?

A and B are the same actually.
I think D is not in syllabus. Don’t think the students will know about this.
Tried setting a question like this last time, was rejected by the senior teachers as this is not required in syllabus. May consider changing to find chiral centres instead…
product?

A reducing ethanoic acid $\text{CH}_3\text{CO}_2\text{H}$ with lithium aluminium hydride $\text{LiAlH}_4$

B heating ethanal $\text{CH}_3\text{CHO}$ with acidified potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$

C complete combustion of ethene $\text{CH}_2=\text{CH}_2$ in air

D heating bromoethane $\text{CH}_3\text{CH}_2\text{Br}$ under reflux with alcoholic potassium hydroxide $\text{KOH}$

24. A mixture of one mole of $\text{CH}_2\text{COC}_2\text{H}_4$ and one mole of $\text{C}_6\text{H}_5\text{Cl}$ is heated under reflux with dilute aqueous $\text{NaOH}$. What are the organic compounds in the final reaction mixture?

A $\text{CH}_2\text{ClCO}_2\text{H}$ and $\text{C}_6\text{H}_5\text{OH}$

B $\text{CH}_2\text{OHCO}_2\text{H}$ and $\text{C}_6\text{H}_5\text{Cl}$

C $\text{CH}_2\text{OHCO}_2\text{H}$ and $\text{C}_6\text{H}_5\text{O}^-$

D $\text{CH}_2\text{OHCO}_2\text{H}$ and $\text{C}_6\text{H}_5\text{Cl}$

24. Under identical conditions, even though it proceeds by the same mechanism, reaction 1 is faster than reaction 2.

reaction 1: $\text{CH}_3\text{CHBrCH}_3 + \text{NaCN} \rightarrow \text{CH}_3\text{CH(CN)CH}_3 + \text{NaBr}$

reaction 2: $\text{CH}_3\text{CHBrCH}_3 + \text{NaI} \rightarrow \text{CH}_3\text{CHI}_2\text{CH}_3 + \text{NaBr}$

What factor will explain this result?

A The C–I bond is a stronger bond than the C–Br bond.

B The C–CN bond is a stronger bond than the C–I bond.

C The cyanide ion is a stronger nucleophile than the iodide ion.

D The bromocyanide ion is a weaker-stronger nucleophile than the iodide-iodide ion.

25. The following compound is a flavoring agent in food.
20

Which of the following reagents will give a positive chemical test result with the above compound?

A  phosphorus pentachloride
B  aqueous alkaline iodine
C  acidified potassium dichromate(VI)
D  Fehling’s solution

21. Which reaction will give 2-chloropropane in the best yield?

A  propene gas with chlorine gas in the presence of ultraviolet light
B  propene-2-ol with dilute NaCl(aq)
C  propene-2-ol with SOCl₂
D  propene with dilute HCl(aq)

25. The following compound is a flavoring agent in food.

Which of the following reagents will react with the above compound?

A  propanoic acid in the presence of concentrated sulfuric acid
B  aqueous alkaline iodine
C  neutral aqueous iron(III) chloride
D  Fehling’s solution

26. When equimolar amounts of organic compounds R, S, T and U are added separately to water, solutions of increasing pH values are obtained. Which set of identities of compounds R to U is correct?
21

27. The reddish brown colour of aqueous bromine is discharged when a solution of phenylamine is added to it. Which statement explains this observation?
A  Bromine displaces hydrogen in the benzene ring.
B  The NH₂ group of phenylamine is substituted by bromine.
C  Bromine forms a colourless complex with phenylamine.
D  Phenylamine reduces Br₂ to Br⁻.

26. Which of the following reagents and conditions to form 2-chloropropane are correct? The reaction conditions for four different reactions are given. Which reaction has the correct conditions?

[(alc) indicates an alcoholic solution.]
A  butaneCH₃CH₃(g) with + C₂Cl₂(aq), presence of ultraviolet light
B  C₂Cl₂(l) butan-2-ol with C₂Cl₂(aq)
C  butan-2-ol with SOC₂Cl(g) + HBr(g) → CH₃CH₂Br
D  CH₃CH₂I(l) + NaOH(alc) → CH₃CH₂OH + NaI + but-1-ene with HCl(aq)

27. Which halogenoalkane will undergo an Sₘ¹ reaction and produce a yellow precipitate when AgNO₃(aq) is added to it?

A  1-chlorobutane
B  1-iodobutane
C  2-chloro-2-methylpropane
D  2-iodo-2-methylpropane
28. Consider the following reaction scheme.

Which of the type of reactions is incorrect?

<table>
<thead>
<tr>
<th>Step</th>
<th>Type of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A I</td>
<td>Electrophilic substitution/Condensation</td>
</tr>
<tr>
<td>B II</td>
<td>Reduction</td>
</tr>
</tbody>
</table>
29. Which mixtures, on heating, will not produce a basic alkaline product containing deuterium, D?

A. \( \text{C}_6\text{H}_5\text{CH}_2\text{CN in D}_2 \) with Ni catalyst
B. \( (\text{ND}_2\text{H}_2)\text{SO}_4 \) and NaOD in D\(_2\)O
C. CH\(_2\)CH=CH\(_2\) with D\(_2\)O(g) in the presence of H\(_3\)PO\(_4\) catalyst
D. CH\(_3\)CH\(_2\)CONH\(_2\) and NaOD in D\(_2\)O

30. Which of the following about the amino acid, methionine, is true?

![Methionine structure]

A. It migrates towards the cathode in a solution of Na\(_2\)CO\(_3\)(aq).
B. It exists predominantly as a zwitterion in a solution of pH 2.
C. It exists as a crystalline solid with high melting point.
D. It forms covalent disulfide linkage with another methionine molecule.

**SECTION B**

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

Decide whether each of the statements is or is not correct.

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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1, 2 and 3 are</td>
<td>1 and 2 only are</td>
<td>2 and 3 only are</td>
<td>1 only is</td>
</tr>
<tr>
<td></td>
<td>correct</td>
<td>correct</td>
<td>correct</td>
<td>correct</td>
</tr>
</tbody>
</table>

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

31. Gaseous particle Y has a proton number of n+1 and a charge of +2. Gaseous particle X has proton number n and is isoelectronic with Y. Which of the following statements are true?

1. X has a larger radius than Y.
2. X requires less energy than Y when an electron is removed from each particle.
3. X releases less energy than Y when an electron is added to each particle.

32. Which of the following statements about 20.3 g of Co₂(SO₄)₃ is correct?

1. It contains 9.6 g of oxygen.
2. It contains 0.15 mol of SO₄²⁻ ions.
3. It contains 1.5 x 10²³ ions.

33. Why does a mixture of nitrogen gas and hydrogen gas react together faster with the addition of a catalyst?

1. The activation energy of the reaction is lowered.
2. There is an increase in frequency of effective collision between the molecules.
3. Nitrogen molecules and hydrogen molecules collide more frequently.

34. The numerical values of the solubility product of strontium carbonate and strontium fluoride are $8.7 \times 10^{-9}$ and $4.0 \times 10^{-11}$ respectively at 25°C.

Which of the following statements is true?

1. Strontium carbonate has a lower solubility than strontium fluoride.
2. Addition of sodium fluoride to a solution containing strontium fluoride does not affect the solubility product of strontium fluoride.
3. Addition of sodium fluoride to a saturated solution of strontium fluoride decreases the solubility of strontium fluoride.

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<tr>
<td></td>
<td>1 and 2 only are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
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</table>

33. Catalysts are used in many reversible reactions. Finely divided iron is used in the Haber process.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

What effect does iron have on this equilibrium?

1. It lowers the value of activation energy for the forward reaction.
2. It increases the rate of the reverse reaction.
3. It increases the average kinetic energy of the reacting particles.

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<tr>
<td></td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

34. The numerical values of the solubility product of strontium carbonate and strontium fluoride are $8.7 \times 10^{-9}$ and $4.0 \times 10^{-11}$ respectively at 25°C.

Which of the following statements are true?

Commented [HZY15]: Thought options 2 & 3 are the same thing...

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<th>A</th>
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<th>D</th>
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Jurong Junior College 9647/01/Prelim 2012
1. Addition of potassium fluoride to a solution containing strontium fluoride does not affect the solubility product of strontium fluoride.

2. Addition of potassium fluoride to a saturated solution of strontium fluoride decreases the solubility of strontium fluoride.

3. Strontium fluoride has a higher solubility than strontium carbonate. Fluoride will not be precipitated when potassium fluoride is added to a solution mixture containing strontium carbonate precipitate.

35. Which of the following statements are correct for the sequence hydrogen chloride, hydrogen bromide and hydrogen iodide?

1. The thermal stability of hydrogen halides decreases. The enthalpy change of formation becomes more exothermic.


3. The enthalpy change of formation becomes more exothermic. The polarity of the hydrogen halide molecule decreases.

36. When the yellow liquid NCl₃ is stirred into aqueous sodium hydroxide, the reaction that occurs can be represented by the following equation.

\[ 2\text{NCl}_3(l) + 6\text{NaOH}(aq) \rightarrow \text{N}_2(g) + 3\text{NaCl}^-,(aq) + 3\text{NaOCl}^-,(aq) + 3\text{H}_2\text{O}(l) \]

Which of the following statements are true will be the result for this reaction?

1. The oxidation state of nitrogen atom changes from -3 to 0 undergoes a redox reaction.

2. A bleaching solution remains produced after the reaction.

3. The final solution gives a precipitate with acidified silver nitrate.
### Table

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<tbody>
<tr>
<td>1</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
<td></td>
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<tr>
<td>2</td>
<td>1, 2 and 3 are correct</td>
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</table>

### Question 37

The diagram shows some laboratory apparatus.

Which preparations could this apparatus be used for?

1. bromoethane, from ethanol, sodium bromide and concentrated sulfuric acid
2. ethanal, from ethanol, sodium dichromate(VI) and sulfuric acid
3. 1,2-dibromoethane, from bromine and ethene
38. With vigorous oxidation using hot concentrated nitric acid, ketones can be oxidised to acids. The chemical equation showing the oxidation of propanone is as follows.

\[
\begin{align*}
H_3C-C=O & \xrightarrow{\text{hot HNO}_3} CH_3COOH + CO_2 \\
H_3C-C=O & \xrightarrow{\text{hot HNO}_3} CH_3CH(COOH)_2 + CO_2
\end{align*}
\]

What are the products formed when butanone undergoes the same type of oxidation?

1. CO₂
2. CH₃CO₂H
3. CH₃CH₂CO₂H

36. Disaccharides, C₁₂H₂₂O₁₁, are important in the human diet. For example, sucrose is found in pastries and lactose occurs in milk products. Both of these compounds can be hydrolysed.

\[
\begin{align*}
sucrose + H_2O & \rightarrow CH_2OH(CHOH)_4CHO + CH_2OH(CHOH)_3COCH₂OH \\
& \quad \text{glucose} \quad \text{fructose} \\
lactose + H_2O & \rightarrow CH₂OH(CHOH)_4CHO + CH₂OH(CHOH)_3CHO \\
& \quad \text{glucose} \quad \text{galactose}
\end{align*}
\]

Which statements about these hydrolysis products are correct?

1. Glucose and fructose have structural isomers.
29

Glucose and galactose are optical isomers.

Glucose and galactose are ketones.

37. Which of the following are the environmental consequences arising from unburnt hydrocarbons produced from the internal combustion engine?
1. Production of photochemical smog.
2. Respiration and breathing difficulties.
3. Formation of 'acid rain'.

38. Ketones are generally resistant to oxidation. With vigorous oxidation using hot nitric acid, ketones can be oxidised to acids.

The chemical equation showing the oxidation of penta-3-one is as follows:

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} = \text{O} + 3 \text{[O]} \\
\text{H}_3\text{C} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3\text{COOH} + \text{CO}_2
\end{array}
\]

What are the products formed when propanone undergoes the same type of oxidation?

1. CO
2. CHCOOH
3. HCOOH

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

\[
\begin{array}{c}
\text{Pravastatin}
\end{array}
\]

Which of the following statements about Pravastatin are correct?

1. 1 mole of Pravastatin reacts with 2 moles of hot NaOH(aq).
2. When 1 mole of Pravastatin is treated with an excess of Na, 2 moles of H₂ are produced.
3. In the presence of a suitable catalyst, 1 mole of Pravastatin reacts with 4 moles of HCl(g).
40. Which of the following statements about compound Z are correct?

![Compound Z]

1. Z can be hydrolysed to produce amino acids.
2. Z gives an orange precipitate with Brady’s reagent.
3. Z forms amide and ester functional groups with ethanoyl chloride.
4. Z forms ester functional groups.

Which of the following statements about this compound are correct?

- 1, 2, and 3 are correct.
- 1 and 2 only are correct.
- 2 and 3 only are correct.
- 1 only is correct.

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

![Pravastatin]

Which of the following statements about pravastatin are correct?

- A.
- B.
- C.
- D.
1. 1 mole of pravastatin reacts with 2 moles of hot NaOH(aq).
2. When 1 mole of pravastatin is treated with an excess of Na, 2 moles of H₂ is produced.
3. When 1 mole of pravastatin is treated with hot SOCl₂, 3 moles of HCl(g) is evolved.

40. The following compound, Z, is a by-product formed in the body that counteracts the effect of the drug administered to patients to treat herpes for treatment of herpes.

\[
\text{H}_2\text{N} - \text{N} - \text{N}\text{H}_2 - \text{O} - \text{NH}_2 - \text{OH}
\]

Which of the following statements about this compound are correct?

1. Z gives an orange precipitate with Brady’s reagent.
2. 1 mole of Z reacts with 4 moles of ethanoyl chloride.
3. One mole of Z can be hydrolyzed to produce 2 moles of amino acids.
Suggested Worked Solutions for 2012 JC2 Prelim Paper 1 (9647/01)

1. \( \text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+} \)
   \( \text{Co} \rightarrow \text{Co}^{2+} + 2e^- \)
   Overall eqn: \( \text{Co} + 2\text{Co}^{3+} \rightarrow 3\text{Co}^{2+} \)
   For the resulting mixture to contain Co\(^{3+}\), Co\(^{3+}\) must be in excess (more than double the amount of Co). When \( x=1, y=3 \),
   \[ \text{Co} + 2\text{Co}^{3+} \rightarrow 3\text{Co}^{2+} \]
   Initial amt/mol 1 3 0
   Final amt/mol 0 1 3
   Ans: B

2. \( \text{charge/mass} \propto \text{angle of deflection} \)
   \begin{align*}
   \text{Particle} & & \text{charge/mass} \\
   ^{157}\text{Gd}^+ & & \frac{1}{157} = 0.00637 \\
   ^{87.6}\text{Sr}^{2+} & & \frac{2}{87.6} = 0.0228 \\
   \end{align*}
   Angle of deflection for \( ^{87.6}\text{Sr}^{2+} = \left( \frac{0.0228}{0.00637} \times 2 \right) = 7.2^\circ \).
   Ans: C

3. |   | I                          | II                          |
<table>
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<tr>
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<tbody>
<tr>
<td>A</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{F} )</td>
<td>( \text{CH}_3\text{CH}_2\text{CHF}_2 )</td>
</tr>
<tr>
<td></td>
<td>Polar molecule. Permanent dipole-permanent dipole forces of attraction between molecules.</td>
<td>Polar molecule with larger dipole moment than ( \text{CH}_3\text{CH}_2\text{CH}_2\text{F} ). \textbf{Stronger} permanent dipole-permanent dipole forces of attraction than that of I.</td>
</tr>
<tr>
<td>B</td>
<td>( \text{trans CH}_3\text{CC}=/\text{CC/CH}_3 )</td>
<td>( \text{cis CH}_3\text{CC}=/\text{CC/CH}_3 )</td>
</tr>
<tr>
<td></td>
<td>Non-polar molecule. van der Waals’ forces of attraction between molecules.</td>
<td>Polar molecule. \textbf{Stronger} permanent dipole-permanent dipole forces of attraction than weaker VDW forces of attraction between I molecules.</td>
</tr>
<tr>
<td>C</td>
<td>( \text{CH}_4 )</td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td></td>
<td>van der Waals’ forces of attraction between molecules</td>
<td>\textbf{Stronger} hydrogen bonding between molecules than the weaker VDW forces of attraction between I molecules.</td>
</tr>
<tr>
<td>D</td>
<td>( \text{CH}_3\text{CH}_2\text{COOH} )</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} )</td>
</tr>
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<td>More extensive hydrogen bonds between molecules as they exist as dimers (formation of more extensive hydrogen bonding between 2 RCO(_2)H molecules) than that of II.</td>
<td>hydrogen bond between molecules.</td>
</tr>
</tbody>
</table>
   Ans: D
4. Given, 
2Y(g) + 6H(g) → Y₂H₆(g) \( \Delta H = -2775 \text{ kJ mol}^{-1} \) 
Y₂H₆(g) → 2Y(g) + 6H(g) \( \Delta H = +2775 \text{ kJ mol}^{-1} \)

\( \Delta H_r = \Delta H_f(Y) + 6\Delta H_f(Y-H) \)

\( \Delta H_f(Y) = +2775 - 6(395) = +405 \text{ kJ mol}^{-1} \)

Ans: D

5. Using the formula, 
\( \Delta H_{\text{rxn}} = \Sigma \Delta H_f(\text{products}) - \Sigma \Delta H_f(\text{reactants}) \)

\( \Delta H_r = 2\Delta H_f(H_2O) - 2\Delta H_f(H_2O_2) \)

\( = 2(-286) - 2(-188) = -196 \text{ kJ mol}^{-1} \)

Note: \( \Delta H_f(O_2) = 0 \text{ kJ mol}^{-1} \) as O₂ is an element.

Ans: B

6. Let x be the volume of NOCl(g) that reacted.

NOCl(g) ⇌ NO(g) + \( \frac{1}{2} \) Cl₂(g)

Eqm volume/cm³ 100–x x \( \frac{1}{2} \)x

Total volume of gases at eqm = (100+\( \frac{1}{2} \)x) cm³

\% of NO at eqm = \( \frac{x}{100+\frac{1}{2}x} \) x 100 \% = 40 \%

Solving, x=50 cm³

Hence, total volume of gases at eqm
=100 + \( \frac{1}{2} \) (50) = 125 cm³

Ans: B

7. HPO₄²⁻(aq) + H₂BO₃⁻(aq) ⇌ H₂PO₄⁻(aq) + HBO₃²⁻(aq)

base conjugate acid conjugate

H₂PO₄⁻ and H₂BO₃⁻ are acids and HBO₃²⁻ and HPO₄²⁻ are bases. Hence option C and D are wrong.

Since the equilibrium constant < 1.0, there will be a higher [HPO₄²⁻(aq)] and [H₂BO₃⁻(aq)] and a lower [H₂PO₄⁻(aq)] and [HBO₃²⁻(aq)] at equilibrium.

- Since [H₂PO₄⁻(aq)] < [H₂BO₃⁻(aq)] \( \Rightarrow \) H₂PO₄⁻ ionises to a greater extent than H₂BO₃⁻ to give H⁺. Hence H₂PO₄⁻ is a stronger acid than H₂BO₃⁻.
- Since [HBO₃²⁻(aq)] < [HPO₄²⁻(aq)] \( \Rightarrow \) HBO₃²⁻ ionises to a greater extent than to give OH⁻. Hence HBO₃²⁻ is a stronger base than HPO₄²⁻.

Strength of acids: H₂PO₄⁻ > H₂BO₃⁻

Strength of bases: HBO₃²⁻ > HPO₄²⁻

Ans: A

8. BaL₂(s) ⇌ Ba²⁺(aq) + 2L⁻(aq)

Given \( K_{sp} = [\text{Ba}^{2+}(aq)][\text{L}^-(aq)]^2 = q \text{ mol}^3 \text{ dm}^{-9} \)

Let [L⁻] at equilibrium be x mol dm⁻³

\( \therefore K_{sp} = \frac{x}{2} (x)^2 = q \)

\( \Rightarrow \frac{x^3}{2} = q \)

\( \Rightarrow x = (2q)^{\frac{1}{3}} \)

Ans: D

9. Given t₁/₂ = 2.0 hour

After first half-life,
mass of X = \( \frac{1}{2} \) (320) = 160 mg

After the second half-life,
mass of X = \( \frac{1}{2} \) (160) = 80 mg

After the third half-life,
mass of X = \( \frac{1}{2} \) (80) = 40 mg

Hence, drug X will still be effective after 3 half-lives (3 x 2.0 = 6.0 hour).

Ans: C
10. Rate = \( k[H_2O_2][I^-] \),
For expt 1: Rate = \( k'[H_2O_2] \) where \( k' = k[I^-] \)
The graph of \([H_2O_2]\) against time is a downward sloping curve with decreasing gradient.
For expt 2: Rate = \( k' \) where \( k' = k[I^-][H_2O_2] \)
The graph of \([H^+]\) against time is a decreasing straight line with a constant gradient.

Ans: B

11. \( E_{Ag^+/Ag} = +0.80 \, V, \ E_{Zn^{2+}/Zn} = -0.76 \, V, \ E_{Cu^{2+}/Cu} = +0.34 \, V \)

A : ( ) \( E(Ag^+/Ag) \) is more positive than \( E(Cu^{2+}/Cu) \) ⇒ Cu has the greater tendency to be oxidised than Ag. Hence, silver is less electropositive (tendency to lose e^- ⇒ undergoes oxidation) than copper.

B : ( ) \( E(Ag^+/Ag) \) is more positive than \( E(Zn^{2+}/Zn) \) ⇒ Zn has the greater tendency to be oxidised than Ag. Hence, zinc displaces silver from a solution containing silver ions.

C : ( ) \( E(Zn^{2+}/Zn) \) is more negative than \( E(Cu^{2+}/Cu) \) ⇒ Zn^{2+} has the lower tendency to be reduced than Cu^{2+}.

D : ( ) \( E(Ag^+/Ag) \) is more positive than \( E(Zn^{2+}/Zn) \) ⇒ Zn has the greater tendency to be oxidised than Ag. Hence, zinc has a higher tendency than silver to form positively charged ions.

Ans: A

12. | Result | Negative terminal (anode) | Positive terminal (cathode) | Voltage (V) |
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<thead>
<tr>
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<tbody>
<tr>
<td>(1)</td>
<td>Pb</td>
<td>x</td>
<td>0.35</td>
</tr>
<tr>
<td>(2)</td>
<td>y</td>
<td>Pb</td>
<td>1.10</td>
</tr>
<tr>
<td>(3)</td>
<td>z</td>
<td>Pb</td>
<td>2.60</td>
</tr>
</tbody>
</table>

Using (1), Pb undergoes oxidation and x undergoes reduction. ⇒ The reducing power of Pb is higher than that of x.

Using (2) and (3), both y and z undergo oxidation and Pb undergoes reduction. ⇒ The reducing power of y and z is higher than that of Pb.

Since the voltage recorded in (3) is higher than that in (2), the reducing power of z is higher than that of y. \( \ldots \) from weakest to strongest reducing power: \( x, \) Pb, \( y, \) z

Ans: D

13. A : ( ) Reactivity of Group II elements with cold water increases down the group. \( \{Mg \, reacts \, slowly; \, Ca \, reacts \, readily; \, Ba \& \, Sr \, react \, vigorously.\} \)

\( \text{M(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{M(OH)}_2(aq) + \text{H}_2(g) \), where M = Ca, Sr and Ba

B : ( ) Solubility of Group II hydroxides and oxides increases down the group. As a result, the pH of the resulting hydroxide solutions increases \( \{\text{from } \text{pH 9 in Mg(OH)}_2 \, \text{to } \text{pH 12 in Ca(OH)}_2 \, \text{to } \text{pH 14 in Ba(OH)}_2\} \).

\( \text{MO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{M(OH)}_2(aq) \), where M = Ca, Sr and Ba

\( \text{MgO(s)} + \text{H}_2\text{O(l)} = \text{Mg(OH)}_2(aq) \)

C : ( ) Second ionisation energy of elements decreases from Be to Ba. This is due to an increase in ionic radii of M^+(g) and the increase in shielding effect which outweighs the effect of increasing nuclear charge.

D : ( ) Down the group, thermal stability of Group II carbonates increases.

\( \text{MCO}_3(s) \rightarrow \text{MO(s)} + \text{CO}_2(g) \)

As the ionic radius of the M^{2+} increases down the Group, the charge density of the M^{2+} decreases. The ability of M^{2+} to polarise the large CO_3^{2-} anion decreases down the group.

Ans: C
14. A: (°) Atomic radius of At is larger than Cl and At–At bond is longer and weaker than Cl–Cl bond and so At₂ dissociates more readily than Cl₂.

B: (°) It reacts explosively with hydrogen.
\[ X_2(g) + H_2(g) \rightarrow 2HX(g), \Delta H \]
(where \( X = Cl, Br \) and I)
\[ \Delta H = E(X-X) + E(H-H) - 2E(H-X) \]
As H–X bond energy decreases, \( \Delta H \) becomes less exothermic (less energetically feasible).

C: (°) Down the group, \( E(X_2/X^-) \) becomes less positive, indicating that the oxidising power decreases down the group. Thus At₂ will not be able to oxidise I⁻ to I₂.

D: (°) Volatility of halogens (\( X_2 \)) decreases down group VII from Cl₂ to I₂. There is an increase in strength of van der Waals' forces between \( X_2 \) molecules as the no. of electrons per \( X_2 \) molecules increases from Cl₂ to At₂. Thus At₂ exists as crystalline solid.

Ans: D

15. From the large drop in 1st ionisation energy from M to N, we can deduce that M is the last element in the 2nd Period (Ne) and N is the first element in the 3rd Period (Na).

A: (°) R is Si. It has the highest melting point. (Giant covalent structure, with strong Si–Si covalent bonds)

B: (°) J is nitrogen and K is oxygen. Both N³⁻ and O²⁻ are isoelectronic, thus as nuclear charge increases from N³⁻ and O²⁻, while the shielding effect by inner shell electrons remains relatively constant, the ionic radius of N³⁻ (J) is larger than that of O²⁻ (K).

C: (°) Q is aluminium. Al forms an insoluble hydroxide, which dissolves in excess dilute NaOH(aq).
\[ Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^- (aq) \]

[Note: Being amphoteric, Al(OH)₃ reacts with both aqueous acids and alkalis.]

\[ Al(OH)_3(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O(l) \]

D: (°) Oxide of P (Mg) gives a lower pH than oxide of N (Na) when reacted with water. Na₂O(s) reacts vigorously with water to form a strongly alkaline NaOH(aq) solution with pH = 13-14.
\[ Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq) \]

MgO(s) is sparingly soluble in water and hence dissolves with water to a small extent to form limited quantity of Mg(OH)₂(aq), a weakly alkaline solution with pH = 9.
\[ MgO(s) + H_2O(l) = Mg(OH)_2(aq) \]
\[ Mg(OH)_2(aq) \rightarrow Mg^{2+}(aq) + 2OH^-(aq) \]

Ans: D

16. A: (°) A change in colour indicates either the possibility of a redox reaction or a ligand exchange reaction.
\[ [Cr(H₂O)₆]^{3+} + 6NH₃ \rightarrow [Cr(NH₃)₆]^{3+} + 6H₂O \]
green-purple

B: (°) Since NH₃ replaces the H₂O ligand, as it forms a stronger dative covalent bond with Cr³⁺ and thus a more stable complex ion than [Cr(H₂O)₆]³⁺.

C: (°) The yellow solution is CrO₄²⁻ (Cr₂O₇²⁻ is orange in colour).

D: (°) 2CrO₄²⁻ + H₂O = Cr₂O₇²⁻ + 2OH⁻
CrO₄²⁻ ionises in water, giving Cr₂O₇²⁻ + 2OH⁻. Thus it reacts with H⁺ to give Cr₂O₇²⁻ and H₂O.
\[ 2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O \]

Ans: C
17. A: \( \text{Fe(CN)}_6^{3-} + e \rightleftharpoons \text{Fe(CN)}_6^{4-} \; \text{+0.36V} \)
\[ \text{Br}_2 + 2e \rightleftharpoons 2\text{Br}^- \; \text{+1.07V} \]
\( E^{\circ}_{\text{cell}} = 0.36 - (+1.07) = -0.71 \text{V} < 0 \) (energetically not feasible). Hence \( \text{Fe(CN)}_6^{3-} \) is not able to oxidise \( \text{Br}^- \) to \( \text{Br}_2 \).

B: (\( \text{in atmosphere} \) ) indicates reaction in presence of \( \text{O}_2 \).
\( \text{O}_2 + 4\text{H}^+ + 4e \rightleftharpoons 2\text{H}_2\text{O} \; +1.23\text{V} \)
\( \text{Cr}^{3+} + e \rightleftharpoons \text{Cr}^{2+} \; -0.41\text{V} \)
\( E^{\circ}_{\text{cell}} = 1.23 - (-0.41) = +1.64\text{V} > 0 \) (energetically feasible). Hence \( \text{CrCl}_2 \) is chemically unstable as it will be oxidised to \( \text{CrCl}_3 \).

C: \( \text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O} \; +1.52\text{V} \)
\( \text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{O}_2 \; +0.68\text{V} \)
\( E^{\circ}_{\text{cell}} = 1.52 - 0.68 = +0.84\text{V} > 0 \) (energetically feasible). On addition of \( \text{H}_2\text{O}_2 \) to acidified \( \text{KMnO}_4 \), the purple solution decolourises.

D: (\( \text{NaOH(aq)} \) and \( \text{FeCl}_3 \)(aq) is mixed, \( \text{Fe(OH)}_3 \)(s) is formed.
\( \text{Fe(OH)}_3 + e \rightleftharpoons \text{Fe(OH)}_2 + \text{OH}^- \; -0.56\text{V} \)
\( \text{O}_2 + 2\text{H}^+ + 4e \rightleftharpoons 4\text{OH}^- \; +0.40\text{V} \)
\( E^{\circ}_{\text{cell}} = -0.56 - (+0.40) = -0.96\text{V} < 0 \) (energetically not feasible). \( \therefore \text{Fe(OH)}_3 \) does not react with \( \text{OH}^- \) to give \( \text{O}_2 \).

Ans: B

18. \( \text{AgCl} + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow 4\text{Na}^+ + \text{Cl}^- + [\text{Ag(S}_2\text{O}_3)_2]^{3-} \)
A: (\( \text{The reaction causes silver ions to} \)
\( \text{dissolve through the formation of a silver} \)
\( \text{complex, [Ag(S}_2\text{O}_3)_2]^{3-} \) which is soluble.

B, C and D: (\( \text{Silver is neither oxidised or} \)
\( \text{reduced as the oxidation state of Ag remains at} \)
\( +1 \) in both \( \text{AgCl} \) and \( [\text{Ag(S}_2\text{O}_3)_2]^{3-} \).

Ans: A

19. Error! Objects cannot be created from editing field codes.

20. With cold, dilute acidified \( \text{KMnO}_4 \):

After mild oxidation, there is an increase in two new chiral carbon atoms.
20. With hot, concentrated acidified KMnO₄:

![Chemical structure image]

This carbon is not chiral after oxidation.
After strong oxidation, there is a decrease in one chiral carbon atom.

Answer: D

21. Note: the three CH₃ groups bonded to C3 are equivalent.

C/• can abstract H atoms from 1 CH₃ of C1, 2 CH₂ of C2 or 3 any of the three CH₃ groups bonded to C3 to form 3 different forms of X•.

![Chemical structure image]

Answer: B

22. X:

![Chemical structure image]

Y:

![Chemical structure image]

Cᵃ, Cᵇ and Cᵈ are sp³ hybridised (ie. 4 electron pair).
Cᵃ is sp hybridized (ie. 2 electron pairs).

Answer: C
23. **Error! Objects cannot be created from editing field codes.**

A: (°)  
120°  
Oxidation  
\[ \text{CH}_3\text{C} = \text{O} \rightarrow \text{CH}_3\text{C} = \text{OH} \]

B: (°)  
120°  
Combustion  
\[ \text{CH}_3\text{C} = \text{C} = \text{H} \rightarrow \text{O} = \text{C} = \text{O} \]

C: (°)  
120°  
Elimination  
\[ \text{H}_3\text{C} = \text{C} - \text{Br} \rightarrow \text{C} = \text{C} - \text{H} \]

D: (°)  
109.5°  
\[ \text{Ans: A} \]

24. **A:** (°) The C–I bond is a weaker bond than the C–Br bond.

**B:** (°) The C–N bond is not broken in the mechanism.

**C:** (°) The cyanide ion is a stronger nucleophile than the iodide ion, hence the substitution proceeds faster.

**D:** (°) The nucleophiles in reaction 1 and 2 are cyanide ion and iodide ion respectively. The bromide ion is not acting as a nucleophile.

\[ \text{Ans: C} \]

25. **A:** (°) Absence of carboxylic acid and alcohol functional groups which could react with PC\(_5\).

**B:** (°) No pale yellow ppt will be formed due to the absence of –COCH\(_3\) (in aldehydes or ketones) or –CH(OH)CH\(_3\) group (in alcohols) in reactant or product.

**C:** (°)  
\[ \text{O} \quad \text{alkaline} \quad \text{hydrolysis} \quad \text{O} \quad \text{O} \quad \text{+ CH}_3\text{CO}_2^- \]

**D:** (°) Fehling’s solution only gives a positive chemical test for aliphatic aldehyde, not for aromatic aldehyde.

\[ \text{Answer: C} \]

26. **A:** (°) \( \text{CH}_3\text{CH}_3(g) + \text{Cl}_2(g) \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl} \)

**B:** (°) \( \text{AlCl}_3(s) \rightarrow \text{Cl}^- + \text{HCl} \)

**D:** (°) \( \text{CH}_3\text{CH}_2\text{I}(l) + \text{NaOH(aq)} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaI} \)

\[ \text{Note if it’s CH}_3\text{CH}_2\text{I}(l) + \text{NaOH(alc)} \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}, \text{elimination occurs.} \]
27. Primary halogenoalkane generally undergoes $S_N2$ reaction. Tertiary halogenoalkane generally undergoes $S_N1$ reaction. The yellow ppt is AgI, hence the halogenoalkane must be iodoalkane (eliminate option A & C).

B: \( \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH}_2\text{C} \quad \text{primary halogenoalkane} \\
\text{H} \\
1\text{ alkyl group}
\end{array} \)

D: \( \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array} \quad \text{tertiary halogenoalkane} \\
3\text{ alkyl groups}
\)

Answer: C

28. This acts as an electrophile and undergoes electrophilic substitution with benzene ring to form M.

Ans: A

29. A: \( \begin{array}{c}
\text{C}_6\text{H}_5\text{CH}_2\text{CN} + \text{D}_2 \quad \text{Ni} \\
\rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CD}_2\text{ND}_2
\end{array} \quad \text{reduction} \)

(remsembles \( \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2 \), primary amine, which is basic)

B: \( \begin{array}{c}
\text{ND}_2\text{H}_2 + \text{OD}^- \\
\rightarrow \text{ND}_2\text{H} (\text{or NDH}_2) + \text{HDO} (\text{or D}_2\text{O})
\end{array} \quad \text{acid-base reaction} \)

(remsembles \( \text{NH}_3 \), which is basic)

C: \( \begin{array}{c}
\text{CH}_3\text{CH} = \text{CH}_2 + \text{D}_2\text{O} (\text{g}) \\
\rightarrow \text{CH}_3\text{CH} (\text{OD})\text{CH}_2\text{D}
\end{array} \quad \text{electrophilic addition} \)

(remsembles \( \text{CH}_3\text{CH} (\text{OH})\text{CH}_3 \), an alcohol, which is not basic)

D: \( \begin{array}{c}
\text{CH}_3\text{CH}_2\text{CONH}_2 \\
\rightarrow \text{CH}_3\text{CH}_2\text{CO}_2^-\text{Na}^+ + \text{NH}_2\text{D}
\end{array} \)

(remsembles \( \text{NH}_3 \), which is basic)

Answer: C

30. A: \( \begin{array}{c}
\text{In Na}_2\text{CO}_3 (\text{aq}), \text{it migrates towards the positively charged anode.}
\end{array} \)

B: \( \begin{array}{c}
\text{It exists as a cation in a solution of pH 1.}
\end{array} \)

C: \( \begin{array}{c}
\text{It exists as a solid with high melting point due to the presence of strong ionic bonds between groups of oppositely charged zwitterions.}
\end{array} \)

2012 JJ Prelim H2 Chemistry (9647) Paper 1 (9647/01) Suggested Worked Solutions Page 8 of 11
### 30. D: (*) To form covalent disulfide linkage with another molecule, it has to be −SH, and not −SCH<sub>3</sub>.

![Disulfide Linkage](image)

**Answer:** C

### 31. Gas particle Y has (n+1) protons and a charge of 2+. Error! Objects cannot be created from editing field codes. No. of electrons = (n+1 – 2) = n – 1

Gas particle X has n protons and (n-1) electrons. Error! Objects cannot be created from editing field codes. Charge of X is 1+.

1. (, ) X has a smaller nuclear charge than Y, hence X has a larger radius than Y.

2. (, ) The electron removed is less tightly bound to the singly charged X than the doubly charged Y. Hence less energy is required to remove the electron.

3. (, ) The electron added is less tightly bound to the singly charged X than the doubly charged Y. Hence less energy is released when the electron is added to X.

**Answer:** A

### 32. (1): (, ) ΔS<0. Decrease in disorder due to precipitation of PbSO₄(s).

(2): (, ) ΔS>0. Increase in disorder since kinetic energy of particles increases causing a broadening of the Boltzmann energy distribution. Error! Objects cannot be created from editing field codes. More ways of arrangement of energy quanta.

(3): (, ) ΔS>0. Increase in disorder as reaction proceeds with an increase in number of gas particles from 0 to 1 mole.

**Answer:** D

### 33. (1) and (2): (, ) The iron catalyst provides an alternative reaction path of lower E<sub>a</sub> than that of the uncatalysed reaction. Thus, the number of molecules with energy greater than the lowered activation energy increases. Frequency of effective collisions between molecules increases and hence rate of reaction increases by the same extend for the forward and backward reaction.

(3): (, ) Catalyst does not increase the kinetic energy of the reacting particles.

**Answer:** B

### 34. (1): (, ) Solubility product, K<sub>sp</sub> is only affected by temperature.

(2): (, ) The presence of the common ion F⁻, increases [F⁻]. Equilibrium position of SrF<sub>2</sub>(s) ⇌ Sr<sup>2+</sup>(aq) 2F⁻(aq) will shift to left, hence decreasing the solubility of strontium fluoride.

(3): (, ) Let solubility of SrCO<sub>3</sub> be x.

\[
x^2 = 8.7 \times 10^{-9}
\]

\[
x = (8.7 \times 10^{-9})^{1/2} = 9.33 \times 10^{-5} \text{ mol dm}^{-3}
\]

Let solubility of SrF<sub>2</sub> be y.

\[
4.0 \times 10^{-11} = (y)(2y)^2 = 4y^3
\]

\[
y = \left(\frac{4.0 \times 10^{-11}}{4}\right)^{1/3} = 2.15 \times 10^{-4} \text{ mol dm}^{-3}
\]

:. SrF<sub>2</sub> is more soluble than SrCO<sub>3</sub>.

**Answer:** A
35. (1) Atomic radius increases from Cl, Br to I. H–X bonds become longer and weaker. Thus, H–X bond energy decreases from HCl, to HBr and HI, and is more easily broken under heating.

(2) As electronegativity decreases from Cl, Br, I, polarity of hydrogen halide decreases from HCl, HBr, HI.

(3) The enthalpy change of formation of HX becomes less exothermic. HF is most energetically stable with respect to F2 and H2, and hence it is most readily formed. Whereas HI is least energetically stable with respect to I2 and H2, and hence it is not readily formed. (H–I bond formed is very weak.)

Answer: B

36. (1) Since N is more electronegative than Cl, o.s of Cl in NC15 = +1. Hence the oxidation state of N in NC15 is –3 and it changes to 0 (in N2).

(2) NaClO(aq) is the bleaching solution.

(3) Cl from NaCl forms AgCl precipitate with AgNO3(aq).

(Note: The acid added is to remove any NaOH left, so as to prevent precipitation of Ag2O.)

Answer: A

37. (1) and (2) To prepare the gaseous products, bromoethane and ethanal, heating is required with their respective reagents and conditions. The products can then be condensed and collected as the distillate.

(3) To prepare 1,2-dibromoethane, heating is not required.

Answer: B

38. Pattern observation:

When this C–C bond is broken, oxidised to HCO2H, which is further oxidised to CO2.

For butanone, oxidised to

When this C–C bond is broken, oxidised to CH3CH2COOH + CO2.
(1), (2) and (3) : ( )

Answer : A

39. (1) : ( ) Alkaline hydrolysis

2 moles of NaOH(aq) are required to react with the ester via alkaline hydrolysis and carboxylic acid via acid-base reaction.

(2) : ( )

4 –OH groups ≡ 2H₂(g)

Redox reaction

Na reacts with 3–OH groups and 1 RCOOH group to produce 2 moles of H₂.

(3) : ( )

Electrophilic addition with alkenes and substitution reaction with alcohol

1 mole of Pravastatin reacts with 5 moles of HCl(g).

Answer : B

40. (1) : ( )
Note: Amino acids contain at least one amino group (–NH₂) and one carboxyl group (–COOH).

(2): (°) There is no aldehyde or ketone functional groups in compound Z.

(3): (°) Ethanoyl chloride forms only amides with the –NH₂ groups in Z. Esters will not be formed.

Answer : D
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 all questions.
A Data Booklet is provided. Do not write anything on the Data Booklet.

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

You are to plan an investigation into the thermal decomposition of caesium nitrate, CsNO₃.

You may make use the following data when planning your investigation.

**Data:**

<table>
<thead>
<tr>
<th>Group I element</th>
<th>cation</th>
<th>Ionic radius / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium</td>
<td>Li⁺</td>
<td>0.060</td>
</tr>
<tr>
<td>sodium</td>
<td>Na⁺</td>
<td>0.095</td>
</tr>
<tr>
<td>potassium</td>
<td>K⁺</td>
<td>0.133</td>
</tr>
<tr>
<td>rubidium</td>
<td>Rb⁺</td>
<td>0.148</td>
</tr>
<tr>
<td>caesium</td>
<td>Cs⁺</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Equation for the thermal decomposition of lithium nitrate and sodium nitrate are given below:

1. \[4\text{LiNO}_3(s) \rightarrow 2\text{Li}_2\text{O}(s) + 4\text{NO}_2(g) + \text{O}_2(g)\]
2. \[2\text{NaNO}_3(s) \rightarrow 2\text{NaNO}_2(s) + \text{O}_2(g)\]

<table>
<thead>
<tr>
<th>Nitrogen dioxide gas</th>
<th>Oxygen gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>O₂</td>
</tr>
<tr>
<td>brown in colour</td>
<td>colourless</td>
</tr>
<tr>
<td>soluble in water</td>
<td>almost insoluble in water</td>
</tr>
<tr>
<td>poisonous</td>
<td>powerful oxidant</td>
</tr>
</tbody>
</table>

1 mol of any gas occupies a volume of approximately 24 dm³ at room temperature and atmospheric pressure.

\[A_r: \text{Cs, 133; N, 14.0; O, 16.0}\]

(a) Predict which of the equations below will represent the thermal decomposition of caesium nitrate. Place a tick against the equation of your choice.

\[4\text{CsNO}_3(s) \rightarrow 2\text{Cs}_2\text{O}(s) + 4\text{NO}_2(g) + \text{O}_2(g)\]
\[2\text{CsNO}_3(s) \rightarrow 2\text{CsNO}_2(s) + \text{O}_2(g)\]

Use the data provided to explain your prediction.

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[2]
1. **(b)** You are to plan an experiment in which

- caesium nitrate is heated
- gas is collected
- the volume of gas collected is measured
- the experimental results are used to confirm or reject your prediction

(i) Draw a diagram of the apparatus you would use in this experiment.

Your apparatus should use only standard items found in college laboratory.

Label each piece of apparatus used, indicating its size or capacity and state the gas or gases collected on your diagram.

(ii) Calculate the volume of gas you would expect to collect at room temperature and atmospheric pressure if 1 mol of caesium nitrate completely decomposed according to your predicted equation in (a).
1. (c) Use your answer to (b)(ii) and the capacity of the apparatus selected in (b)(i) to calculate the maximum mass of CsNO$_3$ that can be used in your experiment.

(d) Outline, in a series of numbered steps, the method to be used in the experiment.

Make certain that the steps you describe are in the correct order.

You need not explain how the apparatus is assembled.

Indicate clearly how you will know when decomposition is complete.

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1. (e) What should be done when decomposition is complete to ensure that the volume of the gas measured in the apparatus is the “correct” volume?

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

(f) Identify a risk present in the method you have described and suggest how you would minimise this risk.

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

[Total: 12]
2. (a) (i) Write an equation for the reaction between chlorine and cold aqueous sodium hydroxide and state the type of reaction that occurs.

Type of reaction: .........................................................

(ii) The resultant solution obtained in (a)(i) is heated and a further reaction occurs. Write an equation for the overall reaction between chlorine and sodium hydroxide.

(b) Chlorine forms a variety of oxides and oxoanions. A series of standard reduction potentials involving the chlorine oxoanions, in alkaline medium, are given below.

<table>
<thead>
<tr>
<th>half-equation</th>
<th>E/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClO(^-) + H(_2)O + 2e(^-) = Cl(^-) + 2OH(^-)</td>
<td>-0.89</td>
</tr>
<tr>
<td>ClO(_2)(^-) + H(_2)O + 2e(^-) = ClO(^-) + 2OH(^-)</td>
<td>-0.67</td>
</tr>
<tr>
<td>ClO(_3)(^-) + H(_2)O + 2e(^-) = ClO(_2)(^-) + 2OH(^-)</td>
<td>-0.33</td>
</tr>
<tr>
<td>ClO(_4)(^-) + H(_2)O + 2e(^-) = ClO(_3)(^-) + 2OH(^-)</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

Using the above data and information in the *Data Booklet*, predict the final product formed when excess zinc metal is added to an alkaline solution of chlorate(V), ClO\(_3\)\(^-\). Support your answer with \(E_{\text{cell}}\) calculations.
2. (c) Chlorine dioxide, $\text{C}/\text{O}_2$, is a highly reactive gas that is used as a disinfectant to kill water-borne bacteria, viruses and fungi.

Draw a ‘dot-and-cross’ diagram to show the arrangement of valence electrons in the $\text{C}/\text{O}_2$ molecule. Hence suggest why chlorine dioxide is highly reactive.

...............................................................................................................................
............................................................................................................................... [2]

(d) Despite having similar relative molecular mass, the boiling point of chlorine is $-34 \, ^\circ\text{C}$ and that of chlorine dioxide is $11 \, ^\circ\text{C}$.

Give an explanation to account for this large difference in boiling points.

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3. (b) The enthalpy change of formation of \( \text{Al}_2\text{O}_3 \) can be calculated from a Born-Haber cycle.

Construct the Born-Haber cycle for the formation of \( \text{Al}_2\text{O}_3 \), using the following data and relevant data from the Data Booklet. Hence, calculate the enthalpy change of formation of \( \text{Al}_2\text{O}_3 \).

<table>
<thead>
<tr>
<th>Term</th>
<th>( \Delta H ) / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy change of atomisation of aluminium</td>
<td>+644</td>
</tr>
<tr>
<td>Sum of 1(^{st}) and 2(^{nd}) electron affinities of oxygen</td>
<td>+702</td>
</tr>
<tr>
<td>Lattice energy of ( \text{Al}_2\text{O}_3 )</td>
<td>−13311</td>
</tr>
</tbody>
</table>

[5]
3. (c) Aluminium chloride exists in two different forms in the vapour state. When some $\text{Al}_2\text{Cl}_6$ was added into a reaction vessel, the following equilibrium is slowly set up.

$$\text{Al}_2\text{Cl}_6(g) = 2\text{AlCl}_3(g)$$

At different times during the experiment, changes were made to the conditions in the reaction vessel. At each time, there was only one change made to the condition in the reaction vessel.

The change in the concentrations in the equilibrium mixture with time is shown in the graph below.

(i) Suggest the changes that caused the equilibrium shifts at time:

$T_1$: ............................................................... ...............................................................

$T_2$: ............................................................... ...............................................................

(ii) Explain whether the conversion of $\text{Al}_2\text{Cl}_6$ to $\text{AlCl}_3$ is expected to be exothermic or endothermic.

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3. (c) (iii) Sketch on the same axes of the given graph on page 9, the changes in the concentration of $\text{Al}_2\text{Cl}_6$ and $\text{AlCl}_3$ when the mixture was cooled at time $T_3$.

Explain your answer with reference to your conclusion made in (c)(ii).

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(iv) At a total pressure of 1 atm and 673 K, $\text{Al}_2\text{Cl}_6$ was 30% dissociated into $\text{AlCl}_3$.

Calculate the equilibrium constant, $K_p$, including its units, at 673 K.
4. (a) Copper is a transition element that forms a rich variety of compounds with varying oxidation states. 

\[
\text{Cu(NO}_3\text{)}_2(\text{aq}) \text{ is a blue solution which can undergo the following reactions.}
\]

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2(\text{aq}) & \xrightarrow{\text{SO}_2} \text{Cu}_2\text{O} (s) & \text{conc HCl} & \rightarrow D \text{ white solid} \\
& \xrightarrow{\text{excess NH}_3(\text{aq})} \text{B pale blue ppt} & \xrightarrow{\text{conc NH}_3(\text{aq})} \text{C colourless solution} \\
& \xrightarrow{\text{excess NH}_3(\text{aq})} \text{B deep blue solution} & \xrightarrow{\text{colourless solution}} \text{E}
\end{align*}
\]

\(\text{B, C and E contain complex ions of copper.} \)

Both compound \(\text{D} \) and complex ion \(\text{E} \) contain copper and chlorine only.

The oxidation number of copper in \(\text{C}, \text{D} \) and \(\text{E} \) are the same.

(i) What are the formulae of the compound \(\text{A} \) and of the cation present in \(\text{B} \)?

A: ........................................  B: ........................................

(ii) Suggest a balanced equation for the formation of \(\text{B} \) from \(\text{A} \).

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

(iii) State the role of SO\(_2\) in the conversion of \(\text{Cu(NO}_3\text{)}_2 \) to \(\text{Cu}_2\text{O} \).

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

(iv) The composition of complex ion \(\text{C} \) by mass is \(\text{Cu}, 65.1\%, \text{ N}, 28.7\%, \text{ H}, 6.2\%\).

Use the data to determine the empirical formula and identity of complex ion \(\text{C} \).
4. (a) (v) Suggest the formulae of compound D and complex ion E, given that the coordination number of Cu in complex ion E is the same as that in C.

D: ……………………………… E: ………………………………………… [8]

(b) Copper forms a very useful group of organic compounds known as Gilman reagents.

Gilman reagents can react with alkyl halides via nucleophilic substitution to form alkanes. An example is shown below:

Step 1: \[ 2\text{CH}_3\text{Li} + \text{CuI} \rightarrow (\text{CH}_3)_2\text{CuLi} + \text{LiI} \]

\[ \text{methyllithium} \quad \text{Gilman reagent} \]

Step 2: \[ \text{CH}_3\text{CH}_2\text{Cl} + (\text{CH}_3)_2\text{CuLi} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_3\text{Cu} + \text{LiCl} \]

\[ \text{chloroethane} \]

(i) Suggest the structural formula of the final organic product formed when phenyllithium, \[ \text{ } \text{ } \text{ } -\text{CH}_2\text{Li} \text{ } \text{ } \text{ } , \]

and bromoethane are used in a similar two-step process.

(ii) Gilman reagents can also react with acyl chlorides to form ketones. An example is shown below:

\[ \text{phenylchloroacetate} + (\text{CH}_3)_2\text{CuLi} \rightarrow \text{phenylacetate} + \text{CH}_3\text{Cu} + \text{LiCl} \]

It is observed that the reaction with acyl chlorides takes place much more readily than that with alkyl chlorides. Explain why this is so.

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5. (a) The Green Fluorescent Protein (GFP) is a protein that can be isolated from the jellyfish, *Aequorea victoria*, and it can exhibit bright green fluorescence when exposed to ultraviolet light. The chromophore is the section of the GFP that fluoresces and contains the amino acid sequence *ser-tyr-gly*.

![Chemical structure of GFP chromophore](image)

(i) Draw the structure of this section of the GFP at pH 14.

(ii) GFP has a beta barrel structure, consisting of one β-pleated sheet and α-helices running through the centre of the barrel structure.

Sketch a labelled diagram to show how the β-pleated sheet structure of proteins is stabilised, showing clearly the stabilising bonds involved.
5. (b) A venomous jellyfish has tentacles containing ‘stinging cells’ that inject venom into the skin of a victim. The venom is made up of a diverse variety of proteins and polypeptides capable of inflicting pain and swelling.

The most common first-aid treatment of jellyfish stings is to get the victim out of water, scrape off any attached tentacles with a hard object and rinse the affected area with hot seawater to deactivate the venom.

Explain how the application of heat is effective in treating jellyfish stings.

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(c) Paracetamol is usually prescribed to the victim to reduce the pain from jellyfish stings.

\[
\text{HO} \quad \begin{array}{c} \text{N} \end{array} \quad \text{COCH}_3
\]

\text{Paracetamol}

A student suggested that paracetamol can be synthesised from phenol, via a three-step reaction sequence as proposed below.

\[
\begin{array}{c}
\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{OH} \\
\end{array}
\quad \begin{array}{c}
\text{C}_6\text{H}_5\text{C} \\
\text{O} \\
\text{O} \\
\text{C} \\
\end{array}
\quad \text{NO}_2 \\
\begin{array}{c}
\text{NH}_2 \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{NH}_2 \\
\end{array}
\text{N} \quad \text{COCH}_3
\]

\text{4-aminophenol} \quad \text{paracetamol}

(i) What types of reaction take place in Step I, II and III?

Step I: ........................................................................................................

Step II: ........................................................................................................

Step III: .................................................................................................................................

5. (c) (ii) State the reagents and conditions needed for Step I and II.

Step I: ........................................................................................................................................

Step II: ........................................................................................................................................

(iii) In actual practice, 4-aminophenol is used instead as the starting material and only Step III is carried out.

Given that both phenol and 4-aminophenol are easily available, suggest a reason why phenol is not used as the starting material.

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.................................................................................................................................................... [7]

Total: 13

6. Lorcaserin (Trade name: Belviq®) is a weight-loss drug developed by Arena Pharmaceuticals in San Diego and is recently approved by the US Food and Drug Administration in June 2012 for use in the treatment of obesity for adults.

(a) Draw the structures of the organic compounds formed when Lorcaserin is treated with the following reagents.

(i) ethanoyl chloride

(ii) excess CH₃Cl
6. (b) An isomer of Lorcaserin (compound Y) is shown below.

\[
\begin{align*}
\text{H}_3\text{C} & \\
\text{Cl} & \\
\text{compound Y} & \\
\end{align*}
\]

Suggest a chemical test that could be used to distinguish compound Y from Lorcaserin. You should state what you would observe for each compound in the test.

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(c) \[
\begin{align*}
\text{NH}_2 & \\
\text{phenylamine} & \\
\end{align*}
\]

Explain how the basicity of Lorcaserin might compare with that of phenylamine.

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[Total: 6]
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 all questions.
A Data Booklet is provided. Do not write anything on the Data Booklet.

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

For Examiner’s Use

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1. Planning (P)

You are to plan an investigation into the thermal decomposition of caesium nitrate, CsNO₃.
You may make use of some or all of the following data when planning your investigation.

**Data:**

<table>
<thead>
<tr>
<th>Group I element</th>
<th>cation</th>
<th>Ionic radius / nm</th>
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<tbody>
<tr>
<td>lithium</td>
<td>Li⁺</td>
<td>0.060</td>
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<tr>
<td>sodium</td>
<td>Na⁺</td>
<td>0.095</td>
</tr>
<tr>
<td>potassium</td>
<td>K⁺</td>
<td>0.133</td>
</tr>
<tr>
<td>rubidium</td>
<td>Rb⁺</td>
<td>0.148</td>
</tr>
<tr>
<td>caesium</td>
<td>Cs⁺</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Equation for the thermal decomposition of lithium nitrate and sodium nitrate are given below:

1. \(4\text{LiNO}_3(s) \rightarrow 2\text{Li}_2\text{O(s)} + 4\text{NO}_2(g) + \text{O}_2(g)\)
2. \(2\text{NaNO}_3(s) \rightarrow 2\text{NaNO}_2(s) + \text{O}_2(g)\)

<table>
<thead>
<tr>
<th>Nitrogen dioxide gas</th>
<th>Oxygen gas</th>
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</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>O₂</td>
</tr>
<tr>
<td>brown in colour</td>
<td>colourless</td>
</tr>
<tr>
<td>soluble in water</td>
<td>almost insoluble in water</td>
</tr>
<tr>
<td>poisonous</td>
<td>powerful oxidant</td>
</tr>
</tbody>
</table>

1 mol of any gas occupies a volume of approximately 24 dm³ at room temperature and atmospheric pressure.

\(A_r: \text{Cs}, 133; \ \text{N}, 14.0; \ \text{O}, 16.0\)

1. Planning (P)

(a) Predict which of the equations below will represent the thermal decomposition of caesium nitrate. Place a tick against the equation of your choice.

\(4\text{CsNO}_3(s) \rightarrow 2\text{Cs}_2\text{O(s)} + 4\text{NO}_2(g) + \text{O}_2(g)\)
\(2\text{CsNO}_3(s) \rightarrow 2\text{CsNO}_2(s) + \text{O}_2(g)\)

\(\text{[1m]}\)

Use the data provided to explain your prediction.

*As the size/ionic radius of Cs⁺ is larger than that of Na⁺, Cs⁺ has a lower charge density and hence has a lower polarising power/less able to polarise the large NO₃⁻ anion than Na⁺.\(\text{[1m]}\)*

(b) You are to plan an experiment in which

- caesium nitrate is heated
• gas is collected
• the volume of gas collected is measured
• the experimental results are used in a calculation to confirm or reject your prediction

(i) Draw a diagram of the apparatus you would use in this experiment.
Your apparatus should use only standard items found in college laboratory. Show clearly how the solid will be heated, the gas collected and its volume measured.
Label each piece of apparatus used, indicating its size or capacity and state the gas or gases collected on your diagram.

[1m] Heat solid CsNO₃ in a hard glass tube or boiling tube with a stoppered delivery tube. Must indicate 'Heat' with or without arrow.

[1m] Collect gas over water into an inverted burette or a measuring cylinder; or collect gas directly into a graduated frictionless gas syringe.

[1m] Connect the two apparatus (no gas loss), label the capacity of apparatus for gas volume measurement, state the gas(es) collected in the set-up.

1. (b) (ii) Calculate the volume of gas you would expect to collect in your apparatus if 1 mol of caesium nitrate completely decomposed according to your predicted equation in (a).

Following equation 2, \(2\text{CsNO}_3 \equiv \text{O}_2\)

Expected amount of \(\text{O}_2 = \frac{1}{2} \times 1 = 0.5 \text{ mol}\)

Expected volume of \(\text{O}_2\) gas at r.t.p. = \(0.5 \times 24 \text{ dm}^3 = 12 \text{ dm}^3\) \[1m\]

OR

Following equation 1 (for direct collection), \(4\text{CsNO}_3 \equiv 4\text{NO}_2 \equiv \text{O}_2\)

Expected amount of gases (\(\text{NO}_2\) and \(\text{O}_2\)) = \(5/4 \times 1 = 1.25 \text{ mol}\)

Expected volume of \(\text{O}_2\) gas at r.t.p. = \(1.25 \times 24 \text{ dm}^3 = 30 \text{ dm}^3\)

Following equation 1 (for collection of gas over water), \(4\text{CsNO}_3 \equiv \text{O}_2\)

Expected amount of \(\text{O}_2\) gas = \(1/4 \times 1 = 0.25 \text{ mol}\)

Expected volume of \(\text{O}_2\) gas at r.t.p. = \(0.25 \times 24 \text{ dm}^3 = 6 \text{ dm}^3\)
Use your answer to (b)(ii) and the size of the apparatus selected in (b)(i) to calculate the maximum mass of CsNO$_3$ that can be used in your experiment.

Following equation 2:

Mass of 1 mol of CsNO$_3$ = 195 g

Using 100 cm$^3$ measuring cylinder or graduated gas syringe,
Maximum volume of gas collected = 100 cm$^3$
Maximum mass of CsNO$_3$ = 100/12000 x 195 = 1.625 g = $1.63$ g (1-2 d.p.)

Or, Using 50.00 cm$^3$ burette or graduated gas syringe,
Maximum volume of gas collected = 50 cm$^3$

Maximum mass of CsNO$_3$ = 50/12000 x 195 = 0.8125 g = $0.81$ g (1-2 d.p.)

OR

Following equation 1 (for direct collection of gas):

Using 100 cm$^3$ measuring cylinder or graduated gas syringe,
Maximum volume of gas collected = 100 cm$^3$
Maximum mass of CsNO$_3$ = 100/30000 x 195 = 0.65 g (1-2 d.p.)

Or, Using 50.00 cm$^3$ burette or graduated gas syringe,
Maximum volume of gas collected = 50 cm$^3$

Maximum mass of CsNO$_3$ = 50/30000 x 195 = 0.325 g = $0.33$ g (1-2 d.p.)

OR

Following equation 1 (for collection of gas over water):

Using 100 cm$^3$ measuring cylinder or graduated gas syringe,
Maximum volume of gas collected = 100 cm$^3$
Maximum mass of CsNO$_3$ = 100/6000 x 195 = 0.65 g (1-2 d.p.)

Or, Using 50.00 cm$^3$ burette or graduated gas syringe,
Maximum volume of gas collected = 50 cm$^3$

Maximum mass of CsNO$_3$ = 50/6000 x 195 = 1.625 g = $1.63$ g (1-2 d.p.)

1. (d) Outline, in a series of numbered steps, the method to be used in the experiment.

Make certain that the steps you describe are in the correct order.
You need not explain how the apparatus is assembled.
Indicate clearly how you will know when decomposed is complete.

1. Weigh accurately $*1.50$ g (should be slightly less than the maximum mass) of solid CsNO$_3$ into a dry boiling tube and record the mass.

2. Stopper the boiling tube with a delivery tube. Measure and record the initial volume reading on the gas syringe (or in the inverted measuring cylinder or burette).

3. Heat the solid sample gently at first and then strongly until a constant volume of gas is collected (or there is no movement of piston of the gas syringe or no more gas bubbles is observed in water).

4. When the whole set-up has been cooled to room temperature, measure...
and record the final volume reading on the gas syringe (or in the inverted measuring cylinder or burette) (e)

(e) What should be done when decomposition is complete to ensure that the volume of the gas measured in the apparatus is the “correct” volume.

The gas or whole set-up needs to be cooled to room temperature before measuring the final volume (or repeat the whole experiment with the same mass of solid and take the average readings) [1m]

(f) Identify a risk present in the method you have described and suggest how you would minimise this risk.

O₂ is a powerful oxidant and support burning. Remove any oxidisable material. (no mark if student commented that O₂ is flammable…..) [1m]

Or,

Only for those who chose equation 1:

NO₂ is poisonous gas. Conduct the experiment inside the fume cupboard.)

Or,

Only for those who collected the gas over water:

Potential suck back may occur and crack the hot tube. Remove the delivery tube from water when heating stops.

[Total: 12]
2. (a) (i) Write an equation for the reaction between chlorine and cold aqueous sodium hydroxide and state the type of reaction that occurs.

**Type of reaction: Disproportionation**

\[ \text{Cl}_2 (g) + 2\text{OH}^- (aq) \rightarrow \text{Cl}^- (aq) + \text{ClO}^- (aq) + \text{H}_2\text{O} (l) \]  
OR \[ \text{Cl}_2 (g) + 2\text{NaOH} (aq) \rightarrow \text{NaCl} (aq) + \text{NaClO} (aq) + \text{H}_2\text{O} (l) \]  

(ii) The resultant solution obtained in (a)(i) is heated and a further reaction occurs. Write an equation for the overall reaction between chlorine and sodium hydroxide.

**Overall eqn:** \[ 3\text{Cl}_2 (g) + 6\text{OH}^- (aq) \rightarrow 5\text{Cl}^- (aq) + \text{ClO}^- (aq) + 3\text{H}_2\text{O} (l) \]  
OR \[ 3\text{Cl}_2 (g) + 6\text{NaOH} (aq) \rightarrow 5\text{NaCl} (aq) + \text{NaClO} (aq) + 3\text{H}_2\text{O} (l) \]

(b) Chlorine forms a variety of oxides and oxoanions. A series of standard reduction potentials involving the chlorine oxoanions, in alkaline medium, are shown:

<table>
<thead>
<tr>
<th>Half-equation</th>
<th>( E/V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ClO}^- + \text{H}_2\text{O} + 2e^- = \text{Cl}^- + 2\text{OH}^- )</td>
<td>-0.89</td>
</tr>
<tr>
<td>( \text{ClO}_2^- + \text{H}_2\text{O} + 2e^- = \text{ClO}^- + 2\text{OH}^- )</td>
<td>-0.67</td>
</tr>
<tr>
<td>( \text{ClO}_3^- + \text{H}_2\text{O} + 2e^- = \text{ClO}_2^- + 2\text{OH}^- )</td>
<td>-0.33</td>
</tr>
<tr>
<td>( \text{ClO}_4^- + \text{H}_2\text{O} + 2e^- = \text{ClO}_3^- + 2\text{OH}^- )</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

Using the above data and information in the *Data Booklet*, predict the final product formed when excess zinc metal is added to an alkaline solution of chlorate(V), \( \text{ClO}_3^- \). Support your answer with \( E_{\text{cell}} \) calculations.

**Reaction of zinc metal with chlorate(V):**

\[ E_{\text{cell}}^\circ = E^{\circ} (\text{ClO}_3^- /\text{ClO}_2^-) - E^{\circ} (\text{Zn}^{2+} /\text{Zn}) \]
\[ = -0.33 - (-0.76) \]
\[ = +0.43 \text{ V} \]

Thus, Zn is able to reduce \( \text{ClO}_3^- \) to \( \text{ClO}_2^- \).

**Reaction of zinc metal with chlorate(III):**

\[ E_{\text{cell}}^\circ = E^{\circ} (\text{ClO}_2^- /\text{ClO}^-) - E^{\circ} (\text{Zn}^{2+} /\text{Zn}) \]
\[ = -0.67 - (-0.76) \]
\[ = +0.09 \text{ V} \]

Thus, Zn is able to reduce \( \text{ClO}_2^- \) to \( \text{ClO}^- \).

**Reaction of zinc metal with chlorate(I):**

\[ E_{\text{cell}}^\circ = E^{\circ} (\text{ClO}^- /\text{Cl}^-) - E^{\circ} (\text{Zn}^{2+} /\text{Zn}) \]
\[ = -0.89 - (-0.76) \]
\[ = -0.13 \text{ V} \]

Rxn between \( \text{ClO}^- \) and \( \text{Zn}^{2+} \) is not energetically feasible

OR Zn is not able to reduce \( \text{ClO}^- \) to \( \text{Cl}^- \).

Hence, zinc will be oxidised to \( \text{Zn}^{2+} \) and chlorate(V) will be reduced to chlorate(I)/\( \text{ClO}^- \).
2. (c) Chlorine dioxide, ClO₂, is a highly reactive gas that is used as a disinfectant to kill water-borne bacteria, viruses and fungi.

Draw a dot-and-cross diagram to show the arrangement of electrons in the ClO₂ molecule. Hence suggest why chlorine dioxide is highly reactive.

![Diagram of ClO₂ molecule]

Chlorine dioxide has an unpaired electron/odd number of electrons. Hence it is highly reactive. [1m]

(d) Despite having similar relative molecular mass, the boiling point of chlorine is –34 °C and that of chlorine dioxide is 11 °C.

Give an explanation to account for this large difference in boiling points.

A larger amount of energy is required to break the stronger permanent dipole-permanent dipole interactions between the ClO₂ molecules than that to break the weaker van der Waals' forces between the Cl₂ molecules. [2m]

[1m] for correct intermolecular forces identified bet. molecules

[1m] for pd-pd stronger than vdw (must compare bet. Correct I.M.F)

[Total: 11]
3. (a) Aluminium is obtained by electrolysis of molten $\text{Al}_2\text{O}_3$ using inert electrodes.

(i) Give ion-electron equations, with state symbols, for the electrode processes:

at the cathode: \[ \text{Al}^{3+}(l) + 3e^- \rightarrow \text{Al}(l) \] \[1\text{m}\]

at the anode: \[ \text{O}_2^-(l) \rightarrow \frac{1}{2}\text{O}_2(g) + 2e^- \] \[1\text{m}\]

s.s. required, reject "=" for wrong or missing s.s. AND half-eqns are correct: 1m only

(ii) Calculate the mass of aluminium produced when a current of 8 A is passed for 100 minutes through the molten $\text{Al}_2\text{O}_3$.

Amount of $e^-$ transferred = $48000/96500 = 0.497 \text{ mol}$ (ignore sf) \[1\text{m}\]

Mass of Al produced = $0.497/3 \times 27.0 = 4.47 \text{ g}$ \[2\text{m}\]

(1st mark ecf from (a)(i) for mole ratio)

(1 - 3 sf for final answer (2nd mark) + correct units)

(b) The enthalpy change of formation of $\text{Al}_2\text{O}_3$ can be calculated from a Born-Haber cycle.

Construct the Born-Haber cycle for the formation of $\text{Al}_2\text{O}_3$, using the following data and relevant data from the Data Booklet. Hence, calculate the enthalpy change of formation of $\text{Al}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Enthalpy change</th>
<th>$\Delta H$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>of atomisation</td>
<td>+644</td>
</tr>
<tr>
<td>of Al</td>
<td>+702</td>
</tr>
<tr>
<td>of $\text{O}_2$</td>
<td>-13311</td>
</tr>
</tbody>
</table>

\[ \text{2 Al}^{3+}(g) + 3 \text{O}^2-(g) \rightarrow \text{Al}_2\text{O}_3(s) \] \[1\text{m}\] for balanced $\text{Al}_2\text{O}_3(s)$ formation equation

$\Delta H_f(\text{Al}_2\text{O}_3(s)) = 2(644) + 2(5137) + (3/2(496)) + 3(702) - 13311 = +1101 \text{ kJ mol}^{-1}$

[1m] for final answer (exact/3 sf), no ecf

Award each (,) only if
- equation is balanced
- state symbol of reactants and products are stated correctly
- process is labelled with correct $\Delta H$ value or symbol (ignore "=" sign)
- $\Delta H_f$ can be accepted (infer to question)
3. (c) Aluminium chloride exists in two different forms in the vapour state and the following conversion exists between them:

\[ \text{Al}_2\text{Cl}_6(\text{g}) = 2\text{AlCl}_3(\text{g}) \]

The conversion was studied using a fixed amount of Al\(_2\)Cl\(_6\) in a reaction vessel. At different times during the experiment, changes were made to the conditions in the reaction vessel. The change in the concentrations in the equilibrium mixture with time is given by the graph below.

(i) Suggest the changes that caused the equilibrium shifts at time:

- **T\(_1\)**: decrease in total volume of reaction vessel/increase in pressure [1m]
- **T\(_2\)**: addition of/increase in concentration/(partial) pressure of Al\(_2\)Cl\(_6\) (OWTTE) [1m]

Reject “decrease in volume of (specific gas)”, accept “decrease in volume of gases”…….. Same for suggestions in pressure

Accept wrongly-written formula of Al\(_2\)Cl\(_6\) (Benefit Of Doubt), and reject “AlCl\(_3\)”
(ii) Explain whether the conversion of $\text{Al}_2\text{Cl}_6$ to $\text{AlCl}_3$ is expected to be exothermic or endothermic.

It is expected to be endothermic. $[1\text{m}]$

This is because there is breaking of (dative covalent) bonding $[1\text{m}]$ between the Cl and Al atoms.

Accept:

"break molecule/ dimer"

3. (c) (iii) Sketch on the same axes of the given graph on page 9, the changes in the concentration of $\text{Al}_2\text{Cl}_6$ and $\text{AlCl}_3$ when the mixture was cooled at time $T_3$. Explain your answer with reference to your conclusion made in (c)(ii).

When temperature is lowered, the equilibrium position will shift to $[1\text{m}]$ the left, favouring the exothermic reaction, so as to increase temperature.

OR

When temperature is lowered, it favours the backward exothermic reaction, so as to increase temperature.

Hence, yield of $\text{Al}_2\text{Cl}_6$ increases and yield of $\text{AlCl}_3$ decreases.

Ecf from c(ii)

(iv) At a total pressure of 1 atm and 673 K, $\text{Al}_2\text{Cl}_6$ was 30% dissociated into $\text{AlCl}_3$.

Calculate the equilibrium constant, $K_p$, including its units, at 673 K.

Let $p$ be the initial partial pressure of $\text{Al}_2\text{Cl}_6$ (g).

$$\text{Al}_2\text{Cl}_6(g) = 2\text{AlCl}_3(g)$$

Initial partial pressure/ atm $p$
Eqm partial pressure/ atm $0.7p$ $0.6p$

$0.7p + 0.6p = 1\text{ atm}$

$p = 0.769\text{ atm}$

At eqm, $P_{\text{Al}_2\text{Cl}_6} = 0.7 \times 0.769 = 0.538\text{ atm}$ $[1\text{m}]$ ignore sf

$P_{\text{AlCl}_3} = 0.6 \times 0.769 = 0.462\text{ atm} (0.461\text{ atm})$ $[1\text{m}]$ ignore sf

$$K_p = \frac{0.462^2}{0.538} [1\text{m}]$$

for correct substitution (ecf from p.p.) in correct $K_p$ expression

$= 0.397\text{ atm} (0.395\text{ atm or 0.396\text{ atm})} [1\text{m}]$ correct answers + units + 3 sf (ecf only for correct $K_p$ expression )
4. (a) Copper is a transition element that forms a rich variety of compounds with varying oxidation states.

Aqueous copper(II) nitrate, \( \text{Cu(NO}_3\text{)}_2 \) is a blue solution which can undergo the following reactions.

\[
\begin{align*}
\text{Cu(NO}_3\text{)}_2(\text{aq}) + \text{SO}_2(\text{aq}) & \rightarrow \text{Cu}_2\text{O}(s) + \text{D} \\
\text{B} + \text{conc } \text{NH}_3(\text{aq}) & \Rightarrow \text{E} \\
\text{C} & \Rightarrow \text{colourless solution}
\end{align*}
\]

B, C and E contain complex ions of copper. Both compound D and complex ion E contain copper and chlorine only.

(i) What are the formulae of the compound A and of the cation present in B?

A: \( \text{Cu(OH)}_2 \)  B: \( [\text{Cu(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^{2+} \)  [2m]

(ii) Suggest a balanced equation for the formation of B from A.

\[
\text{Cu(OH)}_2(s) + 4\text{NH}_3(\text{aq}) + 2\text{H}_2\text{O(l)} \rightarrow [\text{Cu(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^{2+} + 2\text{OH}^-(\text{aq})
\]

s.s not required  [1m]

(iii) State the role of \( \text{SO}_2 \) in the conversion of \( \text{Cu(NO}_3\text{)}_2 \) to \( \text{Cu}_2\text{O} \).

Reducing agent/Reductant (mark for meaning)  [1m]

(iv) The composition of complex ion C by mass is Cu, 65.1%, N, 28.7%, H, 6.2%.

Use the data to determine the empirical formula and identity of complex ion C.

<table>
<thead>
<tr>
<th>( \text{Cu} )</th>
<th>( \text{N} )</th>
<th>( \text{H} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.1</td>
<td>28.7</td>
<td>6.2</td>
</tr>
<tr>
<td>63.5</td>
<td>14.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.025</td>
<td>2.05</td>
<td>6.2</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

Working for empirical formula must be shown

Empirical Formula = \( \text{CuN}_2\text{H}_6 \) or \( [\text{Cu(NH}_3\text{)}_2]^{2+} \) (ignore charge if its given)  [1m]

Identity: \( [\text{Cu(NH}_3\text{)}_2]^{2+} \)  [1m]
(v) The oxidation number of copper in compound D and complex ion E are the same as that in compound C, and both D and E contain copper and chlorine only.

Suggest the formulae of D and E.

D: CuCl  
E: CuCl₂⁻  

4. (b) Copper forms a very useful group of organic compounds known as Gilman reagents.

2CH₃Li + CuI → (CH₃)₂CuLi + LiI  

methyllithium  

Gilman reagent

Alkyl halides (except fluorides) undergo nucleophilic substitution with Gilman reagents.

CH₃CH₂Cl + (CH₃)₂CuLi → CH₃CH₂CH₃ + CH₃Cu + LiCl  

ethyl chloride

(i) Suggest the structural formula of the final organic product formed when phenyllithium, and bromoethane are used in a similar two-step process.

(ii) Gilman reagents can also react with acyl chlorides to form ketones. An example is shown below:

It is observed that the reaction with acyl chlorides takes place much more readily than that with alkyl chlorides. Explain why this is so.

It is because the carbonyl C atom in >C=O of acyl chlorides (the electron-deficient C atom must be clearly specified in the answer) is more/highly electron deficient, due to it being bonded to 2 electronegative/electron-withdrawing atoms, O and Cl. Hence it is more susceptible to nucleophilic attacks.

Or bonded to one more electronegative O atom

OR the trigonal planar sp² hybridised C in -COCl experience less steric hindrance than the tetrahedral sp³ hybridised C in alkyl chloride.

[1m] correct sp² and sp³ assignment (or no. of alkyl groups)  
[1m] steric hindrance comparison
5. (a) The Green Fluorescent Protein (GFP) is a protein that can be isolated from the jellyfish, *Aequorea victoria*, and it can exhibit bright green fluorescence when exposed to ultraviolet light. The chromophore is the section of the GFP that fluoresces and contains the amino acid sequence *ser-tyr-gly*.

![Amino Acid Structure](image)

(i) Draw the structure of this section of the GFP at pH 14.

![Structure at pH 14](image)

[1m] for correct amino acid sequence and fragment of protein drawing

[1m] for acid-base reaction with phenol, forming phenoxide

(ecf 2nd mark: if tripeptide is drawn and must accompany by acid-base reaction with any acidic groups: both phenol and COOH)
(ii) GFP has a beta barrel structure, consisting of one beta-pleated sheet and alpha-helices running through the centre of the barrel structure.

Sketch a labelled diagram to show how two groups in a protein could be involved in maintaining the structure of the beta-pleated sheet.

[1m] correct structure of beta-pleated sheet, showing C=O and N-H groups involved in forming the stabilising forces. N and C must be on the polypeptide backbone, strands of polypeptide chain must be labelled.

[1m] at least 1 hydrogen bond correctly drawn Reject "H-bond".

Accept anti-parallel/parallel diagrams and accept zigzag displayed

Accept "polypeptide strand" in place of "a strand of polypeptide chain"

5. (b) A venomous jellyfish has tentacles containing 'stinging cells' that inject venom into the skin of a victim. The venom is made up of a diverse variety of proteins and polypeptides capable of inflicting pain and swelling.

The most common first-aid treatment of jellyfish stings is to get the victim out of water, scrape off any attached tentacles with a hard object and rinse the affected area with hot seawater to deactivate the venom.

Explain how the application of heat is effective in treating jellyfish stings.

Heat will disrupt the weak interactions: van der Waals' forces in the tertiary and quaternary structures and hydrogen bonds in the secondary, tertiary and quaternary structures of the proteins in the venom (and the nematocysts).

This alters the conformation/(3D) shape of the proteins which causes the polypeptide chain folds differently/this denatures the protein

[1m] : at least one correct R group interaction + structure disrupted

[2m] : for everything stated above("without any other extra R group interaction"

(c) Paracetamol is usually prescribed to the casualty to reduce the pain from the jellyfish sting.

Paracetamol

A student suggested that paracetamol can be synthesised from phenol, via a three-step reaction sequence as proposed below.
(i) What types of reactions take place in Step I, II and III?

Step I: Electrophilic Substitution [1m]
Step II: Reduction [1m]
Step III: Nucleophilic Substitution/Amide formation/Condensation [1m]

No spelling mistake allowed

5. (c) (ii) State the reagents and conditions needed for Step I and II.

Step I: Dilute HNO\(_3\) (aq) [1m] reject "aqueous HNO\(_3\)", "heat"

Step II: Concentrated HCl(aq), Sn, heat [1m], followed by controlled amount of NaOH(aq) [1m]

Reject "HCl(aq)"

(iii) In actual practice, 4-aminophenol is used instead as the starting material and only Step III is carried out.

Given that both phenol and 4-aminophenol are easily available, suggest a reason why phenol is not chosen to be the starting material to prepare paracetamol in actual practice.

This is because 2 isomers will be produced (2-aminophenol & 4-aminophenol)/mixture of isomers will be formed [1m]

and separation of isomers/separation of 4-aminophenol from 2-aminophenol is not easy/extra step for separation to carry out [7]

Thus, resulting in poor yield of product.

[Total: 13]
6. Lorcaserin (Trade name: Belviq®) is a weight-loss drug developed by Arena Pharmaceuticals in San Diego and is recently approved by the US Food and Drug Administration in June 2012 for use in the treatment of obesity for adults.

(a) Draw the structures of the organic compounds formed when Lorcaserin is treated with the following reagents.

(i) ethanoyl chloride

(ii) excess CH₃Cl

(b) An isomer of lorcaserin (Compound Y) is shown below.

Suggest a chemical test (stating reagents and observations) that would distinguish Compound Y from lorcaserin.
Test: 1. Add aqueous NaOH/KOH to each compound separately and heat.
2. Add (aqueous) dilute HNO₃ to acidify the resulting mixtures
   OR Add (aqueous) dilute HNO₃ to the resulting mixtures to remove excess NaOH.
   OR Add EXCESS (aqueous) dilute HNO₃ to the resulting mixtures
3. Then, add (aqueous) AgNO₃ to the resulting mixtures.

White precipitate / ppt. of AgCl is formed with Compound Y, but not with lorcaserin. [1m] mark observations only when reagents (aq. NaOH and aq. AgNO₃) are correct

(c) \[
\text{\includegraphics[width=0.5\textwidth]{structure.png}}
\text{\small phenylamine}
\]

Suggest and explain how the basicity of lorcaserin might compare with that of phenylamine.

Phenylamine will be less basic/a weaker base than lorcaserin. [1m]
The p-p orbital overlap in phenylamine results in delocalisation of the lone pair of electrons on N atom into the benzene ring, making the lone pair less available for protonation, hence phenylamine is a weaker base. [2]

Reject “.. making N less available…”
JURONG JUNIOR COLLEGE  
JC 2 PRELIMINARY EXAMINATION  
Higher 2

CANDIDATE NAME

CLASS EXAM INDEX NUMBER

CHEMISTRY 9647/03
Paper 3 Free Response

27 August 2012
2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper  
Data Booklet

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.

Begin your answer to each new question on a fresh sheet of writing paper. 
At the end of the examination, arrange the answers in numerical order and attach the cover sheet on top.

A Data Booklet is provided. Do not write anything on the Data Booklet.

You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of 10 printed pages and 0 blank pages.  

[Turn over
Answer any four questions.

1. **Use of the Data Booklet is relevant to the question.**

   (a) Hydrogen can play an important role in the future by replacing the petroleum currently used in automobiles. For example, electric cars can be powered by hydrogen-oxygen fuel cells, with its hydrogen fuel kept at extremely high pressures in thick-walled storage tanks.

      (i) State the half equations for the reactions occurring at each of the electrodes in a hydrogen-oxygen fuel cell operating under acidic conditions.

      (ii) Describe one disadvantage of using a hydrogen-oxygen fuel cell over internal combustion engines in automobiles.

      (iii) A quantity of hydrogen gas is confined in a chamber of constant volume. When the chamber is placed at a temperature of 20°C, the pressure of the gas is $3.29 \times 10^5$ Pa.

         What will be the pressure of the gas, in Pa, if the chamber is now placed in a water bath of boiling water to simulate the operating temperature of a certain automobile?

         [5]

   (b) A student designed an ion-specific probe to determine the concentration of $H^+$ ions in solution. He connected a hydrogen electrode to a calomel reference electrode, which comprises a paste of mercury(I) chloride and mercury in a saturated chloride electrolyte solution. The porous glass frit acts as a salt bridge.

      ![Diagram of pH meter](image)

      The hydrogen electrode, sensitive to $H^+$ ion concentration, is the measuring electrode. Therefore, this galvanic cell acts as a pH meter.

      When both electrodes are in contact with the test solution, an electric current flows through the wire and mercury(I) chloride reacts to form liquid mercury and chloride ion at the reference electrode.

      Under standard conditions, the $E^\text{cell}$ of the pH meter is +0.28 V.

      (i) Construct the half equation for the reaction occurring at the reference electrode.

      (ii) Hence write an overall balanced equation for the pH meter.

      (iii) Explain why the cell potential would increase when the pH meter is placed in a solution of a higher pH.

      [3]
1. (c) The student used his probe to analyse a sample of 0.104 mol dm\(^{-3}\) solution of mandelic acid, a bitter almond extract that is used as antibacterial treatment or an oral antibiotic. The student obtained a cell potential reading, \(E_{\text{cell}}\), of +0.41 V.

(i) The *Nerst equation* can be used to calculate the concentration of \(H^+\) ions detected by the probe:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log_{10} \left( \frac{[H^+]^2 [Cl^-]^2}{P_{H_2}} \right)
\]

where \(n\) is the number of moles of electrons transferred in the overall reaction, 
[H+] is the concentration of hydrogen ions detected 
[Cl\(^-\)] is the concentration of Cl\(^-\) ions at the cathode. 
\(P_{H_2}\) is the pressure, in atm, of hydrogen gas passed into the probe,

Assuming that the concentration of Cl\(^-\) is constant at 1 mol dm\(^{-3}\), use the *Nerst equation* to calculate the concentration of \(H^+\) ions in the solution and the pH of the solution.

(ii) Hence calculate the value of acid dissociation constant, \(K_a\), of mandelic acid.

(iii) How would you expect the value of \(K_a\) of mandelic acid to compare with that of phenylacetic acid? Explain your answer.

\[
\begin{align*}
\text{mandelic acid} & : \text{CH(OH)COOH} \\
\text{phenylacetic acid} & : \text{CH_2COOH}
\end{align*}
\]

(iv) Suggest a chemical test (stating reagents and observations) that would distinguish mandelic acid from phenylacetic acid.

(v) Suggest a synthetic route to form mandelic acid from starting material phenylmethanol.

\[
\begin{align*}
\text{phenylmethanol} & \rightarrow \text{CH_2OH} \\
& \rightarrow \text{CH(OH)COOH}
\end{align*}
\]

[Total: 20]
2. (a) Peppermint oil, also known as brandy mint and balm mint, is extracted from mentha piperita of the Labiatae family. Menthol and menthone are the two main components of peppermint oil.

Menthone can be reduced to menthol, which can be easily dehydrated to give 3-menthene as the major product.

Both menthone and menthol exhibit **stereoisomerism** but 3-menthene has no stereoisomer.

(i) Which compound, menthone or menthol, is expected to be more volatile? Give your reasoning.

(ii) Menthol is insoluble in water but is freely soluble in ethers and alcohols. Explain why menthol is insoluble in water.

(iii) Suggest the reagents and conditions required for step 1 and step 2.

(iv) An alkene M is also formed in step 2 in a much lower proportion than 3-menthene. Suggest the structure for M and give the organic product when M is heated with concentrated acidified KMnO₄(aq).

(v) When HCl(g) is bubbled through a solution of 3-menthene, an addition reaction occurs via a 2-stage mechanism.

Suggest the mechanism of this reaction by means of a diagram. Include all whole or partial charges, and represent the movements of electron pairs by curly arrows.

(vi) What do you understand by the term **stereoisomerism**? Explain why 3-menthene does not exhibit any stereoisomerism.

(b) Magnesium nitrate is a hygroscopic salt. In air, it readily forms a hydrate with the formula Mg(NO₃)₂.6H₂O. Barium nitrate, however, does not form any hydrate in air. Both nitrates are soluble in water. Like all soluble barium compounds, barium nitrate is toxic by ingestion. Solutions of sulfate salts such as Epsom salt may be given as first aid for barium poisoning.

(i) Suggest reason(s) why magnesium nitrate readily forms a hydrate whereas barium nitrate does not.

(ii) Describe what you would see when a sample of white crystals of Mg(NO₃)₂.6H₂O is heated in an open test-tube. Write a balanced equation for the reaction.

(iii) Explain why barium nitrate decomposes at a higher temperature than anhydrous magnesium nitrate.
2. (b) (iv) When water is added to the solid residue after barium nitrate has been heated, a colourless solution is obtained. When water is added to the solid residue after magnesium nitrate has been heated, a white suspension is obtained instead. Explain these observations.

(v) Suggest how administering of Epsom salt solution, which contains magnesium sulfate, helps to treat barium poisoning.

[8]

[Total: 20]
3. (a) Amino acids, such as alanine and phenylalanine, are essential building blocks for making proteins. They can be synthesised by a general 2-step reaction as exemplified below:

\[
\text{RCH}_2\text{CO}_2\text{H} \xrightarrow{\text{trace amount of phosphorus}} \text{E} \xrightarrow{\text{excess NH}_3} \text{RCH(NH}_2\text{)CO}_2\text{H}
\]

(i) Suggest the structure of the intermediate organic compound E.

(ii) What type of reaction is occurring in step I?

(iii) Phenylalanine is found naturally in the breast milk of mammals. It is used in the manufacture of food and drink products and is sold as a nutritional supplement. Suggest the structural formula of the starting material needed to synthesise phenylalanine by the above 2-step reaction.

(b) Solutions of amino acids are buffers important in maintaining optimal pH in our body. A food chemist needs to ensure that all infant manufactured food products containing phenylalanine and its salt, simulates the exact composition of human breast milk.

(i) Draw the structural formula of the zwitterionic form of phenylalanine. Hence suggest, with the aid of an equation, how phenylalanine behaves as a buffer when small amount of base is added.

(ii) In order to investigate the composition of a buffer solution of pH 7.4 containing phenylalanine and its salt, the food chemist titrated a sample of this buffer solution with NaOH(aq) and obtained the titration curve below.

The buffer solution operates at its maximum capacity when 39 cm³ of NaOH(aq) is added and the equivalence point is attained when 80 cm³ of NaOH(aq) is added. Show that the ratio of [phenylalanine] : [salt of phenylalanine] is 40 : 1 in the original sample of buffer solution.

(iii) Hence determine the pH value at the maximum buffering capacity of the buffer containing phenylalanine and its salt.
3. (c) Chymotrypsin is a digestive enzyme produced by the pancreas to aid digestion in the small intestine.

(i) A small peptide \( G \) was hydrolysed by chymotrypsin and gave three different amino acids according to the following reaction.

\[
\begin{align*}
\text{NH}_2 & \quad \text{COOH} \\ tyrosine & \quad M_r = 181 \\ \text{OH} \quad + \\
\text{NH}_2 & \quad \text{COOH} \\ tryptophan & \quad M_r = 204 \\
\text{NH} & \quad \text{NH}_2 \\ phenylalanine & \quad M_r = 165 \\
\end{align*}
\]

Calculate the \( M_r \) of peptide \( G \).

(ii) During the hydrolysis of peptide \( G \) by chymotrypsin, the tyrosine residue of peptide \( G \) must first bind to the active site on chymotrypsin.

![Diagram](active_site_chymotrypsin.png)

Copy this diagram onto your answer script and use it to illustrate how one tyrosine residue of peptide \( G \) can bind to the active site on chymotrypsin. Label the type(s) of interaction that could be involved.

(iii) Vomiting is one of the immediate and observable effects of excessive alcohol consumption as the presence of alcohol inhibits the digestive activity of chymotrypsin.

Suggest how the consumption of alcohol inhibits the digestive activity of chymotrypsin.

5

(d) Compound \( H \), an isomer of phenylalanine, with molecular formula \( C_9H_{11}NO_2 \), is a basic compound. When \( H \) is heated under reflux with NaOH(aq) followed by careful neutralisation, compound \( J \) and ethanol are formed. Compound \( J \) reacts with aqueous sodium carbonate and also dissolves in HCl(aq). 0.10 mol of compound \( J \) reacts completely with 0.20 mol of aqueous bromine to give a white precipitate.

Suggest the structures of compounds \( H \) and \( J \) and explain all the reactions involved.

6

[Total: 20]
4. Under the influence of a dilute base or acid, two molecules of an aldehyde or a ketone may combine in a process known as aldol reaction. An example of an aldol reaction between ethanal molecules in dilute alkaline solution is shown below.

\[
2 \text{CH}_3\text{CHO} + \text{OH}^- \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{CHO} \quad \Delta H < 0
\]

A chemist studied the kinetics of the above reaction at 298 K and obtained the following table of results.

<table>
<thead>
<tr>
<th>experiment number</th>
<th>initial [CH$_3$CHO] / mol dm$^{-3}$</th>
<th>initial [OH$^-$] / mol dm$^{-3}$</th>
<th>initial rate / mol dm$^{-3}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.0110</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.15</td>
<td>0.0165</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>0.20</td>
<td>0.0660</td>
</tr>
</tbody>
</table>

(a) (i) Use these data to deduce the order of reaction with respect to both ethanal and OH$^-$, showing how you arrived at your answers.

Hence write the rate equation for the reaction and calculate the value of the rate constant, stating its units.

(iii) The half-life of ethanal in experiment 1 is 9.0 s. Predict the half-life of ethanal in experiment 3.

[6]

(b) The following three-step mechanism has been proposed for the reaction between ethanal molecules.

Step 1: \[ \text{CH}_3\text{C}^- + \text{OH}^- \rightarrow \text{CH}_3\text{C}^- \text{H}
\]

Step 2: \[ \text{CH}_3\text{C}^- \rightarrow \text{CH}_3\text{C}^- \text{H}
\]

Step 3: \[ \text{CH}_3\text{C}^- \text{H} + \text{H}_2\text{O} \rightarrow \text{OH}^- \text{H}
\]

(i) Using your answers in (a), predict which of the three steps is the rate-determining step. Explain your answer.

(ii) Sketch a labelled energy profile diagram for the above proposed mechanism. You are only required to label the reactants, products and the activation energy of forward reaction on your diagram.
4. **(b)** (iii) Name the type of reaction occurring in Step 1.

(iv) Use a diagram to show how the product in Step 2 is formed. In your diagram, include all whole or partial charges, and represent the movements of electron pairs by curly arrows.

Hence explain why the overall reaction produces a racemic mixture of 3-hydroxybutanal.

[7]

(c) In a similar three-step mechanism mentioned in (b), one molecule of 3-hydroxybutanal can react further with one molecule of ethanal to give a mixture of products with six carbon atoms each.

Deduce the structural formula of **two** possible products from this reaction.

[2]

(d) The aldol reaction is a powerful means of forming carbon-carbon bonds and it combines simple molecules to give a more complex one. Copper(I) and copper(II) complexes have been developed successfully to catalyse some aldol reactions.

(i) Write the electronic configuration of copper(I) and copper(II) ions using the s,p,d,f notation.

(ii) Explain why complexes of copper(II) are usually coloured and those of copper(I) are colourless.

[5]

[Total: 20]
5. The halogens and their compounds are useful laboratory reagents.

(a) Iodine trichloride, \( \text{ICl}_3 \), is a bright yellow solid formed by reaction of iodine and chlorine.

(i) Draw and suggest the shape of \( \text{ICl}_3 \) molecule. Include all lone pairs in your diagram.

(ii) Unlike \( \text{ICl}_3 \), the compound \( \text{FICl}_3 \) does not exist. Suggest a reason for this difference.

(iii) Given the following enthalpy changes,

\[
\begin{align*}
\text{I}_2(\text{s}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{ICl}(\text{s}) & \quad \Delta H^\circ = +14 \text{ kJ mol}^{-1} \\
2\text{ICl}(\text{s}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{ICl}_3(\text{s}) & \quad \Delta H^\circ = -88 \text{ kJ mol}^{-1}
\end{align*}
\]

construct an energy cycle to calculate the standard enthalpy change of formation of solid iodine trichloride.

(iv) The standard entropy change of formation of solid iodine trichloride is \(-225 \text{ J mol}^{-1} \text{ K}^{-1}\). Explain why the formation of solid iodine trichloride has a negative entropy change.

(v) Explain why the formation of solid iodine trichloride is spontaneous at low temperatures.

(vi) Predict whether the reaction is spontaneous at 298 K.

(b) Silver chloride and silver iodide are sparingly soluble in water at room temperature. Their solubility products at 298K are given below.

<table>
<thead>
<tr>
<th>Silver halide</th>
<th>Solubility product, ( K_{sp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>( 1.77 \times 10^{-10} )</td>
</tr>
<tr>
<td>AgI</td>
<td>( 8.52 \times 10^{-17} )</td>
</tr>
</tbody>
</table>

(i) Write an expression for the solubility product, \( K_{sp} \), of silver iodide and hence calculate [Ag⁺(aq)] in a saturated aqueous solution of silver iodide at 298K.

(ii) With the aid of relevant equations, suggest explanations for the following observations:

When aqueous silver nitrate is added to aqueous sodium chloride, a white precipitate is formed which is soluble in excess aqueous ammonia, giving a colourless solution.

When aqueous sodium iodide is added to the resultant solution, a yellow precipitate is formed immediately.

(c) Solid halides such as sodium bromide or sodium chloride are commonly used in situ with concentrated sulfuric acid to produce alkyl halides from alcohols.

(i) Describe what would be observed when concentrated sulfuric acid is added to separate portions of NaCl(s) and NaBr(s). Write an equation for any reaction that occurs and explain the differences in their reactions.

(ii) Suggest why sodium iodide is not used in situ with concentrated sulfuric acid to produce alkyl iodide from alcohol.
Mark Scheme for 2012 JC2 Preliminary Examination Paper 3
Minus [1m] overall for P3 for lack of 3 sf. Indicate on Cover page when penalised.

General Comments for Q1
Many candidates probably left this question as their last attempted question, as they ran out of time and thus
(i) did not manage complete answers or
(ii) did not have enough time to calculate their answers or
(iii) made a lot of careless mistakes.
Marks for this question varies greatly from 4-5 to 17-20.

1. (a) (i) Anode: $2\text{H}_2(g) \rightarrow 4\text{H}^+(aq) + 4e^-$  [1m] s.s not penalised
Cathode: $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$  [1m] s.s. not penalised

- Small handful of candidates still make the usual errors:
  - Use of reversible arrows
  - Use of [O] and [R]
  - Wrong electrodes or no labelling of electrodes
- A few wrote equations for alkaline medium
- A few chose half eqn for $\text{H}_2\text{O}_2$ instead.

(ii) Requires a heavy storage tank of $\text{H}_2$ gas on board a car / takes up more storage space / must be kept under high pressure  [1m] for any relevant ans. Do not accept: "explosive" only
- Difficult to refill $\text{H}_2$ fuel due to lack of infrastructure
- $\text{H}_2$ gas is MORE explosive than fuels in internal combustion engines.
- More expensive due to the expensive catalysts etc
- Explosive at high temperatures

Common Mistakes:
- A few listed advantages instead
- A small handful of candidates did not understand what to compare e.g. thinking that the hydrogen-oxygen fuel cell is used together with the internal combustion engine or to supply electricity to the internal combustion engine.

(iii) Using $\frac{P_1}{T_1} = \frac{P_2}{T_2}$, $P_1 = \left(\frac{P_1}{T_2}\right)T_1 = \left(\frac{3.29 \times 10^3}{293}\right)373 = 4.19 \times 10^4 \text{ Pa}$  [1m]: correct ans, 3 s.f.
- Many candidates solved using PV=nRT, which is a longer method.

Common Mistakes:
- Wrong units for Temperature
- Some gave a qualitative answer only, with no calculation.
1. **(b)**

(i) Reference electrode (cathode):

\[ \text{Hg}_2Cl_2(s) + 2e^- \rightarrow 2\text{Hg}(l) + 2\text{Cl}^- (aq) \] [1m full arrow]

(ii) Measuring electrode (anode): \( \text{H}_2(g) \rightarrow 2\text{H}^+ (aq) + 2e^- \)

Overall: \( \text{Hg}_2\text{Cl}_2(s) + \text{H}_2(g) \rightarrow 2\text{Hg}(l) + 2\text{Cl}^- (aq) + 2\text{H}^+ (aq) \) [1m full arrow]

**Common Mistakes for (i) and (ii):**
- Did not seem to understand Qn or were simply confused with ‘Hg’ and ‘H’ e.g.
  - Mixed up ‘Hg’ with ‘H2’ or ‘Hg’ with ‘H’!
  - wrote reduction of chlorine to chloride only
  - wrote eqns for reaction between hydrogen and chlorine only
- Did not notice formula of “Hg₂Cl₂”.
- Did not check their equation for balancing of charges.

(iii) At a higher pH, there is lower \([H^+]\),

- equilibrium in \( 2\text{H}^+ (aq) + 2e^- = \text{H}_2(g) \) shifts to the left (OR eqm shifts to favour oxidation of \( \text{H}_2 \)) and thus
- \( E(\text{H}^+/\text{H}_2) \) becomes (more) negative.

Thus \( E_{\text{cell}} \) becomes more positive.

**Common Mistakes:**
- Thought “higher pH” = “higher \([H^+]\)”
- Did not write reversible arrow for the eqm equation.
- Thought that a reaction between \( \text{H}^+ \) & \( \text{Cl}^- \) will result in an eqm shift!
- Writing "E value" to represent \( E(\text{H}^+/\text{H}_2) \).

(c) **(i)**

\[
E = E^\circ + \frac{0.0592 \log\left(\frac{[\text{H}^+]^2}{P_{\text{H}_2}}\right)}{n}
\]

\[0.41 = 0.28 + \frac{0.0592 \log([H^+])}{2} \]

\[0.41 = 0.28 + \frac{0.0592 \times 2\log[H^+]}{2}\]

\[\log[H^+] = \frac{0.13}{0.0592}\]

Solving, \([H^+] = 6.37 \times 10^{-3} \) (or \(6.38 \times 10^{-3}\)) mol dm⁻³ \[1m 3sf, ecf\]

\[\text{pH} = -\log(6.37 \times 10^{-3}) = 2.20\] \[1m 3sf, ecf\]

- About half of the candidates (who attempted this part) are able to solve and calculate \([H^+]\), using whatever values substituted.

**Common Mistakes:**
- Substituted \(n = \) amount of acid used (or any other strange number)
- Substituted their answer in (a)(iii) for \( P_{\text{H}_2} \)
- Substituted “1.01 \times 10^6” for \( P_{\text{H}_2} \)
1. (c) (ii)

\[ K_a = \frac{[H^+]^2}{c - [H^+]} = (6.37 \times 10^{-3})^2 = 3.90 \times 10^{-4} \text{ mol dm}^{-3} \]

OR

\[ K_a = \frac{[H^+]^2}{c - [H^+]} = (6.37 \times 10^{-3})^2 = 4.15 \times 10^{-4} \text{ mol dm}^{-3} \]

(OR \(4.16 \times 10^{-4} \text{ mol dm}^{-3}\))

If students get \([H^+] = 6.38 \times 10^{-3} \text{ mol dm}^{-3}\),

\[ K_a = \frac{[H^+]^2}{c - [H^+]} = (6.38 \times 10^{-3})^2 = 4.17 \times 10^{-4} \text{ mol dm}^{-3} \]

\[ K_a = \frac{[H^+]^2}{c - [H^+]} = (6.38 \times 10^{-3})^2 = 3.91 \times 10^{-4} \text{ mol dm}^{-3} \]

- Most candidates earned the ecf marks.
- Most candidates (who got this part correct) solved for \(K_a\) using \(K_a = \frac{[H^+]^2}{c - [H^+]}\).
- A few students got all previous calculations correct but were stuck at \(K_a\). Perhaps they did not notice that mandelic acid is a monobasic acid.

(iii) Mandelic acid, being the stronger acid, has a larger \(K_a\) value.

The electron withdrawing O atom of the –OH group disperses the negative charge and stabilises \(\text{CH(OH)COO}^-\), making \(\text{CH(OH)COO}^-\) more stable than \(\text{CH}_2\text{COO}^-\).

**Common Mistakes:**
- Electron donating –OH group
- Weaker acid has a larger \(K_a\)
- ‘stabilising negative charge’
- ‘mandelic anion’ or ‘anion’ or ‘–COO’ anion’
- Using ‘it’ to describe the acid, the anion, the –OH group (basically everything!) and thus making answers vague/unclear/misleading.

(iv) Add acidified \(K_2\text{Cr}_2\text{O}_7\) to each of the unknowns and heat in a hot water bath. (Accept “hot acidified \(K_2\text{Cr}_2\text{O}_7\))

- Mandelic acid turns orange \(K_2\text{Cr}_2\text{O}_7\) green but not phenylacetic acid.

**Common Mistakes:**
- Using \(\text{KMnO}_4\)
- Using \(\text{KMnO}_4\) then Brady’s reagent
- Using \(\text{KMnO}_4\) (or \(K_2\text{Cr}_2\text{O}_7\)), followed by Tollens’ reagent.
- Using \(\text{PCl}_5\)
1. (c) (v)

Acidified K₂Cr₂O₇ (aq), distill (, )

\[
\text{CH}_2\text{OH} \rightarrow \text{CHO} \rightarrow \text{CH(OH)CN}
\]

HCN, trace amt of NaCN/base (, )

dilute H₂SO₄, heat
or H₂SO₄(aq), heat
or dilute HCl, heat
or HCl(aq), heat (, )

OR the less recommended way:

Limited Cl₂, uv light (, )

\[
\text{CH}_2\text{OH} \rightarrow \text{CHOH} \rightarrow \text{CH(OH)COOH}
\]

NaCN in ethanol, heat under reflux (, )

dilute H₂SO₄, heat
or H₂SO₄(aq), heat
or dilute HCl, heat
or HCl(aq), heat (, )

[1m] for each correct intermediate structure

2(, ): 1m ; 3(, ): 2m , only awarded if corresponding structures are correct

Award marks proportionately, for any other long synthesis method suggested.

1m max for any haywire synthesis method but correct cyano-intermediate & reagent and conditions for hydrolysis to get the end product

-1m if answers are correct but not clearly presented

- Have to remind students that Free Radical Substitution is *not* a recommended way of synthesis. It gives a mixture of products.

**Common Mistakes:**

- Some only listed the sequence of reagents & conditions required w/o giving intermediates for ‘synthetic route’
- Suggested step to convert –OH group to –CN group * (MANY STUDENTS)
- Suggested step to convert –OH group to –COOH group * (MANY STUDENTS)
- Using “KmO₄/K₂Cr₂O₇ and heat under reflux” to oxidise alcohol to aldehyde
- Confused on when to use HCN and NaCN (for nucleophilic sub & addition)
- Listed a mixture of two acids for hydrolysis e.g. ‘H₂SO₄, HCl, heat under reflux’
- Did not use ‘dilute’ or ‘aq’ for acid hydrolysis (i.e. simply “H₂SO₄, heat”)
- Used ‘conc’ acid for hydrolysis.
General Comments for Q2

Part (a) was generally well attempted and the average score is 7 out of 12. Students generally lost most marks in (a)(i)(ii)(vi).

Part (b) was poorly attempted and the average score is 3 out of 8. Students generally scored all marks in (b)(iii)(v).

For details, please see the comments under individual subparts.

2. (a)  (i)  **Menthone** is expected to be more volatile. (or **Menthol** is expected to be less volatile) **[1m]**

Less energy is required to overcome the *weaker permanent dipole-permanent dipole interaction** between menthone molecules than the *stronger hydrogen bonds** between menthol molecules.

**Reject:**
- Just mention menthol has a higher boiling point.
- “Methanol/Menthanol” as Menthone/Menthol

**Common mistakes:**
- Menthone and Menthol were spelt wrongly.
- C=O bond is stronger than O-H bond..
- ....van der waals’ forces between menthone molecules
- “between molecules” is often missing
- ...higher b.p.....therefore more volatile

(ii) Menthol is insoluble in water due to the presence of large/bulky non-polar/hydrophobic cyclic alkyl chain/group in menthol molecule which *prevents/hinders effective hydrogen bonding with water* molecules. **[1m]**

**Reject:**
- mention “steric hindrance” without relating to the large alkyl group and hydrogen bonding.

**Common mistakes:**
- Menthol is non-polar/hydrophobic.....cannot form ion-dipole interaction or hydrogen bonding with water ....
- ΔHsoln is highly endothermic....
- Lone pair on O atom of –OH not available for hydrogen bonding as it is delocalised into the benzene ring.
(iii) Step 1: LiA/H₄, dry ether or NaBH₄, methanol or H₂, Ni, heat/200 °C  [1m]
Step 2: concentrated H₂SO₄, heat at 170/180 °C or Al₂O₃, heat/350 °C  [1m]

Reject:
- “heat under reflux” for both steps
- (aq)/wrong state symbol of reagent.
  Except for “conc. H₂SO₄(aq)” (to cancel “[aq]” on student’s script)
- “LiLiH₄” as LiAlH₄

Common mistakes:
- Did not state “170 °C” in step 2 when conc. H₂SO₄ is used.
- Quoted “acidified KMnO₄/K₂Cr₂O₇…” in step 1.
- Quoted “ethanolic KOH/NaOH, heat under reflux” in step 2.

(iv) M:  [1m]

Oxidised product:  [1m]

Common mistakes:
- One missing carbon/one extra carbon atom in the oxidized product.
- Leave out one of more H atoms in the fully expanded structural formula of M/oxidised product.
- Some gave ketone/aldehyde/CO₂ as the oxidised product.
2. (a) (v) 

![Chemical structure and reaction](image)

- (P) full arrow pointing from π bond to +H
- (P) full arrow pointing from H–C bond towards +Cl
- *(P)* correct carbocation structure
- (P) full arrow pointing from lone pair on Cl– towards C+
- *(P)* correct addition product

3-4(P): [1m] 5(P): [2m]

Common mistakes:
- Leave out one or more H atoms in the expanded structural formula of 3-menthene.
- Put (δ+, δ-) on the C=C bond. Penalise under 1st (P).
- Dissociate H–Cl into H+ and Cl– in the first step, then proceed with π electrons attacking the H+ and Cl– attacking the carbocation.
- Lone pair on Cl– is often missing.
- Arrow point from the electrophile (+H) to C=C bond.

(iv) Stereoisomerism occurs when compounds/molecules have the same molecular formula and same structural formula but the *atoms/groups of atoms* of the molecules are directed/arranged differently in 3-dimensional space. 3-menthene **has no chiral centre (or no carbon atom with four different groups/groups of atoms attached)** and so it does not exhibit optical isomerism.

***One form of the geometric isomer (or E-isomer/trans-isomer) is unstable (or does not exist) due to ring strain (or angle strain in the ring).*** Therefore it only exists in one stable form.

Reject:
- ***One form/isomer is unstable …….” without linking to geometric isomerism
- Due to ring strain, 3-menthene does not exhibit geometric isomerism
- 3-menthene has ring strain and cannot exhibit geometric isomerism

Common mistakes:
- For definition of stereoisomerism:
  - …molecules with 4 different groups attached to C/has chiral
centre/give rise to optical isomers that rotate plane polarised light.
  - …different arrangement of molecules/functional group in space.
  - …same molecular/chemical formula but different structural formula.
- Did not use “ring strain” but mentioned “twisting/distortion of ring and failed to relate to unstability of one geometric/trans isomer.
- No geometric isomerism as each C of C=C is bonded to the same group/due to cyclic ring.
- Mostly did not discuss both optical and geometric isomerism.
2. (b) (i) The charge density of Mg²⁺ is greater than that of Ba²⁺, therefore Mg²⁺ has a higher/greater tendency to attract the polar water molecules to itself to form hydrate as compared to Ba²⁺.

Reject:
• “...greater polarising power....”

Common mistakes:
• Many did not know what is a hydrate and discussed solubility of compound in water or reaction of compound with water instead.
• Discussed ΔH_{hyd}/oxidising power of Mg²⁺.
• Discussed high polarising power of Mg²⁺ and polarises the water molecule to great/more extent.
• High charge density Mg²⁺ favours formation of dative covalent bond with water molecules/readily accepts lone pair of electrons from water molecule to form dative covalent bond...
2. (b) (ii) When white crystals of Mg(NO$_3$)$_2$.6H$_2$O is heated in an open test-tube, water droplets condense at the top (P) of the test-tube, followed by evolution of a pungent brown NO$_2$ gas/fumes (P) and a colourless odourless O$_2$ gas which relights a glowing splint. A “white residue/solid/powder (P) of MgO is obtained after heating.

\[
\text{Mg(NO}_3\text{)}_2.6\text{H}_2\text{O(s)} \rightarrow \text{MgO(s)} + 2\text{NO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} + 6\text{H}_2\text{O(g)} \\
\text{or, } 2\text{Mg(NO}_3\text{)}_2.6\text{H}_2\text{O(s)} \rightarrow 2\text{MgO(s)} + 4\text{NO}_2\text{(g)} + \text{O}_2\text{(g)} + 12\text{H}_2\text{O(g)}
\]

Reject:
- "White precipitate/ppt….

Common mistakes:
- Many thought that this was a combustion reaction and wrote - “Mg(NO$_3$)$_2$.6H$_2$O(s) + O$_2$(g) → …”
- “burns with a ________ flame”
- Some gave Mg (instead of MgO) as the product.
- Equation not balanced and “O$_2$” in the product or “.6H$_2$O” in the reactant were often missing.
- MgO residue is black.
- “Water droplets form/condense at the top” was often missing.
- Water vapour is seen.

(iii) The charge density of Ba$^{2+}$ is lower than that of Mg$^{2+}$ since Ba$^{2+}$ has a larger [1m] size/ionic radius/radius (or is bigger) than Mg$^{2+}$.

Ba$^{2+}$ has a lower polarising power (or “Ba$^{2+}$ has a lower ability to distort [1m] the (large) NO$_3^-$/anion). Hence, Ba(NO$_3$)$_2$ is thermally more stable and requires a higher temperature to decompose than Mg(NO$_3$)$_2$.

Reject:
- “polarising power/Charge density of BaNO$_3$”
- “atomic radius of Ba/Ba$^{2+}$/BaNO$_3$”
- “size/ionic radius/radius of Ba/BaNO$_3$”
- “Ba/BaNO$_3$...lower ability to distort/polarise anion”… etc
(Basically, the subject must be Ba$^{2+}$/Mg$^{2+}$, not Ba/Mg or BaNO$_3$/MgNO$_3$)

Common mistakes:
- As mentioned in “Reject”.
(iv) The solid residue after barium nitrate has been heated is BaO. 

*BaO is soluble/dissolves/reacts* (,) readily in water to form a strongly alkaline solution of Ba(OH)$_2$ (,) Hence a colourless solution is observed.

The solid residue after magnesium nitrate has been heated is MgO. *MgO is only sparingly/partially/slightly soluble/not very soluble (or MgO dissolves to a small extent)* (,) and reacts with water to a small extent to form a weakly alkaline solution of Mg(OH)$_2$. Hence a white suspension of MgO (,) is observed.

2. (b) (v) Epson salt contains SO$_4^{2-}$ ions which form an insoluble BaSO$_4$ precipitate with aqueous solution containing Ba$^2+$. Hence, administering of Epson salt helps *to remove Ba$^2+$ ions/reduce [Ba$^2+$] from the solution through precipitation of BaSO$_4$.  

**Common mistakes:**
- Many did not discuss solubility of MgO and BaO, but comment on solubility of Mg(OH)$_2$ and Ba(OH)$_2$.
- Extent of reactivity with water i.e. “BaO reacts readily/completely..... MgO reacts only to a small extent” was not discussed.
- MgO reacts to give Mg(OH)$_2$ which is sparingly soluble to give white Mg(OH)$_2$ suspension.

**Common mistakes:**
- Many are not aware that Ba$^2+$ (aq) is toxic whereas insoluble barium compounds are not.
- Some thought that the barium poisoning is caused by the presence of Ba and discussed
  - reducing power of Mg/Ba
  - displacement reaction: Ba + MgSO$_4$ $\rightarrow$ Mg + BaSO$_4$
- …form soluble BaSO$_4$ and therefore easier to remove (eg. as urine)
- …stronger MgSO$_4$ salt displaces out weaker BaSO$_4$ salt....
General Comments for Q3

This question was one of the popular question that student would choose, however many students made a lot of careless mistakes especially in the proteins section. Marks for this question varies greatly from 2-10, very few students had more than 15. (no full marks)

Part (a) and (b) was generally well attempted and the average score is 5 out of 9. Students generally lost most marks in (b)(iii).

Part (c) was poorly attempted and the average score is 4 out of 11. Students generally scored full marks in (c)(i) only.

3. (a) (i) RCHC/CO₂H
(ii) substitution
(iii) or C₆H₅CH₂CH₂COOH

• Accept
• reject (incomplete structure)

(b) (i) NH₃+ COO⁻

The small amount of OH⁻ added is removed through acid-base reaction, maintaining the pH (or resisting changes in pH) of the buffer mixture.

• A few of candidates still make the usual error of using reversible arrows for the acid-base rxn.

• Small handful of candidates chose as the species present in the buffer to remove the base added.
The solution is a buffer at the start of the titration.

- When 39 \text{ cm}^3 of NaOH(aq) is added
  - the buffer solution is at its maximum buffering capacity
    - Mole ratio of \( \text{NH}_3^+ : \text{COO}^- = 1:1 \)

- A further 41 \text{ cm}^3 of NaOH(aq) is added to reach equivalence point.
  - 41 \text{ cm}^3 of NaOH(aq) was required to neutralise all the acid left in the buffer at the maximum buffering capacity.
  - i.e. at max. buffering capacity,
    - \text{amt of } \text{NH}_3^+ : \text{COO}^- = 41 \text{ x } 41 \text{ cm}^3 \)

  Working backwards, at start of the titration:
    - Mole ratio of \( \text{NH}_3^+ : \text{COO}^- \):
      \[
      \frac{80}{80} : \frac{41 - 39}{2} \text{ x } 40 : 1 \text{ (shown)}
      \]

(iii) In the original sample of buffer,

\[
\text{pH} = \text{p}K_a + \lg \frac{[\text{salt}]}{[\text{acid}]} \]

\[
7.4 = \text{p}K_a + \lg \left( \frac{1}{40} \right) \quad \text{[1m] correct substitution}
\]

Solving, \( \text{p}K_a = 9.00 \text{ [1m] pH can be calculated directly, with clear working} \)

Or, \( \text{K}_a = 10^{7.4 - \frac{1}{40}} \quad \text{[1m]} \)

\[
\text{K}_a = 9.95 \times 10^{-10} \quad \text{[1m]} \]

At the maximum buffering capacity, \( \text{pH} = \text{p}K_a = 9.00 \text{ [1m]} \)

(c) (i) Since 7 amino acids are formed, 6 amide bonds were broken in peptide G with the release of 6 mol of H\(_2\)O.

\[
\text{Moles of G} = (2 \times 181) + (2 \times 204) + (3 \times 165) - 6(18) = 1157 \quad \text{[1m] no units}
\]
(ii) The presence of alcohol reacts with the polar groups/ alcohol and disrupts the hydrogen bonds in the secondary, tertiary and quaternary structures of the protein/ enzyme/ chymotrypsin.

Thus, the conformation (or shape) of the active site of the enzyme is altered/change/destroyed and inhibits its digestive activity.

- Majority of candidates still make the usual errors:
  - Drew the free \(-\text{NH}_2\) and \(-\text{COOH}\) groups from the tyrosine amino acid.
  - Drew hydrogen bonding between the free \(-\text{NH}_2\) and \(-\text{COOH}\) groups from the tyrosine to the serine residue.
  - Indicated hydrogen bonding for the H atoms of the glycine residue.
- Many did not have complete hydrogen bonding diagram.

(iii) The small handful of candidates still make the usual error of stating that the active site is altered, without mentioning that it is the conformation/shape of the active site that is altered.

- Reject: Alcohol interacts/reacts with the serine residue, hence this inhibits the tyrosine from binding to the serine residue… (inhibitor only works if the structure of the inhibitor is almost the same as the substrate, alcohol does not have a structure like tyrosine-so such inhibiting of substrate does not work)
- Alcohol disrupts the hydrogen bonds in the secondary, tertiary and quaternary structures present in the active site of chymotrypsin.

- Small handful of candidates still make the usual error of stating that the active site is altered, without mentioning that it is the conformation/shape of the active site that is altered.
3. (d)

Since J and ethanol are produced after hydrolysis

⇒ H: presence of ester

+ CH₃CH₂OH

alkaline/base hydrolysis

followed by neutralisation

acid-carbonate/acid-base reaction

dissolves

J: presence of carboxylic acid

electrophilic substitution

white ppt

J: presence of phenylamine

since 0.1 mol of J reacts with 0.2 mol of Br₂(aq)

⇒ J: presence of one substituent group on 2 or 4 or 6th position wrt –NH₂ group of phenylamine

OR J contains

side-chain structure

OR Alternative answers:

A few of the candidates concludes for rxn with HCl(aq) that **J is a polar molecule**

Some of the candidates concludes for rxn with Br₂(aq) that **J has a benzene ring** or **J has a benzene ring with more than 2 positions unoccupied** (but forgets about 3,5 position wrt –NH₂ group is also unoccupied)
General Comments for Q4
Many students attempted this question. Generally well-done and answers are well-presented. Most students can achieve at least a pass for this question. Main problem is finding the t1/2 for expt 3 (4aiii) and energy profile diagram (4bii).

4 (a) (i) Compare Expt. 1 and 2:

When \([\text{OH}^-] \) increases to 1.5 \(\times\) times of its original value \((\text{or by } 1.5 \times \text{times})\), rate increases to 1.5 \(\times\) times of its original value \((\text{or by } 1.5 \times \text{times})\). Hence, the order of reaction with respect to \((\text{or w.r.t.) } \text{OH}^-\) is one.

OR:

Accept: \([\text{OH}^-] \) ↑ 1.5 \(\times\), rate ↑ 1.5 \(\times\)

Hence, the order of reaction with respect to \((\text{or w.r.t.) } \text{OH}^-\) is one.

OR rate \(\alpha \) [OH]^{-1}

Compare Expt. 1 and 3:

Let the order of reaction \(w.r.t\) CH₃CHO be \(a\).

Error! Objects cannot be created from editing field codes.

\[a = 6\]

\[a = 3\]

\[a = 1\]

Hence, the order of reaction with respect to \((\text{or w.r.t.) CH}_3\text{CHO is one})\)

OR rate \(\alpha \) [CH₃CHO]^{-1}

OR Alternatively:

Compare Expt 1 and 3:

When \([\text{CH}_3\text{CHO}]\) increases to 3 \(\times\) times of its original value \((\text{or by } 3 \times \text{times})\) and the \([\text{OH}^-]\) increases to 2 \(\times\) times of its original value \((\text{or by } 2 \times \text{times})\), rate increases to 6 \(\times\) times of its original value \((\text{or by } 6 \times \text{times})\).

Hence, the order of reaction with respect to \((\text{or w.r.t.) CH}_3\text{CHO is one})\)

Specific Comments:

Generally well-done. Students who attempted this part mostly achieve full marks. A few made careless mistakes in the calculations. The indices method was the most commonly seen when students compare expt 1(or 2) and 3.
(ii) Rate = \( k \ [\text{CH}_3\text{CHO}] \ [\text{OH}^-] \)

Reject: \( R \text{or r} \text{ate eqn is } k \ [\text{CH}_3\text{CHO}] \ [\text{OH}^-] \)

OR \( R \text{ or r} \text{ate eqn } = k \ [\text{CH}_3\text{CHO}] \ [\text{OH}^-] \)

\( k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}] \ [\text{OH}^-]} \)

From Expt 1: \( k = \frac{0.0110}{(0.10)(0.10)} = 1.10 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1} \)

OR From Expt 2: \( k = \frac{0.0165}{(0.10)(0.15)} = 1.10 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1} \)

OR From Expt 3: \( k = \frac{0.0660}{(0.30)(0.20)} = 1.10 \text{ mol}^{-1}\text{dm}^3\text{s}^{-1} \)

ECF: If student obtains rate eqn = \( k \ [\text{CH}_3\text{CHO}]^2 \ [\text{OH}^-] \)

\( k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^2 \ [\text{OH}^-]} \)

From Expt 1: \( k = \frac{0.0110}{(0.10)^2(0.10)} = 11.0 \text{ mol}^{-2}\text{dm}^8\text{s}^{-1} \)

Specific Comments:
A few still gave rate equation = \( k \ [\text{CH}_3\text{CHO}] \ [\text{OH}^-] \). Some miss out answering this part and move on to the calculations straight away. A small number made mistakes in the units.
4  (a)  (iii) Half-life of CH₃CHO in expt 3 = $\frac{1}{2}(9) = 4.5$ s (or sec/seconds)  

(Explanation:  
From Rate = $k$ [CH₃CHO][OH⁻]  
$\Rightarrow$ Rate = $k''$ [CH₃CHO] where $k'' = k[OH^-]$  
and $t_{1/2}$ of CH₃CHO = $\ln 2/k'' = 9$ s in expt 1  
Comparing expt 1 & 3:  
• [CH₃CHO] is tripled but this has no effect on the half-life of CH₃CHO since the $t_{1/2}$ of CH₃CHO is independent of [CH₃CHO]. The rxn is first order with respect to CH₃CHO.  
• When [OH⁻] is doubled, $k''$ is doubled.  
Thus $t_{1/2}$ of CH₃CHO is halved.  

∴ Half-life of CH₃CHO in expt 3 = $\frac{1}{2}(9) = 4.5$ s  

Specific Comments:  
Not well-done. Many cannot give the correct answers. Only a small number got this right. Students seem to have problem with this type of question asking for $t_{1/2}$.  
Many incorrectly deduce 27s (as well as 9s) as the answer, seeing that the the [CH₃CHO] is tripled.  
Another common value seen was 1.5s. This was due to students pointing out that [CH₃CHO] is tripled and [OH⁻] is doubled.  

(b)  (i) Step 1  

The rate determining step involves only one molecule of CH₃CHO reacting with/and/+ one OH⁻ ion.  

ECF: if student obtains rate = $k$ [CH₃CHO][OH⁻]² in 4a(ii), accept Step 2 supported with appropriate reasoning or derive from equations.  

Specific Comments:  
A small number achieve full marks for the explanation. They miss out ‘one’ molecule and ‘one’ ion. None manage to get this part correct if they got the wrong rate equation from the previous part. Some still regard OH⁻ ion as a molecule.  
The only ECF allowed mentioned above was earned by a small no. of students. This was usually due to them concluding incorrectly rate = $k$ [CH₃CHO]²[OH⁻] in 4a(ii).
Specific Comments:

Many students gave one (or two) humps in their sketch with the labelling of $E_a$, reactants and products, wrong label of x-axis as time or no of molecules (confusing with Boltzmann distribution).

The concept of (overall) $E_a$ of a reaction may need to be reinforced since many students use $E_{a1}$, $E_{a2}$, $E_{a3}$ in their labelling, without recognising that $E_{a1}$ is the (overall) $E_a$ of the forward reaction.

A number of students drew the following energy profile. Students were penalised 1m. It should be reiterated that intermediates, being less stable than reactants and products, usually exist for short period of time (or usually instantaneously) and as such, by drawing the following profile, it seems to indicate that intermediates exist for a significant period of time in the reaction.

<table>
<thead>
<tr>
<th>Energy (kJ mol$^{-1}$)</th>
<th>Accept: reactants</th>
<th>Accept: products</th>
</tr>
</thead>
<tbody>
<tr>
<td>2CH$_3$CHO(+OH$^-$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$CHOHCHO$_2$CHO(+OH$^-$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- X: 3 humps
- Axes labeled
- Reactants and products labelled
- Energy level of pdt < rxt.
- $E_a$ of 1$^{st}$ step $>> E_a$ of 2$^{nd}$ / 3$^{rd}$ step + label $E_a$
- Allow ecf from (b)(i) r.d.s.
Acid-base/Neutralisation reaction [1m]

Specific Comments:
A large number gave 'nucleophilic substitution'. A small number gave 'free-radical substitution'.
In Step 2, there is an equal probability/possibility/chance of the $-\text{CH}_2\text{CHO}$ nucleophile attacking either side (or top or bottom) of the trigonal planar $>\text{C}=\text{O}$ group, producing an equimolar mixture of the two optical isomers.\(\text{[P]}\)

From Organic Summary Handbk (Section 2 pg. 19):
Arrangement around carbonyl C atom is trigonal planar. Hence there is equal probability of $-\text{CH}_2\text{CHO}$ nucleophile attacking either side of the plane, producing a racemic mixture (50:50 proportion of each optical isomer).

Specific Comments:
Some students gave carbocation as intermediate and wrote a 2-step mechanism instead. For the explanation, many students give planar carbonyl compound/molecule. A number drew the wrong nucleophile or the carbonyl compound (replace $-\text{CHO}$ with $-\text{COOH}$).
[1m] for each correct structure for ANY 2 of the 3 structures below

Specific Comments:
A very small number got full marks. Most earned at least 1 mark. Many gave repetition of answers (mirror image of their 1st structure), or give wrong bond linkage. This question involved students using the 3-step mechanism given to deduce the possible products from this reaction.
Specific Comments:
Generally well-done. Most students achieve full marks. There were still some who removed electrons from the 3d first before the 4s orbitals.

(ii) Cu(II) / Cu²⁺ ion has partially-filled d orbitals in its 3d⁹ configuration. Cu(II) / Cu° complexes are coloured because electron transition between d orbitals is possible.

In a Cu(II) / Cu²⁺ complex, the presence of ligands causes the 3d orbitals to split into 2 sets of different energies. (P)*

The difference in energies (ΔE) between these two sets of d orbitals is so small (P)* such that radiation from the visible region/visible light/visible spectrum of the electromagnetic spectrum is absorbed (P)* when an electron moves/transits/excites/promotes/shifts/travels from a d orbital of lower energy to a partially filled/incompletely filled/unfilled (or vacant) d orbital of higher energy. [1m] Hence, copper(II) complexes are coloured.

The colour seen/reflected/transmitted will be the complement/complementary of the colours absorbed. (P)*

Cu(I) / Cu⁺ ion has fully/completely/totally filled 3d orbitals OR no empty or partially filled 3d orbitals.

Thus electron transitions between d-orbitals are not possible. Hence, copper(I) complexes are colourless.

Specific Comments:
Students generally score full marks for this part, if they have studied. Those who did not do well obviously did not study the topic well, especially on the aspect of ligands causing the splitting of d-orbitals.

There were a no. of rather short ans merely describing that Cu(I) / Cu⁺ ion has fully/completely filled 3d orbitals OR no empty or partially filled 3d orbitals

and Cu(II) / Cu²⁺ ion has partially-filled d orbitals in its 3d⁹ configuration.

Students need to recognize the question clearly asks them to “explain...” and take note of the mark allocation in this part of the qns.
**General Comments for Q5**

This is one of the most popular questions. Most students who attempted this question gained close to ten marks.

In this question, we found that most students could correctly identify the concept being tested in each part. However, they are unable to express their ideas using the correct scientific terms. See comments for individual parts for details.

Some students also make careless/ spelling mistakes in this question which caused them to lose a number of marks. Questions in which students demonstrated their carelessness include (a)(v); (b)(i).

5. (a) (i)

![Dotted plane must be drawn](image)

Shape: T-Shaped/T shape (do not accept “t”)  

**Common mistakes:**

1. Many students drew the lone pairs of electrons on the axial position instead of the equatorial positions. Could they have forgotten their year one’s work on shapes of molecules?
2. In addition, a number of students actually written out the number of bond-pairs and lone-pairs correctly (3 bp, 2 lp), yet they cannot produce the correct molecular shape.
3. For those who got the shape right, they drew imprecise dotted lines.
4. Others left out drawing the dotted lines. A few left out the lobes for the lone pairs.
5. A large number of students drew dot-and-cross diagram for the ICl₃ molecule instead of shape of the molecule. Could it be they did not understand the requirement of the question or they do not know the shape at all?
(a) (ii) F is from Period 2 while I is from Period 5. I can expand its octet structure/accommodate more than 8 electrons in its outer shell because it has energetically accessible vacant d orbitals, but F cannot expand its octet structure. Thus FCl₃ does not exist. [Note: circle wrong period no.]

OR F does not have energetically accessible vacant d orbitals and hence it does not allow expansion of octet/ accommodation of more than 8 electrons. Thus FCl₃ does not exist.

Common mistakes:
1. Instead of stating that F does not have energetically accessible vacant 3d orbitals to expand its octet structure, students stated FCl₂.
2. Students omit the word ‘octet’ or ‘configuration’ or ‘structure’ in their explanation.
3. This is the part with the most types of spelling mistakes. ‘Octet’ was frequently spelled as ‘octect’, expand was spelt wrongly too.
4. Students describe the vacant 3d orbitals as energetically ‘feasible’ instead of ‘accessible’.
5. In addition, many students wrote “energetically accessible d orbitals” and forgot to add the word “vacant”.
6. Two common misconceptions from students to account for why FCl₃ does not exist are (a) that ‘F is a very small atom, so it cannot accommodate three Cl atoms around it as the resulting FCl₃ will be unstable’ or (b) F is very electronegative, hence, F does not share its electrons, unlike iodine.

(iii) ¹/₂ I₂(s) + ³/₂ Cl₂(g) -> ICl₃(s) + Cl₂(g)

ΔHᵢ = ΔHᵢ(ICI₃(s)) + ¹/₂(14) - ¹/₂(88) = -ΔHᵢ(I₂(s))

By Hess’ Law: ΔHᵢ(ICI₃) = +14/2 - 88/2 = -37 or -37.0 kJ mol⁻¹

Common mistakes:
1. The energy cycle is very often not balanced. One common type of wrong energy cycle is shown below (where Cl₂ (of various coefficients) is inserted at the arrows):

   ¹/₂ I₂(s) + ³/₂ Cl₂(g) --→ ICl₂(s) + Cl₂(g)

   In the above cycle, we can see another common mistake, that is students did not label ΔHᵢ(ICI₂) although there is no penalty here.
2. One or more state symbols were also left out.
3. A good number of students did not realize that they need to half the value of the enthalpy changes, resulting in many leaving the answer as -74.0 kJ mol⁻¹.
4. A typical area for careless mistakes where the subtraction is incorrectly done for ΔHᵢ(I₂Cl₂).
5 (a) (iv) $\Delta S$ is negative due to a decrease in disorder as reaction proceeds with decrease/drop in the number of gaseous particles/molecules from 1.5 mol to 0 mol.

Common mistakes:
1. Many students missed out on stating ‘there was a decrease in disorder’ when there is a negative entropy change.
2. A common misconception was that some students reasoned that ‘the decrease in disorder is due to the change of states from gaseous reactants to solid products’ or due to ‘mixing’.
3. We did not mark for the numerical value of changes in the amount of gas particles. However, we note that many students got the mark for part (iv) although they have used the wrong equation to deduce the answer. For instance, they often wrote that ‘decrease in disorder……from 2 mol to 0 mol.’ It is highly likely that they are referring to this equation for their answer: $2\text{ICl}(s) + 2\text{Cl}_2(g) \rightarrow 2\text{ICl}_3(s)$ instead of the formation of solid trichloride.
4. A small number of students wrote “gaseous ions” or “gaseous atoms” instead of “gaseous molecules”.

(v) $\Delta H < 0, \Delta S < 0, -T\Delta S > 0$

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

At low temperature, $|T\Delta S| < |\Delta H|$ (or magnitude $-T\Delta S < \Delta H$) and thus $\Delta G < 0$ (or $\Delta G$ is negative). Since $\Delta G < 0$, reaction is spontaneous at low temperature.

Common mistakes:
1. Many did not state the first point, i.e. $-T\Delta S > 0$ or simply just state ‘the sign of $T\Delta S$ is positive’, the second of which is not helpful in their explanation.
2. Many misused the modulus sign, e.g., they stated that $|\Delta H|$ is negative.
3. A good number did not include the ‘$-$’ sign when they are comparing $\Delta H$ with $-T\Delta S$.

(vi) $\Delta G_{f} (\text{ICl}_3) = \Delta H_{f} (\text{ICl}_3) - T\Delta S_{f} (\text{ICl}_3) = -37 - (298)(-225 \times 10^{-3})$ [1m] correct subst in kJ mol\(^{-1}\) or J mol\(^{-1}\) ecf(iii)

$= +30.1 \text{ kJ mol}^{-1}$ [1m] 2 – 4 sf, in kJ mol\(^{-1}\) or J mol\(^{-1}\)

Since $\Delta G_f > 0$, formation of ICl\(_3\) is not spontaneous at 298K. [1m] e.c.f from $\Delta G_f$. Reject: 1. Conclusion on whether the reaction is spontaneous or not if a value for $\Delta G_f$ is not computed by students.
2. ‘energetically feasible’ in place of ‘spontaneous’

Note:
2 marks are lost if the students substitute values that are not of the same units:

$e.g. \Delta G_f (\text{ICl}_3) = -37 - (298)(-225 \times 10^{-3})$

There is ecf from (a)(iii) if the units are consistent for all the values substituted.

Common mistakes:
1. Some did not convert 225 to kJ mol\(^{-1}\) K\(^{-1}\), some carelessly substituted ‘255’ instead of ‘225’.
2. Some thought that a positive $\Delta G$ meant spontaneous reaction!
3. Some used the term, ‘energetically feasible’ instead of ‘spontaneous’
4. Some did not know the requirement of the question despite being a similar question to their tutorial on Entropy. These students did not calculate any value for \( \Delta G \) to predict spontaneity of the reaction. Instead, they gave a qualitative explanation.

5. (b) (i) \( K_{sp} = [Ag^+] [I^-] \) [1m]

Let \( y \) mol dm\(^{-3} \) be the solubility of AgI at 25°C.

\[
Ag(s) = Ag^+(aq) + I^-(aq)
\]

\[
K_{sp} = [Ag^+] [I^-]
\]

\[
8.52 \times 10^{-17} = y^2
\]

\[
\Rightarrow y = 9.23 \times 10^{-9}
\]

\[
[Ag^+] = 9.23 \times 10^{-9} \text{ mol dm}^{-3}
\]

Reject:
1. \( K_{sp} \) [AgI]

Common mistakes:
1. Students wrote expression for AgCl instead of AgI.
2. Even if expression is correct, students substituted wrong \( K_{sp} \) value for calculation.
3. Some also substituted wrong power in the \( K_{sp} \) value for calculation, e.g. \( 10^{-7} \) was used instead of the correct \( 10^{-17} \).

(ii) White ppt: AgCl
Yellow ppt: AgI

When AgNO\(_3\)(aq) is added to NaCl(aq), the white ppt formed is AgCl.

\[
Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)
\]

OR AgCl(s) + 2NH\(_3\)(aq) \rightleftharpoons [Ag(NH\(_3\))\(_2\)]\(^+\) (aq) + Cl\(^-\) (aq)

\[
AgCl(s) = Ag^+(aq) + Cl^-(aq) \quad (*)
\]

When NH\(_3\)(aq) is added, Ag\(^+\) forms a soluble colorless complex \( Ag(NH_3)_2^+ \), resulting in a decrease of \( [Ag^+(aq)] \) causing the equilibrium position of (*) to shift to the right. Thus AgCl dissolves when excess NH\(_3\)(aq) is added.

When NaI(aq) is added to \( [Ag(NH_3)_2]^+ \), the yellow ppt formed is AgI(s).

AgI is formed since
• \( K_{sp} \) of AgI is much smaller than \( K_{sp} \) of AgCl [1m]
• the ionic product of \( [Ag^+] [I^-] \) will be greater than \( K_{sp} \) of AgI.

Common mistakes:
1. Students did not state the identities of white and yellow ppt explicitly. They probably did not understand from the question that they need to give the identities of the two ppt in their answers.
2. The second mark is also difficult to award to students as very few of them knew how to explain why the white ppt dissolves.
3. They also got the formula of the complex wrong, common
wrong formulae include AgOH, AgNH₃ (without the charge), AgNH₄, AgNO₃.

4. For the third mark, instead of quoting the difference in Ksp values for the two silver halides as a reason for the different behaviours with ammonia, students said that the reason was because iodide ions was a stronger reducing agent than chloride ions/iodide is a stronger ligand than chloride.

5. Good students generally can answer the dissolving of AgCl in excess NH₃ but lost that mark due to missing state symbols in the equilibrium equation.

(c) (i) Misty/White fumes(or gas) of HCl will be observed. 
Orange-red/Orange/Orange-brown/Red-brown/brown fumes(or gas) of Br₂ will be observed.

\[
\text{NaX + H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HX} \quad \text{where X = Cl, Br} \quad \text{[accept ionic eqn]}
\]

\[
2\text{HBr + H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{Br}_2
\]

HBr/Br⁻ is a stronger reducing agent (or has greater reducing power) than HCl/Cl⁻. Hence HBr can reduce conc. H₂SO₄ (O.S. of S = +6) to SO₂ (O.S. of S = +4) and itself oxidised to Br₂. But HCl cannot reduce conc. H₂SO₄.

Common mistakes:
1. More students gave the correct observations here.
2. A few of them stated ‘brown solution/liquid’ instead of ‘brown fumes’.
3. Some left out the word, ‘gas’, in their description and hence, lost the mark as it is not clear if the student meant solution or gas.
4. A number of them said that bromide ion is a stronger oxidising agent, instead of it being a stronger reducing agent.
5. Many did not even give an explanation for the difference in observations.
6. Some students wrote “Na₂SO₄” in place of “NaHSO₄” when trying to balance the first equation. A few incorrectly wrote “H₂S” in place of “SO₂” for the 2nd eqn for Br.

(ii) Very little HI left for the reaction with alcohol since most of the HI formed will be oxidised to I₂.

OR

Most of the HI formed will be oxidised to I₂ as HI is an even stronger reducing agent than HBr, while concentrated sulfuric acid is reduced to give mainly H₂S and SO₂. Thus the remaining HI will not be enough (or too little HI left) to react with alcohol to give alkyl iodide.

Common mistakes:
1. Many did not conclude that very little HI is left for the reaction even though they gave a reasonable explanation as to why the specified reaction is not used to prepare alkyl iodides. One logical reason that students propsed is that HI is unstable and hence, decomposes to H₂ and I₂ readily, and hence is hardly available to react with alcohol to give alkyl iodide.
2. Some students commented on the reducing power of HI instead and did not explain clearly how this could lead to the specified reaction not being used to prepare alkyl iodide.
2012 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY

Paper 1

Additional Materials: OMR
Data Booklet

INSTRUCTIONS TO CANDIDATES

1. Do not turn over this question paper until you are told to do so.
2. Write your name, class and admission number in the spaces provided at the top of this page and on the OMR provided.
3. Answer ALL questions and shade the correct answers on the OMR provided using a soft pencil.
4. No extra time will be given for shading.
5. Hand in the question paper and the OMR separately.

INFORMATION FOR CANDIDATES

Marks will not be deducted for wrong answers; your total score will be the number of correct answers given.

FOR EXAMINER’S USE

TOTAL (40 marks)

This question paper consists of 16 printed pages.
Answer all questions on the OMR form provided (40 Marks)

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

1 Zn reacts with VO$_3^-$ ions to give V$^{n+}$. 3.9 g of Zn was required to react completely with 40.0 cm$^3$ of 1.0 mol dm$^{-3}$ of KVO$_3$.

What is the value of n?

A 1  
B 2  
C 3  
D 4

2 In which of the following pairs do the species have different shapes?

A AlCl$_3$ and CO$_3^{2-}$  
B NH$_4^+$ and CH$_4$  
C NH$_3$ and H$_3$O$^+$  
D SeF$_4$ and SO$_4^{2-}$

3 The following graph shows how ionic radius changes across Period 3 for seven elements.

A The sharp increase in ionic radius between the 4th and 5th element is due to an increase in the number of principal quantum shells.

B There is a decrease in ionic radius for the first 4 elements in Period 3 due to decreasing shielding effect.

C There is a decrease in ionic radius for the last 3 elements due to decreasing proton to electron ratio.

D The first 4 elements form anions and hence have lower ionic radii than the last 3 elements which form cations.
4 In which of the following reactions is the acid acting as an oxidant?

A \[ \text{KBr} + \text{H}_3\text{PO}_4 \rightarrow \text{HBr} + \text{KH}_2\text{PO}_4 \]
B \[ \text{MgO} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O} \]
C \[ 12\text{HC}l\text{O}_4 + \text{P}_4\text{O}_{10} \rightarrow 6\text{Cl}_2\text{O}_7 + 4\text{H}_3\text{PO}_4 \]
D \[ \text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2 \]

5 A 1 dm\(^3\) flask containing helium at 2 kPa pressure is connected (at constant temperature) to a 2 dm\(^3\) flask containing neon at 1 kPa pressure. What is the final pressure after connection?

A \( \frac{4}{3} \) kPa
B \( \frac{3}{2} \) kPa
C \( \frac{5}{3} \) kPa
D 2 kPa

6 *The use of the Data Booklet is relevant to this question.*

Phosphorus, \( \text{P}_4 \), has the following molecular structure:

Imagine that nitrogen were to form a similar molecule \( \text{N}_4 \) shown in the reaction below:

\[ 2\text{N}_2(\text{g}) \rightarrow \text{N}_4(\text{g}) \]

What would be the value of \( \Delta H \) (in kJ mol\(^{-1}\)) for the above reaction?

A 1028
B 1348
C 1954
D 2628
7. Which gas shows the greatest deviation from ideal gas behavior?
   A. HCl
   B. He
   C. CH₄
   D. N₂

8. The use of the data booklet is relevant to this question.
   In many areas, tap water is slightly acidic due to dissolved carbon dioxide. Which metal will not be dissolved by tap water containing carbon dioxide?
   A. Cr
   B. Cu
   C. Fe
   D. Pb

9. Which of the following mixtures is not an acid/conjugate base pair?
   A. H₂O/OH⁻
   B. H₂PO₄⁻/HPO₄²⁻
   C. NaH/Na
   D. NH₃/NH₂⁻

10. Which of the following pairs of solutions would form an acidic buffer when mixed?
    A. HCN and NaCN
    B. HNO₃ and NaNO₃
    C. NaOH and NaCl
    D. HCl and NaOH

11. Bleaching solutions are manufactured by dissolving chlorine gas in sodium hydroxide solution to give the following reaction.
    \[ \text{Cl}_2 (g) + 2\text{OH}^- (aq) \rightleftharpoons \text{OCI}^- (aq) + \text{Cl}^- (aq) + \text{H}_2\text{O (l)} \]
    Users are warned not to mix the bleach with other cleaning solutions to prevent evolution of hazardous chlorine gas. Which of the following actions will lead to liberation of chlorine gas?
    A. Addition of water to bleach
    B. Mixing of an alkali with bleach
    C. Shaking bleach with table salt, NaCl
    D. Subjecting bleach to high pressure
12  Given that,

Equilibrium I:  \[ \text{C (s) + O}_2 \text{ (g) } \rightleftharpoons \text{CO}_2 \text{ (g)} \quad K_{c1} = 3 \]
Equilibrium II: \[ \text{C (s) + } \frac{1}{2} \text{O}_2 \text{ (g) } \rightleftharpoons \text{CO (g)} \quad K_{c2} = 2 \]
Equilibrium III: \[ \text{CO (g) + } \frac{1}{2} \text{O}_2 \text{ (g) } \rightleftharpoons \text{CO}_2 \text{ (g)} \quad K_c = \ ? \]

What is the numerical \( K_c \) value for the Equilibrium III?

A  \( \frac{\sqrt{2}}{3} \)  
C  \( \frac{\sqrt{3}}{2} \)
B  \( \frac{2}{3} \)  
D  \( \frac{3}{2} \)

13  The rate of removal of the pain-killing drug paracetamol from the body is a first order reaction with a rate constant, \( k \), of 0.26 h\(^{-1}\).

How long will it take for 6.25% of the paracetamol ingested to remain in the body?

A  2.7 hours  
C  8.1 hours
B  10.6 hours  
D  13.5 hours

14  Sulfates of Group II metals exist as crystalline form as follows:

\[
\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \quad \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad \text{SrSO}_4 \quad \text{BaSO}_4
\]

Which one of the following accounts for this trend in hydration?

A  The atomic radius of the elements increases down the group.
B  The ionic character of these sulfates increases down the group.
C  The ionisation energy of the elements decreases down the group.
D  The radius of the cation increases down the group.

15  \( X \) is a mixture of two compounds. When \( X \) is treated with an excess of dilute hydrochloric acid, a colour gas is evolved and some, but not all of the mixture dissolves.

Which one of the following mixtures could be \( X \)?

A  \( \text{Ba(NO}_3\text{)_2 and Ca(OH)}_2 \)
B  \( \text{Ag}_2\text{SO}_4 \) and \( \text{CaCO}_3 \)
C  \( \text{CaCO}_3 \) and \( \text{MgSO}_4 \)
D  \( \text{Ca(OH)}_2 \) and \( \text{MgCO}_3 \)
A yellow precipitate of cadmium(II) sulfide is formed when H$_2$S is passed into an aqueous solution of cadmium(II) ions, Cd$^{2+}$. This precipitate is also obtained in the presence of dilute hydrochloric acid but not in the presence of concentrated hydrochloric acid nor in excess potassium chloride. Which explanation accounts for all these observations?

A. The presence of a high concentration of H$^+$ (aq) suppresses the ionisation of H$_2$S (aq).
B. The concentration of S$^2-$ (aq) is reduced by the formation of SCl$_4^{2-}$ (aq).
C. CdS (s) is insoluble in concentrated HCl (aq).
D. Cd$^{2+}$ (aq) ions react with Cl$^-$ (aq) to form the complex ion [CdCl$_4$]$^{2-}$ (aq).

A current of 2.0 A is used to plate Ni(s) from 500 cm$^3$ of a 1.00 mol dm$^{-3}$ Ni$^{2+}$(aq) solution. What is the concentration of Ni$^{2+}$(aq) after 3.0 hours?

A. 0.39 mol dm$^{-3}$
B. 0.46 mol dm$^{-3}$
C. 0.78 mol dm$^{-3}$
D. 0.89 mol dm$^{-3}$

Which one of the following statements is correct about a reaction for which the equilibrium constant is independent of temperature?

A. The enthalpy change of reaction is zero.
B. Its rate constants do not vary with temperature.
C. There are equal numbers of moles of reactants and products.
D. The activation energies for both the forward and reverse reactions are zero.
Magnesium iodate(V) undergoes thermal decomposition to yield products as shown by the equation below. The other Group II iodates(V) also undergo similar thermal decomposition.

\[ 2\text{Mg(IO}_3\text{)}_2(s) \rightarrow 2\text{MgO(s) + 2I}_2\text{(g) + 5O}_2\text{(g)} \]

The three graphs given below show the change in mass when 2.00 g each of three Group II iodates(V) are heated separately at a temperature T.

Which three Group II iodates(V) give rise to these graphs?

Graph (1)  Graph (2)  Graph (3)
A  Ca(\text{IO}_3\text{)}_2  Mg(\text{IO}_3\text{)}_2  Ba(\text{IO}_3\text{)}_2
B  Mg(\text{IO}_3\text{)}_2  Ba(\text{IO}_3\text{)}_2  Sr(\text{IO}_3\text{)}_2
C  Ca(\text{IO}_3\text{)}_2  Mg(\text{IO}_3\text{)}_2  Sr(\text{IO}_3\text{)}_2
D  Sr(\text{IO}_3\text{)}_2  Ba(\text{IO}_3\text{)}_2  Ca(\text{IO}_3\text{)}_2

A compound X exhibits structural isomerism, the isomers being members of different homologous series. To which pair of isomers could X belong?

A  acyl chlorides and carboxylic acids
B  carboxylic acids and esters
C  amino acids and ammonium salts
D  amides and amino acids

What is the total number of structural and geometrical isomers for a compound with molecular formula C\textsubscript{3}H\textsubscript{5}F, excluding cyclic structures?

A  3
B  4
C  5
D  6
22 1,2-dibromo-3-chloropropane (DBCP) has been used in the control of earthworms in agricultural land. The structure of DBCP is shown below.

Which of the following reactions will lead to the highest yield of DBCP?

A  \( \text{CH}_2=\text{CHCH}_2\text{Cl} + \text{Br}_2 / \text{CCl}_4 \rightarrow \text{DBCP} \)

B  \( \text{CH}_2=\text{CHCHBr}_2 + \text{HCl} / (\text{g}) \rightarrow \text{DBCP} \)

C  \( \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + 2\text{Br}_2 / \text{uv light} \rightarrow \text{DBCP} + 2\text{HBr} \)

D  \( \text{CH}_3\text{CHBrCH}_2\text{Br} + \text{BrCl} / \text{uv light} \rightarrow \text{DBCP} + \text{HCl} \)

23 Compound J, \( \text{C}_5\text{H}_{11}\text{Cl} / \) undergoes the following reaction.

\[ \text{Ethanolic KOH} \]
\[ \text{C}_5\text{H}_{11}\text{Cl} \quad \text{C}_5\text{H}_{10} \]

Which of the following cannot be Compound J?

A  1-chloropentane

B  2-chloropentane

C  2-chloro-3-methylbutane

D  1-chloro-2,2-dimethylpropane
A polypeptide was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

Digestion using enzyme **N**:
thr-phe-leu
cys-glu-val
ser-glu-cys
asp-cys

Digestion using the enzyme **O**:
val-asp-cys-thr
phe-leu-ser
glu-cys
cys-glu

What is the correct sequence of the polypeptide structure?

A  cys-glu-val-ser-glu-cys-asp-cys-thr-phe-leu

B  cys-glu-val-asp-cys-thr-phe-leu-ser-glu-cys

C  glu-cys-glu-val-asp-cys-thr-phe-leu-ser-glu

D  ser-glu-cys-glu-val-asp-cys-thr-phe-leu-ser
Methylbenzene and bromine, in the ratio of 1:6 were mixed and left under the sun and compound Q was isolated. After which, iron fillings were added to the mixture at room temperature and Compound R was identified to be the final product. Which of the following is likely to be Compounds Q and R?
26 One industrial preparation of ethanoic acid is the direct carbonylation of methanol using a rhodium catalyst.

\[ \text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{rhodium catalyst}} \text{CH}_3\text{CO}_2\text{H} \]

Which compound could be used to produce HC—CH₂CO₂H by this method?

A

\[
\begin{align*}
\text{HC—CH}_2\text{CO}_2\text{H} \\
\text{CO}_2\text{H}
\end{align*}
\]

B

\[
\begin{align*}
\text{HC—CO}_2\text{H} \\
\text{CH}_2\text{OH}
\end{align*}
\]

C

\[
\begin{align*}
\text{OH} \\
\text{HC—CH}_2\text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

D

\[
\begin{align*}
\text{CH}_2\text{OH} \\
\text{HC—CH}_2\text{OH} \\
\text{CH}_2\text{OH}
\end{align*}
\]

27 Tamoxifen is widely used in the treatment of breast cancer.

Tamoxifen

What is the number of \( sp^2 \) and \( sp^3 \) carbon atoms respectively after subjecting Tamoxifen to hydrogen gas under heat and in the presence of nickel?

\[
\begin{array}{c|c|c}
 & sp^2 & sp^3 \\
A & 6 & 20 \\
B & 8 & 18 \\
C & 18 & 8 \\
D & 20 & 6 \\
\end{array}
\]
28  The reduction of a nitrile produces a compound of formula C₃H₇NH₂.
    Which of the following would be produced if the same nitrile is heated with hydrochloric acid?
    A  CH₃CONH₂
    B  CH₃CH₂COOH
    C  (CH₃)₂CHCOOH
    D  CH₃CH₂OH

29  GABA has the structural formula, H₂NCH₂CH₂CH₂CO₂H. It is a neurotransmitter released by red algae to encourage shellfish larvae to settle on the ocean bed. How does GABA differ from amino acids obtained by the hydrolysis of proteins?
    A  It does not form zwitterions.
    B  It is not a 2-aminocarboxylic acid.
    C  It is insoluble in water.
    D  It cannot form a polyamide linkage.

30  Which property enables proteins to function as a pH buffer?
    A  Proteins contain the carboxyl and amino groups.
    B  Proteins are soluble.
    D  Proteins possess secondary and tertiary structures.
For questions 31 – 40, the responses A to D should be selected on the basis of

<table>
<thead>
<tr>
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<th>A</th>
<th>B</th>
<th>C</th>
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<tr>
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<td>1, 2 and 3</td>
<td>1 and 2</td>
<td>2 and 3</td>
<td>1 only</td>
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<td>are correct</td>
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No other combination of statements is to be used as a correct response.

31. Which of the following is/are correct statement(s) about a 12.0 g sample of $^{12}$C?

- **A** The number of atoms is $6.02 \times 10^{23}$.
- **B** The number of atoms is the same as the number of atoms in 4.0 g of $^4$He.
- **C** The number of atoms is the same as the number of atoms in 2.0 g of $^1$H$_2$.

32. The enthalpy change of reaction, $\Delta H_r$, between sodium and water (in excess) to produce sodium hydroxide and hydrogen gas can be measured in the laboratory.

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \xrightarrow{\Delta H_r} 2\text{NaOH}(aq) + \text{H}_2(g)$$

Other than temperature change of the solution, what information is/are needed to calculate a value for the enthalpy change of this reaction?

1. Mass of water
2. Mass of sodium
3. Pressure

33. 0.1 mol of each of the following is separately added to 100 cm$^3$ of water.

Which of the following resulting solution(s) show an increasing order of pH values?

1. **PCl$_3$**, **A/Cl$_3$**, **NaCl**
2. **NH$_3$**, **NaOH**, **Ba(OH)$_2$**
3. **HCl**, **CH$_3$CO$_2$H**, **CH$_3$CH$_2$OH**
34 Which of the following reaction(s) is/are always endothermic?
   1 Hydration of a gaseous ion
   2 The dissociation of a diatomic molecule into atoms
   3 The sublimation of a solid

35 The table below shows the solubility product, in mol dm$^{-3}$ for three metal sulfides. In an acidic solution, $[S^{2-}]_{\text{saturated}} = 10^{-18}$ mol dm$^{-3}$.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Mn$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Ag$^+$</th>
</tr>
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<tbody>
<tr>
<td>$K_{\text{sp}}$ of sulfide</td>
<td>$10^{-16}$</td>
<td>$10^{-21}$</td>
<td>$10^{-36}$</td>
</tr>
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</table>

Which of the metal sulfide(s) would be precipitated from the acidic solution containing 0.010 mol dm$^{-3}$ of the metal ion when the solution is saturated with hydrogen sulfide?

1 Mn$^{2+}$
2 Ni$^{2+}$
3 Ag$^+$

36 The compound 2-ethylhexyl-p-methoxycinnamate (MOC) is used as a sunscreen.

![Structural formula of MOC](image)

Which of the following statement(s) is/are correct?

1 A brown precipitate is formed with cold alkaline KMnO$_4$.
2 A racemic mixture is produced when it is boiled with HCl (g).
3 It is insoluble in organic solvents.
A hydrocarbon, on heating with acidified KMnO$_4$ gives CH$_3$CH$_2$COCH$_2$CH$_2$CH$_2$CH$_2$COOH.

Which of the following is/are possible structure(s) of the hydrocarbon?

1

2

3

Which of the following reaction(s) could have the same intermediate?

1 CH$_3$CH=CH$_2$ $\rightarrow$ intermediate $\rightarrow$ CH$_3$CH(NH$_2$)CH$_3$

2 CH$_3$CH=CH$_2$ $\rightarrow$ intermediate $\rightarrow$ CH$_3$COCH$_3$

3 CH$_3$CO$_2$CH(CH$_3$)$_2$ $\rightarrow$ intermediate $\rightarrow$ CH$_3$CHBrCH$_3$

Psilocin is a psychedelic mushroom alkaloid. It is the active compound that produces hallucinations from ingesting “magic mushrooms” and amplifies sensory experience. Compound Y is a derivative of Psilocin.

Which of the following statement(s) is/are true about Y?

1 It gives white fumes with CH$_3$COCl.

2 It dissolves in both aqueous acids and alkalis.

3 The nitrogen-containing group in the ring has a lower pK$_b$ than the nitrogen-containing group in the side chain.
The Grignard reaction is a very important tool in organic reactions involving the formation of carbon-carbon bond. Grignard reagents are formed by reacting halogenoalkane, R-X, with magnesium in dry ether.

For example, reaction of CH$_3$Cl with Mg,

$$\text{CH}_3\text{Cl} + \text{Mg} \xrightleftharpoons{\text{dry ether}} \text{H}_2\text{C} \delta^- \text{Mg} \delta^+ \text{Cl}$$

Grignard reagents allow the carbon chain of carbonyl compounds to be lengthened.

For example,

$$\text{CH}_3\text{CH} \xrightarrow{1. \text{CH}_3\text{MgCl, ether}} \text{OH} \xrightarrow{2. \text{H}_3\text{O}^+} \text{CH}_3\text{CH}$$

Which compounds could be made from a ketone and a Grignard reagent?

1. CH$_3$C(CH$_2$CH$_3$)$_2$OH
2. CH$_3$CH$_2$CH$_2$CH$_2$OH
3. (CH$_3$CH$_2$)$_2$CHOH
INSTRUCTIONS TO CANDIDATES

1. Do not turn over this question paper until you are told to do so.
2. Write your name, class and admission number in the spaces provided at the top of this page and on the OMR provided.
3. Answer ALL questions and shade the correct answers on the OMR provided using a soft pencil.
4. No extra time will be given for shading.
5. Hand in the question paper and the OMR separately.

INFORMATION FOR CANDIDATES
Marks will not be deducted for wrong answers; your total score will be the number of correct answers given.

FOR EXAMINER’S USE
TOTAL (40 marks)

This question paper consists of 16 printed pages.
Answer all questions on the OMR form provided (40 Marks)

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<td>Al/Cl\textsubscript{3} and CO\textsubscript{3}\textsuperscript{2-}</td>
<td></td>
<td>NH\textsubscript{4}\textsuperscript{+} and CH\textsubscript{4}</td>
<td></td>
<td>NH\textsubscript{3} and H\textsubscript{3}O\textsuperscript{+}</td>
<td></td>
<td>SeF\textsubscript{4} and SO\textsubscript{4}\textsuperscript{2-}</td>
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3 The following graph shows how ionic radius changes across Period 3 for seven elements.

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4 In which of the following reactions is the acid acting as an oxidant?

A  \( \text{KBr} + \text{H}_3\text{PO}_4 \rightarrow \text{HBr} + \text{KH}_2\text{PO}_4 \)

B  \( \text{MgO} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O} \)

C  \( 12\text{HCIO}_4 + \text{P}_4\text{O}_{10} \rightarrow 6\text{Cl}_2\text{O}_7 + 4\text{H}_3\text{PO}_4 \)

D  \( \text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2 \)

5 A 1 dm\(^3\) flask containing helium at 2 kPa pressure is connected (at constant temperature) to a 2 dm\(^3\) flask containing neon at 1 kPa pressure. What is the final pressure after connection?

A  \( \frac{4}{3} \) kPa

B  \( \frac{3}{2} \) kPa

C  \( \frac{5}{3} \) kPa

D  2 kPa

6 The use of the Data Booklet is relevant to this question.

Phosphorus, \( \text{P}_4 \), has the following molecular structure:

Imagine that nitrogen were to form a similar molecule \( \text{N}_4 \) shown in the reaction below:

\[ 2\text{N}_2(g) \rightarrow \text{N}_4(g) \]

What would be the value of \( \Delta H \) (in kJ mol\(^{-1}\)) for the above reaction?

A  1028

B  1348

C  1954

D  2628
7. Which gas shows the greatest deviation from ideal gas behavior?

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<td>A</td>
<td>HCl</td>
</tr>
<tr>
<td>B</td>
<td>He</td>
</tr>
<tr>
<td>C</td>
<td>CH₄</td>
</tr>
<tr>
<td>D</td>
<td>N₂</td>
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</table>

8. The use of the data booklet is relevant to this question.

In many areas, tap water is slightly acidic due to dissolved carbon dioxide. Which metal will not be dissolved by tap water containing carbon dioxide?

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<td>Cr</td>
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<td>B</td>
<td>Cu</td>
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<tr>
<td>C</td>
<td>Fe</td>
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<tr>
<td>D</td>
<td>Pb</td>
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9. Which of the following mixtures is not an acid/conjugate base pair?

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<td>A</td>
<td>H₂O/OH⁻</td>
</tr>
<tr>
<td>B</td>
<td>H₂PO₄⁻/HPO₄²⁻</td>
</tr>
<tr>
<td>C</td>
<td>NaH/Na</td>
</tr>
<tr>
<td>D</td>
<td>NH₃/NH₂⁻</td>
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10. Which of the following pairs of solutions would form an acidic buffer when mixed?

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<tr>
<td>A</td>
<td>HCN and NaCN</td>
</tr>
<tr>
<td>B</td>
<td>HNO₃ and NaNO₃</td>
</tr>
<tr>
<td>C</td>
<td>NaOH and NaCl</td>
</tr>
<tr>
<td>D</td>
<td>HCl and NaOH</td>
</tr>
</tbody>
</table>

11. Bleaching solutions are manufactured by dissolving chlorine gas in sodium hydroxide solution to give the following reaction.

\[
\text{Cl}_2 (g) + 2\text{OH}^-(aq) \rightarrow \text{OC}^- (aq) + \text{Cl}^- (aq) + \text{H}_2\text{O (l)}
\]

Users are warned not to mix the bleach with other cleaning solutions to prevent evolution of hazardous chlorine gas. Which of the following actions will lead to liberation of chlorine gas?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Addition of water to bleach</td>
</tr>
<tr>
<td>B</td>
<td>Mixing of an alkali with bleach</td>
</tr>
<tr>
<td>C</td>
<td>Shaking bleach with table salt, NaCl</td>
</tr>
<tr>
<td>D</td>
<td>Subjecting bleach to high pressure</td>
</tr>
</tbody>
</table>
Given that,

Equilibrium I: \[ C (s) + O_2 (g) \rightleftharpoons CO_2 (g) \quad K_{c1} = 3 \]
Equilibrium II: \[ C (s) + \frac{1}{2} O_2 (g) \rightleftharpoons CO (g) \quad K_{c2} = 2 \]
Equilibrium III: \[ CO (g) + \frac{1}{2} O_2 (g) \rightleftharpoons CO_2 (g) \quad K_c = ? \]

What is the numerical \( K_c \) value for the Equilibrium III?

<table>
<thead>
<tr>
<th></th>
<th>( \frac{\sqrt{2}}{3} )</th>
<th>( \frac{\sqrt{3}}{2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \frac{2}{3} )</td>
<td>( \frac{3}{2} )</td>
</tr>
<tr>
<td>B</td>
<td>( \frac{2}{3} )</td>
<td>( \frac{3}{2} )</td>
</tr>
</tbody>
</table>

The rate of removal of the pain-killing drug paracetamol from the body is a first order reaction with a rate constant, \( k \), of 0.26 h\(^{-1}\).

How long will it take for 6.25% of the paracetamol ingested to remain in the body?

<table>
<thead>
<tr>
<th></th>
<th>2.7 hours</th>
<th>8.1 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.6 hours</td>
<td>13.5 hours</td>
</tr>
<tr>
<td>B</td>
<td>10.6 hours</td>
<td>13.5 hours</td>
</tr>
</tbody>
</table>

Sulfates of Group II metals exist as crystalline form as follows:

\[ \text{MgSO}_4.7\text{H}_2\text{O} \quad \text{CaSO}_4.2\text{H}_2\text{O} \quad \text{SrSO}_4 \quad \text{BaSO}_4 \]

Which one of the following accounts for this trend in hydration?

<table>
<thead>
<tr>
<th></th>
<th>The atomic radius of the elements increases down the group.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>The ionic character of these sulfates increases down the group.</td>
</tr>
<tr>
<td>B</td>
<td>The ionisation energy of the elements decreases down the group.</td>
</tr>
<tr>
<td>C</td>
<td>The radius of the cation increases down the group.</td>
</tr>
</tbody>
</table>

\( X \) is a mixture of two compounds. When \( X \) is treated with an excess of dilute hydrochloric acid, a colour gas is evolved and some, but not all of the mixture dissolves.

Which one of the following mixtures could be \( X \)?

<table>
<thead>
<tr>
<th></th>
<th>Ba(NO(_3))(_2) and Ca(OH)(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ag(_2)SO(_4) and CaCO(_3)</td>
</tr>
<tr>
<td>B</td>
<td>CaCO(_3) and MgSO(_4)</td>
</tr>
<tr>
<td>C</td>
<td>Ca(OH)(_2) and MgCO(_3)</td>
</tr>
<tr>
<td>D</td>
<td>Ca(OH)(_2) and MgCO(_3)</td>
</tr>
</tbody>
</table>
A yellow precipitate of cadmium(II) sulfide is formed when $\text{H}_2\text{S}$ is passed into an aqueous solution of cadmium(II) ions, $\text{Cd}^{2+}$. This precipitate is also obtained in the presence of dilute hydrochloric acid but not in the presence of concentrated hydrochloric acid nor in excess potassium chloride. Which explanation accounts for all these observations?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>The presence of a high concentration of $\text{H}^+$ (aq) suppresses the ionisation of $\text{H}_2\text{S}$ (aq).</td>
</tr>
<tr>
<td>B</td>
<td>The concentration of $\text{S}^{2-}$ (aq) is reduced by the formation of $\text{SCl}_4^{2-}$ (aq).</td>
</tr>
<tr>
<td>C</td>
<td>$\text{CdS}$ (s) is insoluble in concentrated HCl (aq).</td>
</tr>
<tr>
<td>D</td>
<td>$\text{Cd}^{2+}$ (aq) ions react with $\text{Cl}^-$ (aq) to form the complex ion $[\text{CdCl}_4]^{2-}$ (aq).</td>
</tr>
</tbody>
</table>

A current of 2.0 A is used to plate Ni(s) from 500 cm$^3$ of a 1.00 mol dm$^{-3}$ $\text{Ni}^{2+}$ (aq) solution. What is the concentration of $\text{Ni}^{2+}$ (aq) after 3.0 hours?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.39 mol dm$^{-3}$</td>
</tr>
<tr>
<td>B</td>
<td>0.46 mol dm$^{-3}$</td>
</tr>
<tr>
<td>C</td>
<td>0.78 mol dm$^{-3}$</td>
</tr>
<tr>
<td>D</td>
<td>0.89 mol dm$^{-3}$</td>
</tr>
</tbody>
</table>

Which one of the following statements is correct about a reaction for which the equilibrium constant is independent of temperature?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>The enthalpy change of reaction is zero.</td>
</tr>
<tr>
<td>B</td>
<td>Its rate constants do not vary with temperature.</td>
</tr>
<tr>
<td>C</td>
<td>There are equal numbers of moles of reactants and products.</td>
</tr>
<tr>
<td>D</td>
<td>The activation energies for both the forward and reverse reactions are zero.</td>
</tr>
</tbody>
</table>
Magnesium iodate(V) undergoes thermal decomposition to yield products as shown by the equation below. The other Group II iodates(V) also undergo similar thermal decomposition.

\[ 2\text{Mg(IO}_3\text{)}_2(\text{s}) \rightarrow 2\text{MgO(s)} + 2\text{I}_2(\text{g}) + 5\text{O}_2(\text{g}) \]

The three graphs given below show the change in mass when 2.00 g each of three Group II iodates(V) are heated separately at a temperature T.

Which three Group II iodates(V) give rise to these graphs?

<table>
<thead>
<tr>
<th>Graph (1)</th>
<th>Graph (2)</th>
<th>Graph (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ca(IO}_3\text{)}_2</td>
<td>Mg(IO}_3\text{)}_2</td>
</tr>
<tr>
<td>B</td>
<td>Mg(IO}_3\text{)}_2</td>
<td>Ba(IO}_3\text{)}_2</td>
</tr>
<tr>
<td>C</td>
<td>Ca(IO}_3\text{)}_2</td>
<td>Mg(IO}_3\text{)}_2</td>
</tr>
<tr>
<td>D</td>
<td>Sr(IO}_3\text{)}_2</td>
<td>Ba(IO}_3\text{)}_2</td>
</tr>
</tbody>
</table>

A compound X exhibits structural isomerism, the isomers being members of different homologous series.

To which pair of isomers could X belong?

| A | acyl chlorides and carboxylic acids |
| B | **carboxylic acids and esters** |
| C | amino acids and ammonium salts |
| D | amides and amino acids |

What is the total number of structural and geometrical isomers for a compound with molecular formula C}_3\text{H}_7\text{F}, excluding cyclic structures?

| A | 3 |
| B | 4 |
| C | 5 |
| D | 6 |
1,2-dibromo-3-chloropropane (DBCP) has been used in the control of earthworms in agricultural land. The structure of DBCP is shown below.

Which of the following reactions will lead to the highest yield of DBCP?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₂=CHCH₂Cl + Br₂ / CCl₄ → DBCP</td>
</tr>
<tr>
<td>B</td>
<td>CH₂=CHCHBr₂ + HCl (g) → DBCP</td>
</tr>
<tr>
<td>C</td>
<td>CH₃CH₂CH₂Cl + 2Br₂ / uv light → DBCP + 2HBr</td>
</tr>
<tr>
<td>D</td>
<td>CH₃CHBrCH₂Br + BrCl / uv light → DBCP + HCl</td>
</tr>
</tbody>
</table>

Compound J, C₅H₁₁Cl undergoes the following reaction.

\[
\text{C}_5\text{H}_11\text{Cl} \xrightarrow{\text{Ethanolic KOH}} \text{C}_5\text{H}_{10}
\]

Which of the following cannot be Compound J?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1-chloropentane</td>
</tr>
<tr>
<td>B</td>
<td>2-chloropentane</td>
</tr>
<tr>
<td>C</td>
<td>2–chloro-3-methylbutane</td>
</tr>
<tr>
<td>D</td>
<td>1-chloro-2,2-dimethypropane</td>
</tr>
</tbody>
</table>
A polypeptide was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

<table>
<thead>
<tr>
<th>Digestion using enzyme N:</th>
</tr>
</thead>
<tbody>
<tr>
<td>thr-phe-leu</td>
</tr>
<tr>
<td>cys-glu-val</td>
</tr>
<tr>
<td>ser-glu-cys</td>
</tr>
<tr>
<td>asp-cys</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Digestion using the enzyme O:</th>
</tr>
</thead>
<tbody>
<tr>
<td>val-asp-cys-thr</td>
</tr>
<tr>
<td>phe-leu-ser</td>
</tr>
<tr>
<td>glu-cys</td>
</tr>
<tr>
<td>cys-glu</td>
</tr>
</tbody>
</table>

What is the correct sequence of the polypeptide structure?

<table>
<thead>
<tr>
<th>Option</th>
<th>Sequence</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>cys-glu-val-ser-glu-cys-asp-cys-thr-phe-leu</td>
</tr>
<tr>
<td>B</td>
<td>cys-glu-val-asp-cys-thr-phe-leu-ser-glu-cys</td>
</tr>
<tr>
<td>C</td>
<td>glu-cys-glu-val-asp-cys-thr-phe-leu-ser-glu</td>
</tr>
<tr>
<td>D</td>
<td>ser-glu-cys-glu-val-asp-cys-thr-phe-leu-ser</td>
</tr>
</tbody>
</table>
Methylbenzene and bromine, in the ratio of 1:6 were mixed and left under the sun and compound Q was isolated. After which, iron fillings were added to the mixture at room temperature and Compound R was identified to be the final product. Which of the following is likely to be Compounds Q and R?

<table>
<thead>
<tr>
<th></th>
<th>Compound Q</th>
<th>Compound R</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>B</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>C</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>D</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
</tbody>
</table>
One industrial preparation of ethanoic acid is the direct carbonylation of methanol using a rhodium catalyst.

\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{rhodium catalyst}} \text{CH}_3\text{CO}_2\text{H}
\]

Which compound could be used to produce \(\text{HC}—\text{CH}_2\text{CO}_2\text{H}\) by this method?

(A) \(\text{OH} \quad \text{HC}—\text{CH}_2\text{CO}_2\text{H} \quad \text{CO}_2\text{H}\)

(B) \(\text{CO}_2\text{H} \quad \text{HC}—\text{CO}_2\text{H} \quad \text{CH}_2\text{OH}\)

(C) \(\text{OH} \quad \text{HC}—\text{CH}_2\text{OH} \quad \text{CH}_2\text{OH}\)

(D) \(\text{CH}_2\text{OH} \quad \text{HC}—\text{CH}_2\text{OH} \quad \text{CH}_2\text{OH}\)

Tamoxifen is widely used in the treatment of breast cancer.

What is the number of \(sp^2\) and \(sp^3\) carbon atoms respectively after subjecting Tamoxifen to hydrogen gas under heat and in the presence of nickel?

(A) 6 20

(B) 8 18

(C) 18 8

(D) 20 6
**28** The reduction of a nitrile produces a compound of formula C₃H₇NH₂. Which of the following would be produced if the same nitrile is heated with hydrochloric acid?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₃CONH₂</td>
</tr>
<tr>
<td>B</td>
<td>CH₃CH₂COOH</td>
</tr>
<tr>
<td>C</td>
<td>(CH₃)₂CHCOOH</td>
</tr>
<tr>
<td>D</td>
<td>CH₃CH₂OH</td>
</tr>
</tbody>
</table>

**29** GABA has the structural formula, H₂NCH₂CH₂CH₂CO₂H. It is a neurotransmitter released by red algae to encourage shellfish larvae to settle on the ocean bed. How does GABA differ from amino acids obtained by the hydrolysis of proteins?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>It does not form zwitterions.</td>
</tr>
<tr>
<td>B</td>
<td>It is not a 2-aminocarboxylic acid.</td>
</tr>
<tr>
<td>C</td>
<td>It is insoluble in water.</td>
</tr>
<tr>
<td>D</td>
<td>It cannot form a polyamide linkage.</td>
</tr>
</tbody>
</table>

**30** Which property enables proteins to function as a pH buffer?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Proteins contain the carboxyl and amino groups.</td>
</tr>
<tr>
<td>B</td>
<td>Proteins are soluble.</td>
</tr>
<tr>
<td>D</td>
<td>Proteins have high molecular mass.</td>
</tr>
<tr>
<td>D</td>
<td>Proteins possess secondary and tertiary structures.</td>
</tr>
</tbody>
</table>
For questions 31 – 40, the responses A to D should be selected on the basis of

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>1,2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31. Which of the following is/are correct statement(s) about a 12.0 g sample of $^{12}$C?

A. The number of atoms is $6.02 \times 10^{23}$.

B. The number of atoms is the same as the number of atoms in 4.0 g of $^4$He.

C. The number of atoms is the same as the number of atoms in 2.0 g of $^1$H$_2$.

32. The enthalpy change of reaction, $\Delta H_r$, between sodium and water (in excess) to produce sodium hydroxide and hydrogen gas can be measured in the laboratory.

$$2\text{Na(s) + 2H}_2\text{O(l)} \underset{\Delta H_r}{\rightarrow} 2\text{NaOH(aq) + H}_2(\text{g})$$

Other than temperature change of the solution, what information is/are needed to calculate a value for the enthalpy change of this reaction?

1. Mass of water
2. Mass of sodium
3. Pressure

33. 0.1 mol of each of the following is separately added to 100 cm$^3$ of water.

Which of the following resulting solution(s) show an increasing order of pH values?

1. PCl$_3$, AlCl$_3$, NaCl
2. NH$_3$, NaOH, Ba(OH)$_2$
3. HC$_3$, CH$_3$CO$_2$H, CH$_3$CH$_2$OH
34 Which of the following reaction(s) is/are always endothermic?

1. Hydration of a gaseous ion
2. The dissociation of a diatomic molecule into atoms
3. The sublimation of a solid

35 The table below shows the solubility product, in mol dm\(^{-3}\), for three metal sulfides. In an acidic solution, \([S^{2-}]_{\text{saturated}} = 10^{-18}\) mol dm\(^{-3}\).

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Mn(^{2+})</th>
<th>Ni(^{2+})</th>
<th>Ag(^{+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{sp}) of sulfide</td>
<td>10(^{-16})</td>
<td>10(^{-21})</td>
<td>10(^{-36})</td>
</tr>
</tbody>
</table>

Which of the metal sulfide(s) would be precipitated from the acidic solution containing 0.010 mol dm\(^{-3}\) of the metal ion when the solution is saturated with hydrogen sulfide?

1. Mn\(^{2+}\)
2. Ni\(^{2+}\)
3. Ag\(^{+}\)

36 The compound 2-ethylhexyl-p-methoxycinnamate (MOC) is used as a sunscreen.

\[
\text{CH}_3\text{O}-\text{CH}\equiv\text{CHCO}_2\text{C}_8\text{H}_{17}
\]

Which of the following statement(s) is/are correct?

1. A brown precipitate is formed with cold alkaline KMnO\(_4\).
2. A racemic mixture is produced when it is boiled with HCl (g).
3. It is insoluble in organic solvents.
37 A hydrocarbon, on heating with acidified KMnO₄ gives CH₃CH₂COCH₂CH₂CH₂CH₂COOH. Which of the following is/are possible structure(s) of the hydrocarbon?

1

2

3

38 Which of the following reaction(s) could have the same intermediate?

1 CH₃CH=CH₂ → intermediate → CH₃CH(NH₂)CH₃

2 CH₃CH=CH₂ → intermediate → CH₃COCH₃

3 CH₃CO₂CH(CH₃)₂ → intermediate → CH₃CHBrCH₃

39 *Psilocin* is a psychedelic mushroom alkaloid. It is the active compound that produces hallucinations from ingesting “magic mushrooms” and amplifies sensory experience. Compound Y is a derivative of *Psilocin*.

![Psilocin](image)

Which of the following statement(s) is/are true about Y?

1 It gives white fumes with CH₃COCl.

2 It dissolves in both aqueous acids and alkalis.

3 The nitrogen-containing group in the ring has a lower pKₐ than the nitrogen-containing group in the side chain.
The Grignard reaction is a very important tool in organic reactions involving the formation of carbon-carbon bond. Grignard reagents are formed by reacting halogenoalkane, R-X, with magnesium in dry ether.

For example, reaction of CH$_3$Cl with Mg,

\[
\text{CH}_3\text{Cl} + \text{Mg} \xrightarrow{\text{dry ether}} \text{H}_2\text{C} \text{MgCl}
\]

Grignard reagents allow the carbon chain of carbonyl compounds to be lengthened.

For example,

\[
\text{CH}_3\text{CH} \xrightarrow{1. \text{CH}_3\text{MgCl, ether}} \text{CH}_3\text{CH} \xrightarrow{2. \text{H}_3\text{O}^+} \text{CH}_3\text{CH} - \text{CH}_3
\]

Which compounds could be made from a ketone and a Grignard reagent?

1. CH$_3$C(CH$_2$CH$_3$)$_2$OH
2. CH$_3$CH$_2$CH$_2$OH
3. (CH$_3$CH$_2$)$_2$CHOH

END OF PAPER
2012 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY
9647/02

Paper 2
18 Sept 2012
2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

1. Do not turn over this question paper until you are told to do so.
2. Write your name, class and index number in the spaces provided at the top of this page.
3. Write in dark blue or black pen in the spaces provided on the Question Paper.
4. You may use a soft pencil for any diagrams or graphs.
5. DO NOT use paper clips, highlighters, glue or correction fluid or tape.
6. Answer ALL the questions.
7. Give non-exact numerical answers correct to 3 significant figures, or 1 decimal place in the case of M, and A, unless a different level of accuracy is specified in the question.
8. The number of marks is given in brackets [ ] at the end of each question or part question.
9. You are reminded of the need for clear presentation in your answers and to show all working in calculations.
10. The use of a calculator is expected, where appropriate.

<table>
<thead>
<tr>
<th>Question No</th>
<th>Marks Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (12m)</td>
<td></td>
</tr>
<tr>
<td>2 (9m)</td>
<td></td>
</tr>
<tr>
<td>3 (10m)</td>
<td></td>
</tr>
<tr>
<td>4 (16m)</td>
<td></td>
</tr>
<tr>
<td>5 (10m)</td>
<td></td>
</tr>
<tr>
<td>6 (15m)</td>
<td>72</td>
</tr>
</tbody>
</table>

This question paper consists of 16 printed pages.

[Turn over
1 **Planning**

The benzenediazonium ion, \( \text{C}_6\text{H}_5\text{N}_2^+ \), reacts with water as shown in the equation.

\[
\text{C}_6\text{H}_5\text{N}_2^+ (\text{aq}) + \text{H}_2\text{O} (l) \rightarrow \text{C}_6\text{H}_5\text{OH} (\text{aq}) + \text{N}_2 (g) + \text{H}^+ (\text{aq})
\]

At temperatures below 10 °C, the reaction is very slow. However, nitrogen gas is evolved at a measurable rate at temperatures of 20 °C and above.

In this experiment, you are provided with an aqueous solution containing 0.100 mol dm\(^{-3}\) of the benzenediazonium ion at a temperature below 10 °C.

You are required to design an experiment to deduce the order of reaction with respect to \( \text{C}_6\text{H}_5\text{N}_2^+ \) of an aqueous solution at 20 °C and an atmospheric pressure of 101 kPa.

(a) Define the term *order of reaction*.

................................................................................................................................................
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(b) Outline the steps you would take to determine the order of reaction with respect to \( \text{C}_6\text{H}_5\text{N}_2^+ (\text{aq}) \) at 20 °C. In your plan, include the following details:

- a suitable volume of \( \text{C}_6\text{H}_5\text{N}_2^+ (\text{aq}) \) used,
- measurement(s) to be taken,
- plotting of a suitable graph, if any.
(c) Draw a labelled diagram of the experimental set-up.
[You may assume that you are given common apparatus found in a school laboratory.]

(d) Describe how you will use the results obtained to determine the order of reaction with respect to C₆H₅N₂⁺ (aq).

(e) Identify one potential hazard in this experiment and suggest the safety precaution you would take to overcome this.

[Total: 12 marks]
2 (a) A lower secondary Science student described an atom of Silicon as having ‘fourteen bees buzzing around a space the size of a football stadium, as though they are being trapped.’

(i) Explain using Chemistry concepts, what do the bees in the description represent and what stopped the bees from flying away from the stadium?

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(b) Amongst all the elements in Period 3 of the periodic table, Silicon has the highest melting point. Sketch a graph to illustrate the trend of the melting points of elements in Period 3. Explain your sketch.
(c) Silicon reacts with oxygen to form silicon dioxide as a possible product. In dentistry, a composite material based on SiO₂ has been developed to be used as dental fillings.

(i) State one property of SiO₂ that makes it suitable for use as dental fillings.

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(ii) Draw a diagram to illustrate the type of bonding involved in SiO₂. [2]

3 Ammonia gas decomposes into nitrogen and hydrogen when passed over a platinum gauze. The rate of decomposition is found to be independent of the partial pressure of ammonia at very high pressures, but the rate was directly proportional to the partial pressure of ammonia at low pressures.

(a) Explain this observation as far as you can. [2]

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(b) Given that 45% of ammonia dissociated into nitrogen and hydrogen at moderately high temperatures, and a total pressure of 1 atm, calculate the value of $K_p$, stating its units. [3]

(c) Ammonia, nitrogen and hydrogen are non-ideal gases.

(i) State two assumptions of the kinetic theory as applied to an ideal gas.

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(ii) Which of these three gases deviates the most from an ideal gas? Explain your answer.

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(iii) For a given fixed mass of an ideal gas, sketch graphs of:

I: $P$ against $V$ at constant $T$ (where $P$ represents pressure)

II: $V$ against $pV$ at constant $T$ (where $p$ represents density) [5]

[Total: 10 marks]
4 The reaction between phenol and benzoyl chloride produces an ester with the formula C₆H₅COOC₆H₅. Hydrogen chloride is also formed in this reaction.

<table>
<thead>
<tr>
<th>Name of Compound</th>
<th>Chemical formula</th>
<th>M_r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>C₆H₅OH</td>
<td>94.0</td>
</tr>
<tr>
<td>Benzoyl chloride</td>
<td>C₆H₅COCl</td>
<td>140.5</td>
</tr>
<tr>
<td>?</td>
<td>C₆H₅COOC₆H₅</td>
<td>198.0</td>
</tr>
</tbody>
</table>

The crude (impure) ester produced in the reaction can be purified by recrystallisation in ethanol. A typical yield, based on benzoyl chloride is 70%.

[Additional info:
Melting point of ester: 68- 70 ºC
Boiling point of ester: 298- 299 ºC]

(a) State the name of the ester that is produced in the reaction. [1]

(b) Explain why this reaction will not occur if benzoic acid was used instead of benzoyl chloride. [1]

(c) In this experiment, only 70% of benzoyl chloride is converted into the ester.
(i) Calculate the minimum mass of benzoyl chloride needed to form 5 g of the ester.
(ii) Hence, calculate the minimum mass of phenol needed in the reaction. [2]

(d) Briefly describe how the crude (impure) ester produced can be purified by recrystallisation in ethanol.

(i) ................................................................. .................................................................
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(ii) Suggest and explain a method that can be used to check the purity of the ester produced. [4]

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Another ester, \( P \) \((M_r = 116)\) used in synthetic fruit flavors, is subjected to hydrolysis to give a monoprotic acid, \( Q \) and an alcohol, \( R \).

When 1.00 g of \( Q \) is titrated with 0.500 mol dm\(^{-3}\) NaOH, 33.0 cm\(^3\) of NaOH is required for neutralization. \( R \) reacts with alkaline aqueous iodine to give a precipitate \( S \). Compound \( R \) exists as a pair of isomers, both of which are oxidized to give \( T \) which also reacts with alkaline aqueous iodine to give the same precipitate \( S \), and a solution \( U \).

Identify the structures \( P \), \( Q \), \( R \), \( S \), \( T \) and \( U \), explaining your deductions clearly.

[Total: 16 marks]
This question discusses metals in Group I and Group II of the Periodic table.

(a) For a group I element, the ease with which the following reaction occurs is indicated by its electrode potential, $E^0$. 

$$\text{M(s)} \rightarrow \text{M}^+ (aq) + e^-$$  

-------- Reaction (I)

Calculate the enthalpy change of Reaction (I) for Li and Na, using values given below as well as relevant data from the data booklet.

<table>
<thead>
<tr>
<th>Element (M)</th>
<th>$\Delta H_{\text{at}} (\text{M})$ / kJ mol$^{-1}$</th>
<th>$\Delta H_{\text{hydration}} (\text{M}^+) /$ kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>159</td>
<td>-957</td>
</tr>
<tr>
<td>Na</td>
<td>107</td>
<td>-841</td>
</tr>
</tbody>
</table>

(b) Comment on the relationship between the enthalpy change of Reaction (I) obtained in (a) and the $E^0$ values given in the data booklet for Li and Na.
(c) The melting points of Group II oxides are given in the table below.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Melting point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>2852</td>
</tr>
<tr>
<td>CaO</td>
<td>2614</td>
</tr>
<tr>
<td>SrO</td>
<td>2430</td>
</tr>
<tr>
<td>BaO</td>
<td>1918</td>
</tr>
</tbody>
</table>

Explain the trend in the melting points. [2]

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(d) Describe the reactions, if any, for magnesium and calcium with cold water, writing equations, with state symbols, for any reactions taking place. [3]

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[Total: 10 marks]
Synthetic detergents (anionic, cationic and non-ionic) consist of a hydrocarbon chain and polar group. As a surfactant, the synthetic detergent is more effective than conventional soap in hard water – water that contains dissolved minerals such as Ca\(^{2+}\) and Mg\(^{2+}\).

**Anionic detergents**

Anionic detergents contain groups with a negative charge such as Na\(^+\)SO\(_3\)^\(-\). An example of synthesis of a detergent sodium-n-dodecylbenzenesulfonate is as follows:

\[
\begin{align*}
Benzene & \xrightarrow{H_2SO_4} \text{HO}_3S
\end{align*}
\[
\text{HO}_3S & \xrightarrow{\text{Reaction I}} \text{Na}^+\text{O}_3S
\]

**Cationic detergents**

Cationic detergents contain positively charged groups and can be found in hair conditioners. Keratin, a protein which contains negatively-charged groups which can be found on the surface of hair, binds strongly to the hydrophilic ends of cationic detergents. The hydrophobic ends of the surfactant molecules then act as the new hair surface. One example of such a detergent is trimethylhexadecylammonium chloride, \([\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+\text{Cl}^-\).

**Non-ionic detergents**

Non-ionic detergents are commonly used in dish-washing liquids. An example is pentaerythritol palmitate:
(a) State possible reagents and conditions to synthesize \([\text{CH}_3(\text{CH}_2)_{15}\text{N(CH}_3)_3]^+\) from (i) \(\text{CH}_3(\text{CH}_2)_{15}\text{NH}_2\).

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(ii) Name and draw the mechanism for the following synthesis.

\[
\begin{array}{c}
\text{苯} \\
\text{CH}_3(\text{CH}_2)_{15} \\
\end{array} \rightarrow \begin{array}{c}
\text{苯} \\
\text{HO}_3\text{S} \\
\end{array}
\]
[5]

(b) Suggest why non-ionic detergents are commonly used in dish-washing liquids.

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(c) Describe a chemical test that can be used to distinguish between sodium-n-dodecylbenzenesulfonate and pentaerythritol palmitate.
You are to include all reagents, conditions and expected observations. [2]

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(d) Apart from detergents or soap, cleaning products may also contain enzymes to degrade protein-based stains. Enzymes are proteins with a specific biological activity that are determined by their primary, secondary, tertiary and quaternary structures.
(i) Apart from its function as an enzyme, state one other function of proteins.
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(ii) Briefly describe with a well-labeled diagram, one example of a secondary structure of a protein. [3]
(e) The effectiveness of enzymes can be reduced by the addition of heavy metal ions such as Hg\(^+\) or Pb\(^{2+}\).

(i) Explain this phenomenon.

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(ii) Pb\(^{2+}\) typically forms complexes that are coloured. Explain why this is so. [4]

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[Total: 15 marks]

END OF PAPER
2012 Preliminary Examination II
Pre-university 3

H2 CHEMISTRY

Paper 2

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

1. Do not turn over this question paper until you are told to do so.
2. Write your name, class and index number in the spaces provided at the top of this page.
3. Write in dark blue or black pen in the spaces provided on the Question Paper.
4. You may use a soft pencil for any diagrams or graphs.
5. DO NOT use paper clips, highlighters, glue or correction fluid or tape.
6. Answer ALL the questions.
7. Give non-exact numerical answers correct to 3 significant figures, or 1 decimal place in the case of \( M \), and \( A_r \), unless a different level of accuracy is specified in the question.
8. The number of marks is given in brackets [ ] at the end of each question or part question.
9. You are reminded of the need for clear presentation in your answers and to show all working in calculations.
10. The use of a calculator is expected, where appropriate.

<table>
<thead>
<tr>
<th>Question No</th>
<th>1 (12m)</th>
<th>2 (9m)</th>
<th>3 (10m)</th>
<th>4 (16m)</th>
<th>5 (10m)</th>
<th>6 (15m)</th>
<th>Marks Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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<td>72</td>
</tr>
</tbody>
</table>

This question paper consists of 13 printed pages.
**Planning**

The benzenediazonium ion, $C_6H_5N_2^+$, reacts with water as shown in the equation.

$$C_6H_5N_2^+ (aq) + H_2O (l) \rightarrow C_6H_5OH (aq) + N_2 (g) + H^+ (aq)$$

At temperatures below 10 °C, the reaction is very slow. However, nitrogen gas is evolved at a measurable rate at temperatures of 20 °C and above.

In this experiment, you are provided with an aqueous solution containing 0.100 mol dm$^{-3}$ of the benzenediazonium ion at a temperature below 10 °C.

You are required to design an experiment to deduce the order of reaction with respect to $C_6H_5N_2^+$ of an aqueous solution at 20 °C and an atmospheric pressure of 101 kPa.

(a) Define the term *order of reaction*.

Order of reaction with respect to a reactant is the power of the concentration of that reactant in the experimentally determined rate equation. 

(b) Outline the steps you would take to determine the order of reaction with respect to $C_6H_5N_2^+$ (aq) at 20 °C. In your plan, include the following details:

- a suitable volume of $C_6H_5N_2^+$ (aq) used,
- measurements to be taken,
- plotting of a suitable graph, if any.

Assume 50 cm$^3$ of nitrogen gas to be collected. (Volume chosen has to be large enough for sufficient volume of $C_6H_5N_2^+$ solution used)

Using $pV = nRT$,

Amount of nitrogen gas to be collected = 0.002074 mol

= Amount of $C_6H_5N_2^+$ required

Thus, minimum volume of $C_6H_5N_2^+$ needed = 0.002074 / 0.1 = 20.7 cm$^3$

(To use 25 cm$^3$ of $C_6H_5N_2^+$ )

Use a water bath (no naked flame) to maintain a temperature of 20 °C for the reaction mixture.

Record the volume of nitrogen produced over regular time intervals of 5 minutes.

A graph of volume of nitrogen produced against time is plotted.
(c) Draw a labelled diagram of the experimental set-up.
[You may assume that you are given common apparatus found in a school laboratory.]

1 mark for suitable apparatus (use of well-greased gas syringe to collect nitrogen gas), well-labeled. 
1 mark for feasibility of set-up

(d) Describe how you will use the results obtained to determine the order of reaction with respect to C₆H₅N₂⁺ (aq).

From the graph of volume of nitrogen produced against time plotted, determine the time taken for nitrogen to be produced. (time taken for ½ of total volume, then ¾ of total volume, then all of nitrogen produced) 
If the time taken is constant, order of reaction with respect to C₆H₅N₂⁺ (aq) is one.

(e) Identify one potential hazard in this experiment and suggest the safety precaution you would take to overcome this.

The organic compounds are toxic and may cause irritation when in contact with the skin. 
Gloves should be worn during the experiment. 
OR 
Conduct the experiment in a fume cupboard to prevent inhaling of toxic fumes.

[Total: 12 marks]
A lower secondary Science student described an atom of Silicon as having ‘fourteen bees buzzing around a space the size of a football stadium, as though they are being trapped.’

(i) Explain using Chemistry concepts, what do the bees in the description represent and what stopped the bees from flying away from the stadium?

The bees represent electrons and the electrostatic attraction of the positively charged protons in the nucleus for the electrons presents the electrons from being lost.

(ii) The teacher commented that the student’s description of Silicon was incomplete. What is missing from the student’s description of Silicon?

The positively charged nucleus.

(iii) $^{28}$Si, $^{29}$Si, $^{30}$Si are isotopes of Silicon.

Explain why isotopes of Silicon undergo identical chemical reactions?

Chemical reactions depend on the electronic configuration of the substance.

Since isotopes have the same number of electrons but different number of neutrons, they still have identical chemical properties.

(b) Amongst all the elements in Period 3 of the periodic table, Silicon has the highest melting point. Sketch a graph to illustrate the trend of the melting points of elements in Period 3. Explain your sketch.

Na to Al

\begin{itemize}
  \item giant metallic structure
  \item strong electrostatic forces of attraction between metal cations and delocalised electron
  \item large amount of energy required to overcome those forces
  \item \begin{align*}
    \text{delocalised electrons} & \uparrow, \text{size of cations} \downarrow, \text{(charge on cation} \uparrow
  \end{align*}
\end{itemize}

\[ \begin{array}{c}
  \text{melting point} \\
  \text{proton no.}
\end{array} \]

\begin{itemize}
  \item Na, Mg, Si, Al, S, Cl, Ar
  \item high m.p.
\end{itemize}
strength of metallic bond $\uparrow$ $\therefore$ m.p. $\uparrow$

Si
giant covalent structure
large amount of energy required to break strong covalent bonds between Si atoms. $\therefore$ high m.p.

P to Ar
Simple molecular structure
weak temporary dipole – induced dipole forces of attraction between molecules relatively smaller amount of energy required to overcome those forces $\therefore$ low m.p.

size of electron cloud of molecules varies, $S_8>P_4>Cl_2>Ar$
size of electron cloud of molecules $\uparrow$, strength of temporary dipole – induced dipole forces of attraction $\uparrow$. $\therefore$ m.p.: $S_8>P_4>Cl_2>Ar$

(c) Silicon reacts with oxygen to form silicon dioxide as a possible product.
In dentistry, a composite material based on SiO$_2$ has been developed to be used as dental fillings.

(i) State one property of SiO$_2$ that makes it suitable for use as dental fillings.

SiO$_2$ is hard and resistant to chemical attack (Unreactive towards acids in food or saliva) $\therefore$

(ii) Draw a diagram to illustrate the type of bonding involved in SiO$_2$.[2]

Tetrahedral, similar to diamond.
Each Si is bonded to 4 O atoms, and each O is bonded to 2 Si atoms $\therefore$ [Total: 9 marks]

3 Ammonia gas decomposes into nitrogen and hydrogen when passed over a platinum gauze. The rate of decomposition is found to be independent of the partial pressure of ammonia at very high pressures, but the rate was directly proportional to the partial pressure of ammonia at low pressures.

(a) Explain this observation as far as you can.[2]

$2NH_3 \leftrightarrow N_2 + 3H_2$
When the pressure is high enough, the catalyst surface would be saturated with adsorbed ammonia molecules (By LCP, equilibrium shifts left at high pressure). Any decomposition products that are desorbed from the surface would immediately be replaced by incoming
adsorbed ammonia. Hence, rate of decomposition is constant.
At low pressure, the catalyst surface is not saturated with adsorbed ammonia molecules. Hence, rate of decomposition depends on the partial pressure of ammonia.

(b) Given that 45% of ammonia dissociated into nitrogen and hydrogen at moderately high temperatures, and a total pressure of 1 atm, calculate the value of $K_p$, stating its units.

\[
2\text{NH}_3 \leftrightarrow \text{N}_2 + 3\text{H}_2
\]

<table>
<thead>
<tr>
<th>I / mol</th>
<th>2</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C / mol</td>
<td>-0.9</td>
<td>+0.45</td>
<td>+1.35</td>
</tr>
<tr>
<td>E / mol</td>
<td>1.1</td>
<td>0.45</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Total amount at eqm = 2.90

\[P_{\text{NH}_3} = 1.1 / 2.9 = 0.3793 \text{ atm}
\]

\[P_{\text{N}_2} = 0.1552 \text{ atm}
\]

\[P_{\text{H}_2} = 0.4655 \text{ atm}
\]

\[K_p = (0.1552) (0.4655)^3 / 0.3793^2 = 0.109 \text{ atm}^{-2} \text{ (3s.f.) (with units stated)}
\]

(c) Ammonia, nitrogen and hydrogen are non-ideal gases.

(i) State two assumptions of the kinetic theory as applied to an ideal gas.

Gas particles have negligible volume as compared to the volume of the whole gas.
Gas particles have negligible intermolecular forces of attraction.

(ii) Which of these three gases deviates the most from an ideal gas? Explain your answer.

Ammonia, due to formation of hydrogen bonding (strongest intermolecular force) between its molecules. Thus, the intermolecular forces of attraction are significant.

(iii) For a given fixed mass of an ideal gas, sketch graphs of:

I: $P$ against $V$ at constant $T$ (where $P$ represents pressure)
II: $V$ against $pV$ at constant $T$ (where $p$ represents density)

[Total: 10 marks]
The reaction between phenol and benzoyl chloride produces an ester with the formula $C_6H_5COOC_6H_5$. Hydrogen chloride is also formed in this reaction.

<table>
<thead>
<tr>
<th>Name of Compound</th>
<th>Chemical formula</th>
<th>$M_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>$C_6H_5OH$</td>
<td>94.0</td>
</tr>
<tr>
<td>Benzoyl chloride</td>
<td>$C_6H_5COC_1$</td>
<td>140.5</td>
</tr>
<tr>
<td>?</td>
<td>$C_6H_5COOC_6H_5$</td>
<td>198.0</td>
</tr>
</tbody>
</table>

The crude (impure) ester produced in the reaction can be purified by *recrystallisation in ethanol*. A typical yield, based on benzoyl chloride is 70%.

[Additional info:  
Melting point of ester: 68 - 70 °C  
Boiling point of ester: 298 - 299 °C]

(a) State the name of the ester that is produced in the reaction. [1]

Phenyl Benzoate

(b) Explain why this reaction will not occur if benzoic acid was used instead of benzoyl chloride. [1]

Phenol is weakly acidic. In the presence of a stronger acid (benzoyl acid), phenol can act as a base to react with benzoyl chloride to form esters.

(c) In this experiment, only 70% of benzoyl chloride is converted into the ester. Calculate the minimum mass of benzoyl chloride needed to form 5 g of the ester. [1]

Amount of ester = $\frac{5}{198} = 0.02525 \text{ mol} = \text{amount of benzoyl chloride}$  
Minimum mass of benzoyl chloride required = $100/70 \times 0.02525 \times 140.5 = 5.07 \text{ g (3s.f)}$

(ii) Hence, calculate the minimum mass of phenol needed in the reaction. [2]

Mass of phenol required = $100/70 \times 0.02525 \times 94.0 = 3.39 \text{ g (3s.f)}$

(d) Briefly describe how the crude (impure) ester produced can be purified by *recrystallisation in ethanol*. [1]
Dissolve the crude ester in hot ethanol, until a saturated solution is obtained. Filter and allow the hot solution to cool. Crystals will form upon cooling. Dry the crystals using filter paper.

(ii) Suggest and explain a method that can be used to check the purity of the ester produced.

Use of melting point to check purity of the ester.
If a pure ester is obtained, a sharp and distinct melting point will be obtained. If the ester is impure, the ester will melt over a range of temperatures.

(e) Another ester, \( P \) (\( M_r = 116 \)) used in synthetic fruit flavors, is subjected to hydrolysis to give a monoprotic acid, \( Q \) and an alcohol, \( R \).

When 1.00 g of \( Q \) is titrated with 0.500 mol dm\(^{-3}\) NaOH, 33.0 cm\(^3\) of NaOH is required for neutralization. \( R \) reacts with alkaline aqueous iodine to give a precipitate \( S \). Compound \( R \) exists as a pair of isomers, both of which are oxidized to give \( T \) which also reacts with alkaline aqueous iodine to give the same precipitate \( S \), and a solution \( U \).

Identify the structures \( P, Q, R, S, T \) and \( U \), explaining your deductions clearly.

<table>
<thead>
<tr>
<th>Observations</th>
<th>Deductions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol of acid = mol of NaOH = 0.0165</td>
<td>( Q ) is CH(_3)CO(_2)H</td>
</tr>
<tr>
<td>( M_r ) of ( Q ) = 1 / 0.0165 = 60.6</td>
<td></td>
</tr>
<tr>
<td>Calculating ( M_r ):</td>
<td>( R ) is an alcohol with 4 carbon atoms.</td>
</tr>
<tr>
<td>( 116 + 18.0 = R + 60.06 )</td>
<td></td>
</tr>
<tr>
<td>( M_r ) of ( R ) = 73.4</td>
<td></td>
</tr>
<tr>
<td>( R ) oxidizes to give ( T ), and both react with alkaline aqueous iodine to give a yellow ppt ( S ) and a solution ( U ).</td>
<td>( S ) is CH(_3)I(_3) (yellow ppt) and solution ( U ) contains a sodium salt with 3 carbon atoms.</td>
</tr>
<tr>
<td>( R ) contains a 2º alcohol and ( T ) contains a ketone.</td>
<td></td>
</tr>
<tr>
<td>( R ) exists as a pair of isomers</td>
<td>( R ) contains a chiral center (optical isomers)</td>
</tr>
</tbody>
</table>

\( P: \) CH\(_3\)COOCH(CH\(_3\))CH\(_2\)CH\(_3\)
\( Q: \) CH\(_3\)CO\(_2\)H
(a) For a group I element, the ease with which the following reaction occurs is indicated by its
electrode potential, \( E^0 \).
\[ \text{M(s)} \rightarrow \text{M}^+ (\text{aq}) + \text{e}^- \] Reaction (I)

Calculate the enthalpy change of reaction (I) for Li and Na, using values given below as well as relevant data from the data booklet.

<table>
<thead>
<tr>
<th>Element (M)</th>
<th>( \Delta H_{\text{at}} (\text{M}) / \text{kJ mol}^{-1} )</th>
<th>( \Delta H_{\text{hydration}} (\text{M}^+) / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>159</td>
<td>-957</td>
</tr>
<tr>
<td>Na</td>
<td>107</td>
<td>-841</td>
</tr>
</tbody>
</table>

By Hess’ Law,
\[ \Delta H = \Delta H_{\text{at}} + \text{1st IE} - \Delta H_{\text{hyd}} \]
For Li, \( \Delta H = 159 + 519 - 957 = -279 \text{ kJ mol}^{-1} \); For Na, \( \Delta H = 107 + 494 - 841 = -240 \text{ kJ mol}^{-1} \); 

(b) Comment on the relationship between the enthalpy change of Reaction (I) obtained in (a) and the \( E^0 \) values given in the data booklet for Li and Na.

Li\(^+\) (aq) + e\(^-\) \rightarrow Li (s) \quad E^0 = -3.04 \text{ V}
Na\(^+\) (aq) + e\(^-\) → Na (s) \( E^0 = -2.71 \text{ V} \)

The \( E^0 \) values mirror the calculated \( \Delta H \) values.

The more exothermic \( \Delta H \) value for Li calculated in (a) shows that the reaction is energetically more favourable to form Li\(^+\). The more negative \( E^0 \) value also indicates that Li is readily oxidized to Li\(^+\).

(c) The melting points of Group II oxides are given in the table below.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Melting point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>2852</td>
</tr>
<tr>
<td>CaO</td>
<td>2614</td>
</tr>
<tr>
<td>SrO</td>
<td>2430</td>
</tr>
<tr>
<td>BaO</td>
<td>1918</td>
</tr>
</tbody>
</table>

Explain the trend in the melting points.

The melting point of the oxides decrease down the group.

\[ \text{L.E.} \propto \frac{q^+ q^-}{r^+ + r^-} \]

Down the group, cationic size increases, thus lattice energy decreases.

This results in decreasing electrostatic forces of attraction between the cation and O\(^2-\), hence melting point decreases.

(d) Describe the reactions, if any, for magnesium and calcium with cold water, writing equations, with state symbols, for any reactions taking place.

Mg does not react with cold water.

Calcium reacts vigorously with cold water to give effervescence of hydrogen gas and a white ppt of Ca(OH)\(_2\).

\[
\text{Ca (s) + H}_2\text{O (aq) → Ca(OH)}_2 (s) + \text{H}_2 (g)
\]

[Total: 10 marks]

6 Synthetic detergents (anionic, cationic and non-ionic) consist of a hydrocarbon chain and polar group. As a surfactant, the synthetic detergent is more effective than conventional soap in hard water – water that contains dissolved minerals such as Ca\(^{2+}\) and Mg\(^{2+}\).

Anionic detergents
Anionic detergents contain groups with a negative charge such as Na\(^+\)SO\(_3\)\(^-\). An example of synthesis of a detergent sodium-n-dodecylbenzenesulfonate is as follows:

\[
\text{HO}_3\text{S} \quad \text{Na}^+ \quad \text{O}_3\text{S} \quad \text{Cationic detergents}
\]

Cationic detergents contain positively charged groups and can be found in hair conditioners. Keratin, a protein which contains negatively-charged groups which can be found on the surface of hair, binds strongly to the hydrophilic ends of cationic detergents. The hydrophobic ends of the surfactant molecules then act as the new hair surface. One example of such a detergent is trimethylhexadecylammonium chloride, \([\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+ \text{ Cl}^-\).

Non-ionic detergents
Non-ionic detergents are commonly used in dish-washing liquids. An example is pentaerythrityl palmitate:

\[
\text{CH}_3(\text{CH}_2)_{14} \text{O} \quad \text{H}_2\text{C} \text{--OH}\n\]

(a) State possible reagents and conditions to synthesize \([\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+\) from \(\text{CH}_3(\text{CH}_2)_{15}\text{NH}_2\).

(i) \[\text{CH}_3(\text{CH}_2)_{14} \text{O} \quad \text{H}_2\text{C} \text{--OH}\]

(ii) Name and draw the mechanism for the following synthesis.
**Reagents:** Add *excess* CH₃Cl

**Conditions:** Heat ; (without stating excess, no marks)

**Mechanism:** Electrophilic substitution ;

1 mark for correct intermediate
1 mark for clearly shown arrows
1 mark for indicating that the electrophile is HSO₃⁺
*(students need not know how to generate the electrophile)*

**b)** Suggest why non-ionic detergents are commonly used in dish-washing liquids.

*They do not possess charges and thus do not react with hard water.*

**c)** Describe a chemical test that can be used to distinguish between sodium-n-dodecylbenzenesulfonate and pentaerythrityl palmitate.

You are to include all reagents, conditions and expected observations.

| Reagent: PCl₅ | Conditions: room temperature | Observations: white fumes of HCl gas evolved for pentaerythrityl palmitate, absence of white fumes for sodium-n-dodecylbenzenesulfonate |

**d)** Apart from detergents or soap, cleaning products may also contain enzymes to degrade protein-based stains. Enzymes are proteins with a specific biological activity that are determined by their primary, secondary, tertiary and quaternary structures.

(i) Apart from its function as an enzyme, state one other function of proteins.

*Transport and storage OR structure and shape OR regulation and defense OR Receptors*

(ii) Briefly describe with a well-labeled diagram, one example of a secondary structure of a protein.

*Either a diagram of β-sheet or α-helix with a brief description.*

**α-helix:**

Helix is stabilized by hydrogen bonds which are arranged such that the O of the C=O group of the nᵗʰ residue points along the helix axis towards the N of the N-H group of the (n + 4)ᵗʰ residue

**Parallel β-sheet:**

Formed when segments of polypeptide chains lie adjacent to one another. Hydrogen bonds are formed between the C=O and N-H groups of adjacent chains, and are perpendicular to the direction of the sheet. R groups of adjacent amino acid residues points up or down of the sheet
(e) The effectiveness of enzymes can be reduced by the addition of heavy metal ions such as Hg\(^+\) or Pb\(^{2+}\).

(i) Explain this phenomenon.

Heavy metal ions disrupt salt bridges (in R groups) that are held together by opposite charges, thus causing the protein structure to unfold.

(ii) Pb\(^{2+}\) typically forms complexes that are coloured. Explain why this is so.

Transition element complexes are coloured because of electron transition between d orbitals. In a complex, the presence of ligands causes the 3d orbitals to split into 2 sets of different energies. Radiation from the visible region of the electromagnetic spectrum is absorbed when an electron moves from a d orbital of lower energy to another partially filled / unfilled d orbital of higher energy. Hence, transition element complexes are coloured. The colour seen is the complement of the colours absorbed.

[Total: 15 marks]
This question paper consists of 7 printed pages.
Answer ANY FOUR questions

1. (a) When studying Hydrocarbons, we recognised the environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine.

Because of these environmental concerns, alongside with high oil prices and oil being a limited natural resource, development of cleaner alternative fuels and advanced power systems for vehicles has become a high priority for many governments and vehicle manufacturers around the world.

An alternative fuel vehicle is a vehicle that runs on a fuel other than "traditional" petroleum fuels (petrol or diesel); and also refers to any technology of powering an engine that does not involve solely petroleum (e.g. electric car, hybrid electric vehicles, solar powered).

One such source of alternative fuel is the hydrogen / oxygen fuel cell, which is increasingly used in space crafts.

Describe, providing details, the hydrogen / oxygen fuel cell.

Include the following in your answer:

- Draw a well-labeled diagram for the cell.
- Outline the reactions taking place at each electrode, assuming an alkaline medium.
- State one advantage of using this fuel cell. [6]

(b) Cyanogen is a highly toxic gas, composing of 46.2% carbon and 53.8% nitrogen by mass. At 25 ºC and 1 atm, 1.05 g of cyanogen occupies 0.500 dm³.

(i) Determine the molecular formula of cyanogen.
(ii) Draw the dot-and-cross diagram for cyanogen. Hence, state its shape.
(iii) ‘Cyanogen is soluble in ethanol.’ Explain this statement with the aid of a suitable diagram. [7]

(c) Sketch and explain the trend observed for the atomic and ionic radii of the elements (from Na to Cl) in Period 3. [4]

(d) Phosphine, PH₃, a gas at room temperature can be prepared by action of sodium hydroxide on phosphonium iodide, PH₄I. When 1.00 g of phosphonium iodide reacted with solid sodium hydroxide, 0.925 g of white solid was formed, together with steam and 150 cm³ of PH₃ gas.

All measurements were taken at room temperature and pressure.

Identify the white solid and use the information given to write a balanced equation with state symbols, for the preparation of PH₃. [3]

[Total: 20 marks]
2 (a) Halogen derivatives can be used to synthesize alcohols.

The overall reaction is shown below:

\[
\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}
\]

State the type of reaction mechanism for the above reaction and illustrate how the reaction proceeds via the mechanism you stated. [3]

(b) Describe the reactions of chloride, bromide and iodide ions with the following reagents:
   I. Aqueous silver nitrate, followed by aqueous ammonia
   II. Concentrated sulfuric acid

You are required to write equations where appropriate and give explanations for the differences in their reactions. [7]

(c) When a primary aromatic amine is treated with nitrous acid in a cool solution, the product is unstable compound, known as a diazonium salt.

\[
\text{Error! Objects cannot be created from editing field codes.}
\text{Error! Objects cannot be created from editing field codes.}
\]

\[
\text{+ HNO}_2 + \text{HCl} \rightarrow + \text{H}_2\text{O}
\]

One reaction the diazonium cation undergoes is the substitution of halides.

The reaction is shown below, where X represents the halogen.

\[
\text{C}_6\text{H}_5\text{N}_2^+ + \text{KX} \rightarrow \text{C}_6\text{H}_5\text{X} + \text{K}^+ + \text{N}_2
\]

diazonium salt

Compound P can be synthesised from benzoic acid in the reaction shown below.

Suggest a synthetic route for the conversion of benzoic acid to compound P.

In each case, identify all the intermediate compounds and state clearly the reagents and conditions used for each transformation.

[*Note: In your proposed synthesis route, two of the stages of the synthesis requires the formation of the diazonium ion and the substitution of the halide.]

(d) Arrange the following halogen containing compounds according to increasing pK\text{a} values. Explain your answer.

\[
\text{CH}_3\text{CHC/COOH , CH}_3\text{CCl}_2\text{COOH , CH}_3\text{CHBrCOOH}
\]

[3]
(e) Explain the following physical property trends of transition metals across the Period.

I: relatively constant atomic radius

II: very high melting point

[Total: 20 marks]
(a) An Ellingham diagram shows how the change in Gibbs free energy for a particular reaction varies with temperature.

The following shows a sketch of an Ellingham diagram for three reactions:

I: \[ 2C (s) + O_2 (g) \rightarrow 2CO (g) \quad \Delta G = (-223 - 0.18T) \text{ kJ mol}^{-1} \]

II: \[ 2Fe (s) + O_2 (g) \rightarrow 2FeO (s) \quad \Delta G = (-525 + 0.13T) \text{ kJ mol}^{-1} \]

III: \[ \frac{2}{3}Al (s) + O_2 (g) \rightarrow \frac{2}{3}Al_2O_3 (s) \quad \Delta G = (-1116 + 0.21T) \text{ kJ mol}^{-1} \]

(i) Predict and explain what will happen to the value of \( \Delta G \) when the pressure of the system in reaction I is reduced.

(ii) Explain why the gradient for reaction I is negative (downward sloping), while the gradient for reactions II and III are positive (upward sloping)?

(iii) Calculate \( \Delta G \) of the following reaction at 1000K:

\[ \text{FeO} (s) + C (s) \rightarrow \text{Fe} (s) + \text{CO} (g) \]

(iv) Hence, what is the minimum temperature at which the reduction of iron (II) oxide by carbon becomes thermodynamically feasible?

(v) Aluminium oxide and carbon have high melting points. With reference to the Ellingham diagram, explain why carbon is not used to line vessels that are used to contain molten steel saturated with oxygen.

[The melting point of steel is 1800 K] [14]

(b) The manipulation and rearrangement of the Gibbs free energy equation shows a relation between the change in Gibbs free energy and the standard electrode potential of a cell.

(i) Define the term standard electrode potential of a cell.

(ii) With the use of relevant data from the data booklet, state and illustrate how the relative stabilities of the Fe (II) / Fe (III) oxidation states are affected by the following changes:

I. CN⁻ ligands

II. pH

[Total: 20 marks]
4 (a) Compound K is formed when phenylhydroxylamine, C₆H₅NHOH, is warmed with dilute sulfuric acid. Compound K has the following properties:

- K is not very soluble in water, but dissolves in HCl (aq)
- K dissolves in NaOH (aq) but not in Na₂CO₃ (aq)
- K reacts with 1 mol of ethanoyl chloride to give compound L, C₈H₉O₂N, which is not soluble in HCl (aq), but is soluble in NaOH (aq).
- L reacts with Br₂ (aq) to give compound M, C₈H₇O₂NBr₂.
- K reacts with 2 mol of ethanoyl chloride to give compound N, C₁₀H₁₁O₃N, which is not soluble in HCl (aq) or NaOH (aq).

(i) Suggest structures for compounds K, L, M and N. Present your reasoning clearly by explaining the Chemistry involved.

(ii) Write balanced chemical equations for each of the bullet points above to show how the reactions proceeded. [12]

(b) A student was given 4 unlabelled bottles and each bottle contains one of the following organic compounds with a different functional group:

- 2° Alcohol
- Aldehyde
- Ketone
- 1° Amide

Outline a sequence of simple chemical tests by which you could identify each of the above organic substances.

[Note: you are not allowed to identify the substances by elimination. You must give a positive test to prove the presence of each functional group present.] [8]

[Total: 20 marks]
5 (a) To study the rate of reaction between sodium and ethanol, a student added a freshly cut piece of sodium (of known mass) to a large excess of ethanol and measured the total volume of gas liberated every minute. The results obtained are given below:

<table>
<thead>
<tr>
<th>Time / min</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total vol. of gas produced / cm³</td>
<td>0</td>
<td>23.0</td>
<td>36.5</td>
<td>46.0</td>
<td>51.0</td>
<td>54.5</td>
<td>57.0</td>
<td>58.5</td>
<td>58.5</td>
</tr>
</tbody>
</table>

(i) Write an equation with state symbols for the above reaction.
(ii) Give two reasons why sodium must be freshly cut?
(iii) By plotting a suitable graph on graph paper, explain why the experimental results indicate that the overall kinetics is first order.
(iv) Hence, suggest why the reaction appears to be zero order with respect to ethanol in this experiment.
(v) The student modified the experiment by changing the concentration of ethanol. With the aid of a suitable equation, explain why water should not be used to dilute ethanol.

(b) A solution containing ethanoic acid and sodium ethanoate functions as a buffer.
(i) Explain what is meant by the term *buffer solution*, and write suitable equations to show how this solution functions as a buffer.
(ii) Calculate the pH of the resulting solution when 25 cm³ of 0.10 mol dm⁻³ of ethanoic acid was added to 10 cm³ of 0.20 mol dm⁻³ of NaOH.

\[ K_a \text{ of ethanoic acid} = 1.8 \times 10^{-5} \text{ mol dm}^{-3} \]

(c) A solution X is saturated with the soluble salts, NaNO₃ and Mg(NO₃)₂.
(i) When solution X is heated strongly, the salts start to decompose. State which salt will begin to decomposes first, and the expected observations you will see to indicate that decomposition has taken place. Explain your answer.
(ii) A student conducted an experiment to dissolve magnesium carbonate in solution X. She noted down her observations as follows: ‘The solubility product of magnesium carbonate decreased in solution X. Only a small amount of magnesium carbonate dissolved.’

Discuss in detail the validity of this statement, making corrections to the observations where necessary.

[Total: 20 marks]
READ THESE INSTRUCTIONS FIRST

1. Do not turn over this question paper until you are told to do so.

2. Write your name, class and index number in the spaces provided at the top of this page and on all the work you hand in.

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

4. You may use a soft pencil for any diagrams or graphs.

5. DO NOT use staples, paper clips, highlighters, glue or correction fluid or tape.

6. Answer any four questions.

7. Give non-exact numerical answers correct to 3 significant figures, or 1 decimal place in the case of $M_r$ and $A_r$, unless a different level of accuracy is specified in the question.

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

9. You are reminded of the need for good English and clear presentation in your answers and to show all working in calculations.

10. The use of a calculator is expected, where appropriate.

This question paper consists of 16 printed pages.
When studying Hydrocarbons, we recognised the environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine.

Because of these environmental concerns, alongside with high oil prices and oil being a limited natural resource, development of cleaner alternative fuels and advanced power systems for vehicles has become a high priority for many governments and vehicle manufacturers around the world.

An alternative fuel vehicle is a vehicle that runs on a fuel other than “traditional” petroleum fuels (petrol or diesel); and also refers to any technology of powering an engine that does not involve solely petroleum (e.g. electric car, hybrid electric vehicles, solar powered).

One such source of alternative fuel is the hydrogen / oxygen fuel cell, which is increasingly used in space crafts.

<table>
<thead>
<tr>
<th>1</th>
<th>(a)</th>
<th>When studying Hydrocarbons, we recognised the environmental consequences of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine.</th>
<th>Because of these environmental concerns, alongside with high oil prices and oil being a limited natural resource, development of cleaner alternative fuels and advanced power systems for vehicles has become a high priority for many governments and vehicle manufacturers around the world.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>An alternative fuel vehicle is a vehicle that runs on a fuel other than “traditional” petroleum fuels (petrol or diesel); and also refers to any technology of powering an engine that does not involve solely petroleum (e.g. electric car, hybrid electric vehicles, solar powered).</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>One such source of alternative fuel is the hydrogen / oxygen fuel cell, which is increasingly used in space crafts.</td>
<td></td>
</tr>
</tbody>
</table>

Describe, providing details, the hydrogen / oxygen fuel cell.

Include the following in your answer:

- Draw a well-labeled diagram for the cell.
- Outline the reactions taking place at each electrode, assuming an alkaline medium.
- State one advantage of using this fuel cell.[6]

![Diagram of hydrogen / oxygen fuel cell]

(1 mark for correct electrolyte, 1 mark for labelled anode, 1 mark for labelled cathode)

In alkaline electrolyte

<table>
<thead>
<tr>
<th>Reaction at anode:</th>
<th>H₂(g) + 2OH⁻(aq) → 2H₂O(l) + 2e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction at cathode:</td>
<td>½O₂(g) + H₂O(l) + 2e⁻ → 2OH⁻(aq)</td>
</tr>
<tr>
<td>Overall cell reaction:</td>
<td>H₂(g) + ½O₂(g) → H₂O(l)</td>
</tr>
</tbody>
</table>
Advantage:
Clean products are produced. OR
Water produced in hydrogen-oxygen fuel cell used in spacecraft can be used for drinking and washing.

(b) Cyanogen is a highly toxic gas, composing of 46.2% carbon and 53.8% nitrogen by mass. At 25 °C and 1 atm, 1.05 g of cyanogen occupies 0.500 dm³.

(i) Determine the molecular formula of cyanogen.

<table>
<thead>
<tr>
<th>% mass</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mole ratio</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Simple ratio</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Empirical formula of cyanogen is CN.

Using PV = nRT

\[ 1.01 \times 10^5 \times 0.5 \times 10^{-3} = \frac{1.05}{Mr} \times 8.31 \times 298 \]

\[ Mr = 51.5 \text{ (1 d.p)} \]

Thus, molecular formula of Cyanogen = C₂N₂

(ii) Draw the dot-and-cross diagram for cyanogen. Hence, state its shape.

N≡C-C≡N, linear

(iii) 'Cyanogen is soluble in ethanol.' Explain this statement with the aid of a suitable diagram.

Cyanogen can form hydrogen bonds with ethanol as it has a lone pair of electrons on nitrogen, thus soluble in ethanol.

\[
\begin{align*}
\text{CH}_3\text{CH}_2^+ & \quad \text{O}^– \\
\quad \delta^– & \quad \delta^+ \\
\text{N≡C–C≡N:} & \\
\quad \delta^+ & \quad \delta^– \\
\quad \text{H} & \\
\text{CH}_2\text{CH}_3 & \\
\end{align*}
\]

(lone pairs on N and O, δ+, δ- must all be clearly shown)

(c) Sketch and explain the trend observed for the atomic and ionic radii of the elements (from Na to Cl) in Period 3.

[4]
Atomic Radius:
Across the period, nuclear charge ↑ as proton number ↑
change in the screening effect is negligible (Same no. of inner shells of e−s across the period). Thus the outer e−s are more strongly attracted by the nucleus ∴ atomic radii ↓

Cations (Na⁺ to Si⁴⁺)
cations have one shell less than neutral atoms. Thus, the outer e−s are more strongly attracted by the nucleus therefore having a smaller radius than its parent atoms.

Anions (P³⁻ to C⁻)
• anions have more e−s than protons and so, the effective attractive force on the outer e−s is less than that in neutral atoms.
⇒ the outer e−s are less strongly attracted by the nucleus, thus having a radius that is larger than its parent atoms.

(d) Phosphine, PH₃, a gas at room temperature can be prepared by action of sodium hydroxide on phosphonium iodide, PH₄I. When 1.00 g of phosphonium iodide reacted with solid sodium hydroxide, 0.925 g of white solid was formed, together with steam and 150 cm³ of PH₃ gas.
All measurements were taken at room temperature and pressure.

Identify the white solid and use the information given to write a balanced equation with state symbols, for the preparation of PH₃. [3]

The white solid is NaI.
Molar mass of PH₄I = 162.0
Amount of PH₄I = 1 / 162 = 0.00617 mol
Amount of Na I = 0.925 / (23.0 + 127.0) = 0.00617 mol
Amount of PH₃ = 150 / 24000 = 0.00625 mol
Mole ratio of PH₄I : PH₃ : Na I ≈ 1 : 1 : 1
Thus,
PH₄ I (s) + NaOH (s) → Na I (s) + PH₃ (g) + H₂O (g)
(state symbols must be correct to earn this mark)
Halogen derivatives can be used to synthesize alcohols. The overall reaction is shown below:

\[
\text{CH}_3\text{CH}_2\text{Br} + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{NaBr}
\]

State the type of reaction mechanism for the above reaction and illustrate how the reaction proceeds via the mechanism you stated.

**Nucleophilic Substitution, S\textsubscript{N}2**

1 mark for name of mechanism S\textsubscript{N}2
1 mark for clearly shown arrow pushing
1 mark for correct intermediate and the final product must have the structure of an ‘inverted umbrella’

(b) Describe the reactions of chloride, bromide and iodide ions with the following reagents:

I. Aqueous silver nitrate, followed by aqueous ammonia

II. Concentrated sulfuric acid

You are required to write equations where appropriate and give explanations for the differences in their reactions.

<table>
<thead>
<tr>
<th>Ppt</th>
<th>Colour</th>
<th>Reaction with NH\textsubscript{3} (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>White</td>
<td>(\text{AgCl(s)} + 2\text{NH}_3\text{(aq)} \rightarrow [\text{Ag(NH}_3)_2]^+ \text{(aq)} + \text{Cl}^- \text{(aq)}) \text{diamine silver (I) ion}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>White precipitate readily dissolves in NH\textsubscript{3} (aq) to give a colourless solution, diamine silver (I) ion.</td>
</tr>
<tr>
<td>AgBr</td>
<td>Pale yellow/Cream</td>
<td>(\text{AgBr (s)} + 2\text{NH}_3\text{(aq)} \rightarrow [\text{Ag(NH}_3)_2]^+ \text{(aq)} + \text{Br}^- \text{(aq)}) \text{diamine silver (I) ion}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cream precipitate ONLY dissolves in Conc. NH\textsubscript{3} solution.</td>
</tr>
<tr>
<td>AgI</td>
<td>Deep yellow</td>
<td>Precipitate insoluble in NH\textsubscript{3} (aq)</td>
</tr>
</tbody>
</table>
NaCl + H₂SO₄ → HCl + NaHSO₄

NaBr + H₂SO₄ → HBr + NaHSO₄
2HBr + H₂SO₄ → Br₂ + SO₂ + 2H₂O

NaI + H₂SO₄ → HI + NaHSO₄
6HI + H₂SO₄ → 3I₂ + S + 4H₂O OR
8HI + H₂SO₄ → 4I₂ + H₂S + 4H₂O

The ease of oxidation of halide ions, X⁻ → X₂, increases from Cl⁻ to I⁻ (as the reducing power of the halides increases from Cl⁻ to I⁻). Hence, I⁻ is readily oxidised by conc. sulphuric acid to I₂, Br⁻ is oxidised to Br₂ to a lesser extent and Cl⁻ is not oxidised at all.

(Students can also quote E° values to substantiate their answers)

(c) When a primary aromatic amine is treated with nitrous acid in a cool solution, the product is unstable compound, known as a diazonium salt.

\[
\text{NH}_2 + \text{HNO}_2 + \text{HCl} \rightarrow \text{diazonium salt}
\]

One reaction the diazonium cation undergoes is the substitution of halides.

The reaction is shown below, where X represents the halogen.

\[
\text{C}_6\text{H}_5\text{N}_2^+ + \text{KX} \rightarrow \text{C}_6\text{H}_5\text{X} + \text{K}^+ + \text{N}_2
\]

diazonium ion

Compound P can be synthesised from benzoic acid in the reaction shown below. Suggest a synthetic route for the conversion of benzoic acid to compound P. In each case, identify all the intermediate compounds and state clearly the reagents and conditions used for each transformation.

[*Note: In your proposed synthesis route, two of the stages of the synthesis requires the formation of the diazonium ion and the substitution of the halide.]
(d) Arrange the following halogen containing compounds according to increasing pKₐ values. Explain your answer.

\[ \text{CH}_3\text{CHClCOOH, CH}_3\text{CCl}_2\text{COOH, CH}_3\text{CHBrCOOH} \]

Increasing pKₐ value: \( \text{CH}_3\text{CCl}_2\text{COOH} > \text{CH}_3\text{CHClCOOH} > \text{CH}_3\text{CHBrCOOH} \)

\( \text{CH}_3\text{CCl}_2\text{COOH} \) has the smallest pKₐ (thus most acidic) as there is the presence of two electron withdrawing Cl atoms. This, the negative charge on the O atom in \((\text{CH}_3\text{CCl}_2\text{COO}^-)\) is more dispersed than in \((\text{CH}_3\text{CHClCOO}^-)\). Thus the \(\text{CH}_3\text{CCl}_2\text{COO}^-\) anion is more stable, and the acid is more willing to donate a proton, increasing the acidity of the solution.

\( \text{CH}_3\text{CHBrCOOH} \) has the largest pKₐ value (least acidic) as Br is less electronegative than Cl. Thus, the electron withdrawing ability of Br is less than Cl. Thus the \(\text{CH}_3\text{CHBrCOO}^-\) anion is less stable, and the acid is less willing to donate a proton, decreasing the acidity of the solution.

(no marks for correct arrangement without explanation)

(e) Explain the following physical property trends of transition metals across the Period.

I: relatively constant atomic radius
II: very high melting point

⇒ Electrons are being added to inner 3d subshell.
⇒ Screening effect of 3d electrons effectively cancels almost all increase in nuclear charge across series.

Hence, there is a relatively small difference in the effective nuclear charge and atomic radius remains relatively constant.

⇒ Strong metallic bonding in transition elements due to availability of both the 4s and 3d electrons for delocalisation, thus melting point increases.

[Total: 20 marks]
(a) An Ellingham diagram shows how the change in Gibbs free energy for a particular reaction varies with temperature.

The following shows a sketch of an Ellingham diagram for three reactions:

I: \[ 2\text{C (s)} + \text{O}_2 (g) \rightarrow 2\text{CO (g)} \quad \Delta G = (-223 - 0.18T) \text{kJ mol}^{-1} \]

II: \[ 2\text{Fe (s)} + \text{O}_2 (g) \rightarrow 2\text{FeO (s)} \quad \Delta G = (-525 + 0.13T) \text{kJ mol}^{-1} \]

III: \[ \frac{4}{3}\text{Al (s)} + \text{O}_2 (g) \rightarrow \frac{2}{3}\text{Al}_2\text{O}_3 (s) \quad \Delta G = (-1116 + 0.21T) \text{kJ mol}^{-1} \]

(i) Predict and explain what will happen to the value of \( \Delta G \) when the pressure of the system in reaction I is reduced.

When pressure in reaction I is reduced, by LCP the system will counteract by increasing pressure, thus equilibrium will shift to the right where more amount of gas will be produced. Thus, \( \Delta S > 0 \).

Since \( \Delta G = \Delta H - T\Delta S \), and \( \Delta S > 0 \), \( \Delta G \) then becomes more negative, as pressure is reduced.

(ii) Explain why the gradient for reaction I is negative (downward sloping), while the gradient for reactions II and III are positive (upward sloping)?

The gradient of the graph represents \( -\Delta S \).

In reaction I, there is an increase in the disorderliness as number of moles of gaseous increased from 1 to 2 moles. Thus, \( \Delta S > 0 \) and the overall gradient is negative.

In reactions II and III, there is an increase in the orderliness of the system as number of moles of gases decreased from 1 to 0 moles. Thus, \( \Delta S < 0 \), and the overall gradient is positive.

(iii) Calculate \( \Delta G \) of the following reaction at 1000K:

\[ \text{FeO (s)} + \text{C (s)} \rightarrow \text{Fe (s)} + \text{CO (g)} \]
Hence, what is the minimum temperature at which the reduction of iron (II) oxide by carbon becomes thermodynamically feasible?

\[
\Delta G^\circ = -223 - 0.18T = -525 + 0.31T
\]
Solving, \( T = 974 \text{ K} \)

Aluminium oxide and carbon have high melting points. With reference to the Ellingham diagram, explain why carbon is not used to line vessels that are used to contain molten steel saturated with oxygen.

[The melting point of steel is 1800 K]

From the Ellingham diagram, at \( T=1800\text{K} \), reaction I is still thermodynamically feasible.

\[
\Delta G = -223 - 0.18 \times 1800 = -547 \text{ kJ mol}^{-1}
\]
Thus oxygen can react with carbon to form CO since \( \Delta G < 0 \) and reaction is spontaneous. Thus carbon is not used as a lining material at such a high temperature in the presence of oxygen gas.

The manipulation and rearrangement of the Gibbs free energy equation shows a relation between the change in Gibbs free energy and the standard electrode potential of a cell.

(i) Define the term standard electrode potential of a cell.

Standard electrode potential, \( E^\circ \) of a cell is the relative potential of this cell under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as zero.

(ii) With the use of relevant data from the data booklet, state and illustrate how the relative stabilities of the Fe (II) / Fe (III) oxidation states are affected by the following changes:

I. CN⁻ ligands

\[
\begin{align*}
\text{Fe}^{3+} + e^- &\rightleftharpoons \text{Fe}^{2+} \\
& \text{Postive reduction potential}
\end{align*}
\]

Fe³⁺ is stabilised with respect to Fe²⁺ when complexed with CN⁻, resulting in a less positive reduction potential.
Fe³⁺ is stabilised with respect to Fe²⁺ by an alkaline medium, resulting in a less positive reduction potential.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Electron Transfer</th>
<th>E⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(H₂O)₆]³⁺ + e ⇌ [Fe(H₂O)₆]²⁺</td>
<td></td>
<td>E⁰ = +0.77 V</td>
</tr>
<tr>
<td>Fe³⁺ + e ⇌ Fe²⁺</td>
<td></td>
<td>E⁰ = +0.77 V</td>
</tr>
<tr>
<td>Fe(OH)₂ + e ⇌ Fe(OH)₂⁺ + OH⁻</td>
<td></td>
<td>E⁰ = -0.56 V</td>
</tr>
</tbody>
</table>

[Total: 20 marks]
(a) Compound K is formed when phenylhydroxylamine, C₆H₅NHOH, is warmed with dilute sulfuric acid. Compound K has the following properties:

- K is not very soluble in water, but dissolves in HCl (aq)
- K dissolves in NaOH (aq) but not in Na₂CO₃ (aq)
- K reacts with 1 mol of ethanoyl chloride to give compound L, C₈H₉O₂N, which is not soluble in HCl (aq), but is soluble in NaOH (aq).
- L reacts with Br₂ (aq) to give compound M, C₈H₇O₂NBr₂.
- K reacts with 2 mol of ethanoyl chloride to give compound N, C₁₀H₁₁O₃N, which is not soluble in HCl (aq) or NaOH (aq).

(i) Suggest structures for compounds K, L, M and N.

(ii) Write balanced chemical equations for each of the bullet points above to show how the reactions proceeded.

<table>
<thead>
<tr>
<th>Observations</th>
<th>Deductions</th>
</tr>
</thead>
<tbody>
<tr>
<td>K is not very soluble in water, but dissolves in HCl (aq)</td>
<td>K contains a hydrophobic group. K contains a basic group.</td>
</tr>
<tr>
<td>K dissolves in NaOH (aq) but not in Na₂CO₃ (aq)</td>
<td>K contains an acidic group that is not a carboxylic group. Hence, K contains a phenol group.</td>
</tr>
<tr>
<td>K reacts with 1 mol of ethanoyl chloride to give compound L, C₈H₉O₂N, which is not soluble in HCl (aq), but is soluble in NaOH (aq).</td>
<td>L is acidic (contains the phenol group from K) and also contains an amide.</td>
</tr>
<tr>
<td>L reacts with Br₂ (aq) to give compound M, C₈H₇O₂NBr₂.</td>
<td>Electrophilic substitution occurs readily as the benzene ring is activated by the phenol group.</td>
</tr>
<tr>
<td>K reacts with 2 mol of ethanoyl chloride to give compound N, C₁₀H₁₁O₃N, which is not soluble in HCl (aq) or NaOH (aq).</td>
<td>N is neutral and N contains both ester and amide functional groups.</td>
</tr>
</tbody>
</table>
Balanced Equations:

\[
\text{OH} + \text{HCl} \rightarrow \text{OH} + \text{NH}_3^+\text{Cl}^- \\
\text{OH} + \text{NaOH} \rightarrow \text{OH} + \text{NH}_2\text{Na}^+ + \text{H}_2\text{O} \\
\text{OH} + \text{CH}_3\text{COCl} \rightarrow \text{OH} + \text{NHCOCH}_3 + \text{HCl} \\
\text{OH} + 2\text{Br}_2 \rightarrow \text{OH} + \text{NHCOCH}_3 + 2\text{HBr} \\
\text{OH} + 2\text{CH}_3\text{COCl} \rightarrow \text{OH} + \text{NHCOCH}_3 + 2\text{HCl}
\]

1 mark for each unknown structure
3 marks (max) for explaining the deductions
1 mark for each equation for each bullet point.
A student was given 4 unlabelled bottles and each bottle contains one of the following organic compounds with a different functional group:

- $2^o$ Alcohol
- Aldehyde
- Ketone
- $1^o$ Amide

Outline a sequence of simple chemical tests by which you could identify each of the above organic substances.

[Note: you are not allowed to identify the substances by elimination. You must give a positive test to prove the presence of each functional group present.]

<table>
<thead>
<tr>
<th>No.</th>
<th>Test for aldehyde</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Add tollen’s reagent to 4 test tubes each of the unknown, warm.</td>
<td>Silver mirror will be formed in the test tube containing the aldehyde only.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Test for ketone</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Add brady’s reagent to new samples of the remaining 3 unknowns, warm.</td>
<td>Orange ppt observed in the test tube containing the ketone only.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Test for $2^o$ alcohol</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Add KrCr$_2$O$_7$ / H$_2$SO$_4$ to the remaining two unknowns. Heat under reflux.</td>
<td>Orange solution of Cr$_2$O$_7^{2-}$ decolorize for test tube containing the $2^o$ alcohol only. [\text{\textit{\small (KMnO_4) accepted, iodoform test not accepted}}]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Test for $1^o$ amide</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Add NaOH (aq) to a new sample of the remaining test tube. Warm.</td>
<td>Effervescence, colourless, pungent gas evolved that turned moist red litmus blue.</td>
</tr>
</tbody>
</table>

[Total: 20 marks]
To study the rate of reaction between sodium and ethanol, a student added a freshly cut piece of sodium (of known mass) to a large excess of ethanol and measured the total volume of gas liberated every minute. The results obtained are given below:

<table>
<thead>
<tr>
<th>Time / min</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total vol. of gas produced / cm(^3)</td>
<td>0</td>
<td>23.0</td>
<td>36.5</td>
<td>46.0</td>
<td>51.0</td>
<td>54.5</td>
<td>57.0</td>
<td>58.5</td>
<td>58.5</td>
</tr>
</tbody>
</table>

(i) Write an equation with state symbols for the above reaction.

\[
\text{Na (s) + C}_2\text{H}_5\text{OH (l)} \rightarrow \text{C}_2\text{H}_5\text{O}^-\text{Na}^+ (\text{aq}) + \frac{1}{2} \text{H}_2 (\text{g})
\]

(ii) Give two reasons why sodium must be freshly cut?

Na must be freshly cut because it rapidly oxidised by \( \text{O}_2 \) in air to form a layer of oxide (\( \text{Na}_2\text{O} \)) on its surface.

Na also reacts with the water vapour present in air.

(iii) By plotting a suitable graph on graph paper, explain why the experimental results indicate that the overall kinetics is first order.

1 mark for correct axis chosen (graph of total volume of gas produced against time)
1 mark for collect plotting
1 mark for indicating on graph that half-life of the reaction is first order (must state the value of half-life to be 1.5 min)
(half-life measured from 0 - 29.3 cm\(^3\), and from 29.3 - 43.9 cm\(^3\) of \( \text{H}_2 \))

(iv) Hence, suggest why the reaction appears to be zero order with respect to ethanol in this experiment.

Since ethanol is present in large excess, the concentration of ethanol does not change. Thus rate is independent on concentration of ethanol / reaction is zero order with respect to ethanol.

(v) The student modified the experiment by changing the concentration of ethanol.

With the aid of a suitable equation, explain why water should not be used to dilute ethanol.

\[
\text{Na (s) + H}_2\text{O (l)} \rightarrow \text{NaOH (aq)} + \frac{1}{2} \text{H}_2 (\text{g})
\]
(b) A solution containing ethanoic acid and sodium ethanoate functions as a buffer.

(i) Explain what is meant by the term buffer solution, and write suitable equations to show how this solution functions as a buffer.

A buffer solution is a solution whose pH remains relatively unchanged when a small amount of acid or alkali is added to it.

When a small amount of base is added,
\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

When a small amount of acid is added,
\[ \text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH} \]

(ii) Calculate the pH of the resulting solution when 25 cm³ of 0.10 mol dm⁻³ of ethanoic acid was added to 10 cm³ of 0.20 mol dm⁻³ of NaOH.

[\text{Ka of ethanoic acid} = 1.8 \times 10^{-5} \text{ mol dm}^{-3}]  

<table>
<thead>
<tr>
<th>Amount of ethanoic acid</th>
<th>0.00250 mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of NaOH</td>
<td>0.00200 mol</td>
</tr>
</tbody>
</table>

The limiting reagent is NaOH.

- Amount of CH₃COO⁻ formed = 0.00200 mol
- \([\text{CH}_3\text{COO}^-]_{\text{eqm}} = 0.002 / 0.035 = 0.05714 \text{ mol} \]
- \([\text{CH}_3\text{COOH}]_{\text{eqm}} = (0.0025-0.002) / 0.035 = 0.01428 \text{ mol} \]
- \(\text{pH} = \text{pK}_a + \lg \left( \frac{0.05714}{0.01428} \right) \]
  \[= -\lg (1.8\times10^{-5}) + \lg(0.05714)/(0.01428) \]
  \[= 5.35 \text{ (3s.f)} \]

(c) A solution \(X\) is saturated with the soluble salts, \(\text{NaNO}_3\) and \(\text{Mg(NO}_3\text{)}_2\).

(i) When solution \(X\) is heated strongly, the salts start to decompose. State which salt will begin to decomposes first, and the expected observations you will see to indicate that decomposition has taken place. Explain your answer.

\(\text{Mg(NO}_3\text{)}_2\) will decompose first.

\(\text{Mg}^{2+}\) has a higher charge density as compared to \(\text{Na}^+\) due to its higher charge and smaller ionic radius. Thus, its polarising power increases.

\(\text{Mg}^{2+}\) will polarise the electron cloud of \(\text{NO}_3^-\), distorting the N-O bonds, releasing \(\text{O}_2\) and \(\text{N}_2\).

Brown fumes of \(\text{N}_2\) will be observed to indicate that the reaction has occurred.

(ii) A student conducted an experiment to dissolve magnesium carbonate in solution \(X\).

She noted down her observations as follows: ‘The solubility product of magnesium carbonate decreased in solution \(X\). Only a small amount of magnesium carbonate dissolved.’

Discuss in detail the validity of this statement, making corrections to the observations where necessary.
The statement recorded by the student is wrong. The solubility product of magnesium carbonate does not decrease in Solution X. The solubility product remains the same in solution X, as solubility product is only affected by changes in temperature. However, in solution X, due to the presence of the common ion, Mg\(^{2+}\), the solubility of magnesium carbonate decreases.
Chemistry 9647/1

Paper 1 Multiple Choice 20 September 2012

1 hour

Additional Materials: OMR Sheet
Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page. Write your calculator brand and model/number in the box provided above.

There are forty questions in this section. Answer all questions. For each question, there are four possible answers labelled A, B, C and D. Choose the one you consider correct and record your choice in soft pencil on the OMR answer sheet.

Read very carefully the instructions on the use of the OMR answer sheet.

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

Use of OMR Answer Sheet

Ensure you have written your name, class register number and class on the OMR Answer Sheet.

Use a 2B pencil to shade your answers on the OMR sheet; erase any mistakes cleanly. Multiple shaded answers to a question will not be accepted.

For shading of class register number on the OMR sheet, please follow the given examples:
If your register number is 1, then shade 01 in the index number column.
If your register number is 21, then shade 21 in the index number column.

This document consists of 19 printed pages and 1 blank page.
Section A

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

1 Which of the following statements contains one mole of the stated particle?
   A Molecules in 19.0 g of fluorine gas.
   B Electrons in 24.0 dm$^3$ of hydrogen gas at room temperature and pressure.
   C Neutrons in 1.00 g of helium gas.
   D Protons in 2.02 g of neon gas.

2 Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas at constant $T$?

   A $p$ vs $pV$
   B $pV/T$ vs $p$
   C $pV/T$ vs $p$
   D $pV$ vs $p$
Two elements X and Y have the following properties.

- X and Y form ionic compounds Na₂X and Na₂Y respectively.
- Element Y forms YF₆ molecule whereas X is unable to do so.

Which pair of electronic configurations of X and Y is correct?

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[He]2s²2p²</td>
<td>[Ne]3s²3p²</td>
</tr>
<tr>
<td>B</td>
<td>[He]2s²2p²</td>
<td>[Ne]3s²3p⁴</td>
</tr>
<tr>
<td>C</td>
<td>[He]2s²2p⁴</td>
<td>[Ne]3s²3p²</td>
</tr>
<tr>
<td>D</td>
<td>[He]2s²2p⁴</td>
<td>[Ne]3s²3p⁴</td>
</tr>
</tbody>
</table>

Ions of the two most common isotopes of zinc are shown below:

\[ ^{64}_{30} \text{Zn}^{2+} \quad ^{66}_{30} \text{Zn}^{2+} \]

Which of the following statements is correct?

A Both these Zn²⁺ ions have the same number of electrons but different number of protons.

B Both these Zn²⁺ ions have the same electron configuration \(1s^22s^22p^63s^23p^63d^84s^2\).

C The \(^{64}_{30}\)Zn²⁺ ion has fewer neutrons in its nucleus than the \(^{66}_{30}\)Zn²⁺ ion.

D The \(^{66}_{30}\)Zn²⁺ ion will be deflected more than the \(^{64}_{30}\)Zn²⁺ ion in an electric field of the same strength.

For the pairs of species shown below, in which does the first species have a larger bond angle than the second?

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>PH₃, NH₃</td>
<td>SO₃²⁻, CO₃²⁻</td>
</tr>
<tr>
<td>B</td>
<td>CH₂Cl₂, OCl₂</td>
<td>BrF₂⁻, BeCl₂</td>
</tr>
</tbody>
</table>
In an experiment, a radioactive sample of the sodium thiosulfate, \( \text{Na}_2\text{S}_2\text{O}_3 \) was prepared by boiling solid sulfur containing \( ^{35}\text{S} \) with sodium sulfite, \( \text{Na}_2^{32}\text{SO}_3 \). Adding \( \text{HCl} \) (aq) to this sample causes all the \( ^{35}\text{S} \) to precipitate as sulphur, leaving a resulting solution that contains non-radioactive sulfite ions.

Which of the following depicts the correct displayed formula of the thiosulfate ion produced?

![Diagram A](image)

![Diagram C](image)

![Diagram B](image)

![Diagram D](image)

An experiment is conducted to investigate the kinetics of reaction between bromopropane and 0.1 mol dm\(^{-3}\) sodium hydroxide.

The rate equation is as follows:

\[
\text{Rate} = k \ [\text{bromopropane}] \ [\text{OH}^-]
\]

The half-life of bromopropane in one of the experiments is \( t \) minutes.

What is the new half-life (in minutes) of bromopropane when the concentration of bromopropane is doubled and concentration of sodium hydroxide is reduced to 0.01 mol dm\(^{-3}\)?

A. 0.05\( t \)
B. 0.1\( t \)
C. 5\( t \)
D. 10\( t \)
Consider the following equilibrium system:

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g) \quad \Delta H = +53 \text{ kJ mol}^{-1}$$

Which of the following change is incorrect?

A. Numerical value of $K_p$ is not equal to $K_c$ at 25 °C.
B. Increasing the mass of $H_2$ will not cause the equilibrium constant to increase.
C. Increasing temperature increases the rate constant and equilibrium constant.
D. Rate of forward reaction is equal to rate of backward reaction when equilibrium is reached.

The graph shows the change in pH when 0.25 mol dm$^{-3}$ acid is gradually added to $V$ cm$^3$ of 0.25 mol dm$^{-3}$ base.

Which pair of solutions will give the result as shown in the graph?

A. $\text{HNO}_3$ and $\text{NH}_3$
B. $\text{H}_2\text{SO}_4$ and $\text{CH}_3\text{NH}_2$
C. $\text{CH}_3\text{COOH}$ and $\text{Ca(OH)}_2$
D. $\text{CH}_2(\text{COOH})_2$ and $\text{NaOH}$
The solubility product of iron(II) carbonate is $2.1 \times 10^{-11}$ while that of silver carbonate is $8.1 \times 10^{-12}$ at 25°C.

Which of the following statements is true?

A  Addition of silver nitrate increases the solubility of silver carbonate.

B  Addition of sulfuric acid to a solution containing iron(II) carbonate increases the solubility product of iron(II) carbonate.

C  Iron(II) carbonate precipitates first when sodium carbonate is added to a solution containing equal concentrations of iron(II) and silver ions.

D  The solubility of iron(II) carbonate is higher than the solubility of silver carbonate.

Liquid E has an $\Delta H^\circ$ of vapourisation of $+10.0$ kJ mol$^{-1}$ and a boiling point of 266 K.

What is the $\Delta S^\circ$ of condensation of vapour E?

A  $-26.6$ J mol$^{-1}$ K$^{-1}$

B  $-37.6$ J mol$^{-1}$ K$^{-1}$

C  $+26.6$ J mol$^{-1}$ K$^{-1}$

D  $+37.6$ J mol$^{-1}$ K$^{-1}$

Which of the following has an exothermic enthalpy change?

A  $\text{Ca (g)} \rightarrow \text{Ca}^{2+} (g) + 2e$

B  $\text{CaO (s)} \rightarrow \text{Ca}^{2+} (g) + \text{O}^2^- (g)$

C  $\frac{1}{2}\text{O}_2 (g) \rightarrow \text{O} (g)$

D  $\text{O (g)} + e \rightarrow \text{O}^- (g)$
When a solution of concentrated sodium carboxylate is electrolysed, the equation for the reaction is

$$2\text{RCO}_2\text{Na (aq)} + 2\text{H}_2\text{O (l)} \rightarrow \text{R–R (l)} + 2\text{CO}_2 (\text{g}) + 2\text{NaOH (aq)} + \text{H}_2 (\text{g})$$

Which statement regarding the electrolysis is correct?

A. Carbon dioxide is liberated at the cathode.
B. Hydrogen is liberated at the cathode.
C. R–R is liberated at the cathode.
D. The solution around the anode turns red litmus blue.

When a large current was passed through acidified aqueous copper(II) sulfate, there was simultaneous liberation, at the cathode, of $x$ mol of copper and $y$ dm$^3$ of hydrogen (measured at s.t.p.).

How many moles of electrons passed through the solution?

A. $x + \frac{y}{11.2}$
B. $x + \frac{y}{22.4}$
C. $2x + \frac{y}{11.2}$
D. $2x + \frac{y}{22.4}$

Two cells, one containing a molten chloride of manganese and the other containing molten chromium(II) chloride were connected in series. 11.0 g of manganese and 15.6 g of chromium were deposited.

What is the oxidation state of manganese ion in the chloride?

A. +2
B. +3
C. +4
D. +5
Element **G** is in the third period of the Periodic Table. The chloride of **G** has a simple molecular structure while the oxide of **G** has a giant ionic structure.

Which of the following statements is true about **G**?

A. The atomic radius of **G** is smaller than that of **Cl**.
B. The first ionisation energy of **G** is higher than that of **Mg**.
C. The chloride of **G** dissolves in water to give a neutral solution.
D. The oxide of **G** reacts with excess aqueous sodium hydroxide to form a colourless complex.

**17**  
**J**, **K** and **L** are elements in Period 3. **K** has a larger ionic radius than **J**, and **L** has a less endothermic first ionisation energy than **K**.

What are elements **J**, **K** and **L**?

<table>
<thead>
<tr>
<th></th>
<th>J</th>
<th>K</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>P</td>
<td>S</td>
<td>C/</td>
</tr>
<tr>
<td>B</td>
<td>P</td>
<td>A/</td>
<td>Mg</td>
</tr>
<tr>
<td>C</td>
<td>A/</td>
<td>Mg</td>
<td>Si</td>
</tr>
<tr>
<td>D</td>
<td>A/</td>
<td>P</td>
<td>S</td>
</tr>
</tbody>
</table>

**18**  
Beryllium is a Group II metal and has the smallest ionic radius among the Group II metals.

Which of the following statements is **incorrect**?

A. Beryllium chloride has the highest melting point among the Group II chlorides.
B. Beryllium ions have the highest charge density amongst the Group II metals ions.
C. Beryllium has the highest melting point among the Group II metals.
D. Beryllium has the highest electronegativity among the Group II metals.
19 Which of the following statements is most likely to be true for astatine, the element below iodine in Group VII of the Periodic Table?

A Astatine reacts with aqueous iron(II) ions to give iron(III) ions.

B Astatine reacts with aqueous sodium bromide to given aqueous sodium astatide and bromine.

C Hydrogen iodide is more acidic than hydrogen astatide.

D Silver astatide has a lower $K_{sp}$ value than silver iodide.

20 Which process is not involved in the catalytic hydrogenation of ethene?

A Absorption

B Activation

C Desorption

D Diffusion

21 How many stereoisomers does this organic molecule have?

A 8  B 16  C 32  D 64
22 2-methylpropane can react with bromine in the presence of sunlight to give two monosubstituted halogenoalkanes, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane.

Given the relative rates of abstracting H atoms are:

<table>
<thead>
<tr>
<th>Type of H atom</th>
<th>primary</th>
<th>secondary</th>
<th>tertiary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative rate of abstraction</td>
<td>1</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

What is the expected ratio of 1-bromo-2-methylpropane to 2-bromo-2-methylpropane formed?

A  9 : 1  
B  3 : 2  
C  6 : 1  
D  1 : 1

23 Why does hydrogen cyanide undergo addition reaction with propanone but not with propene?

A  Propanone is more susceptible to CN⁻ attack than propene.
B  Propene is less susceptible to H⁺ attack than propanone.
C  The addition product formed with propene would not be stable.
D  The two methyl groups in propanone exert a stronger electron-donating effect than the single methyl group in propene.
The following compound was heated with ethanolic sodium hydroxide.

Which of the following represents the structure of the organic product?

A

B

C

D
Esters can be converted to alcohols using lithium aluminium hydride followed by the addition of water.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H}_2 & \quad \text{C}_2 \text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{H}^- & \quad \text{H}^- \\
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H}_2 & \quad \text{C}_2 \text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \\
\text{H} & \quad \text{C} \\
\text{H}_2 & \quad \text{C}_2 \text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{H}_2 & \quad \text{C}_2 \text{H}_5
\end{align*}
\]

Which of the following reaction does **not** occur in this process?

A. Hydrolysis  
B. Hydrogenation  
C. Nucleophilic addition  
D. Nucleophilic substitution

When organic compounds P, Q, R and S are added separately to water, solutions of increasing pH values are obtained. The possible identities of the compounds P to S (not necessarily in that order) are given.

CH₃CH₂COOH  CH₃CH₂COCl  (CH₃)₂CHNH₂  H₂NCH₂CH₂COOH

Which is the correct set of identities of compounds P to S?

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₃CH₂COCl</td>
<td>CH₃CH₂COOH</td>
<td>H₂NCH₂CH₂COOH</td>
<td>(CH₃)₂CHNH₂</td>
</tr>
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<td>B</td>
<td>CH₃CH₂COCl</td>
<td>CH₃CH₂COOH</td>
<td>(CH₃)₂CHNH₂</td>
<td>H₂NCH₂CH₂COOH</td>
</tr>
<tr>
<td>C</td>
<td>CH₃CH₂COOH</td>
<td>CH₃CH₂COCl</td>
<td>H₂NCH₂CH₂COOH</td>
<td>(CH₃)₂CHNH₂</td>
</tr>
<tr>
<td>D</td>
<td>CH₃CH₂COOH</td>
<td>CH₃CH₂COCl</td>
<td>(CH₃)₂CHNH₂</td>
<td>H₂NCH₂CH₂COOH</td>
</tr>
</tbody>
</table>
One of the chemicals giving blue cheese its unique aroma is heptan-2-one.

The diagram shows reactions involving heptan-2-one.

Which is the correct identification of compound T, reagent U and compound V?

A  heptane  NaBH₄  heptanoic acid
B  heptan-2-ol  NaBH₄  heptanoic acid
C  heptanal  hydrogen gas  heptan-2-one
D  heptan-2-ol  LiA/H₄ in dry ether  heptan-2-one

The compound C₄H₆O₂ gives butter its distinctive flavour.

It reacts with hydrogen cyanide to form C₆H₈N₂O₂ but does not form a silver mirror with ammoniacal silver nitrate.

What is the structural formula of this compound in butter?

A  CH₃COCH₂CHO
B  CH₃COCOCH₃
C  CH₃COCH=CHOH
D  CH₂=CHCOCH₂OH
The two-stage reaction sequence given shows a possible mechanism for the reaction between hydroxide and ethanoyl chloride.

\[
\begin{align*}
\text{HO}^- & \quad \text{CH}_3 \text{C} \quad \text{Cl} \quad \rightarrow \quad \text{HO} \quad \text{CH}_3 \text{C} \quad \Theta \quad \rightarrow \quad \text{HO} \quad \text{CH}_3 \text{C} \quad \Theta \text{Cl}^- \\
\end{align*}
\]

In what way should the overall reaction be classified?

A. Electrophilic addition  
B. Nucleophilic addition  
C. Electrophilic substitution  
D. Nucleophilic substitution

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

What is the purpose of the sodium hydroxide?

A. to dry the product  
B. to liberate phenylamine  
C. to lower the boiling point for subsequent distillation  
D. to precipitate tin(II) hydroxide
Section B

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

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

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

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 In which sequences are the molecules quoted in order of decreasing boiling points?
1 CH₃(CH₂)₃CH₃, (CH₃)₂CHCH₂CH₃, CH₃C(CH₃)₂CH₃
2 AlBr₃, AlCl₃, AlF₃
3 SO₂, SiO₂, CO₂

32 Beryllium difluoride reacts readily with trimethylamine, (CH₃)₃N to form a stable addition product. Nitrogen trifluoride has no reaction with trimethylamine.

Which of the following statements are true?

1 Nitrogen trifluoride does not react as the nitrogen atom lacks energetically accessible orbitals for reaction.
2 The bond angle in the addition product is 109.5°.
3 The molar ratio for the reaction between beryllium difluoride and (CH₃)₃N is 1:1.
The responses A to D should be selected on the basis of

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</table>

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

33 The graph for the equilibrium,

\[ W (g) + X (g) \rightleftharpoons 3Y (g) \quad \Delta H < 0 \]

is given below:

Which of the following changes could account for the change from Graph 1 to Graph 2?

1. Addition of catalyst
2. Increase in temperature
3. Increase in pressure

34 A cell consisting of a \( V^{2+} \text{(aq)}, V^{3+} \text{(aq)} \) | Pt (s) half-cell and a \( \text{Au}^{3+} \text{(aq)} \) | Au (s) half-cell is shown below using conventional notation.

\[
\text{Pt (s)} | \text{V}^{2+} \text{(aq)}, \text{V}^{3+} \text{(aq)} || \text{Au}^{3+} \text{(aq)} | \text{Au (s)} \quad E^{\circ}_{\text{cell}} = +1.76 \text{ V}
\]

Which of the following statements is true?

1. The mass of the Au electrode increase.
2. The negative electrode is the Pt electrode.
3. The standard electrode potential for \( \text{Au}^{3+} \text{(aq)} \) | Au (s) is +2.02 V.
The responses A to D should be selected on the basis of

<table>
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<td></td>
</tr>
</tbody>
</table>

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

35 The graph shows the first thirteen ionisation energies for element Z.

[Graph showing ionisation energy vs number of electrons removed]

What can be deduced about element Z from the graph?

1 An oxide of Z dissolves in water to form an alkaline solution.
2 A chloride of Z undergoes hydrolysis to form a solution of pH 3.
3 The element Z reacts with steam to form an oxide.

36 Which of the following statements are correct with respect to the trend of the thermal stability of hydrogen halides, HX?

1 The enthalpy change of atomisation of the halogens becomes more endothermic from chlorine to iodine.
2 The enthalpy change of formation of the hydrogen halides becomes less exothermic from hydrogen chloride to hydrogen iodide.
3 The bond energy of the H–X bond becomes less endothermic from hydrogen chloride to hydrogen iodide.
The responses A to D should be selected on the basis of

<table>
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</tr>
<tr>
<td></td>
<td>correct</td>
<td>correct</td>
<td>correct</td>
<td></td>
</tr>
</tbody>
</table>

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

37  Alkanes can be prepared from chloroalkanes by heating under reflux with sodium (in ether) according to the equation:

\[ 2RCI + 2Na \rightarrow R-R + 2NaCl \]

Which alkanes will be produced if a mixture containing equal amounts of \( \text{CH}_3\text{CH}_2\text{Cl} \) and \( \text{CH}_3\text{CHClCH}_3 \) are used?

1. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
2. \( \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2 \)
3. \( \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2 \)

38  Oxytetracycline is a class of broad-spectrum antibiotics used to treat a variety of infections.

Which of the following statements about oxytetracycline is correct?

1. One mole of oxytetracycline reacts with three moles of thionyl chloride.
2. One mole of oxytetracycline reacts with two moles of hot sodium hydroxide to liberate one mole of ammonia gas.
3. One mole of oxytetracycline reacts with six moles of ethanoyl chloride.
The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

39 Benzoylglycine (hippuric acid) was first isolated from stallions’ urine.

\[
\text{CONHCH}_2\text{CO}_2\text{H}
\]

Which of the following reactions about hippuric acid are correct?

1. It can be made by reacting benzoyl chloride with aminoethanoic acid.
2. It can be made by reacting hot benzoic acid with aminoethanoic acid.
3. It can be hydrolysed with cold aqueous sodium hydroxide to produce an amino acid.

40 Amylase is an enzyme that converts complex carbohydrates into simple sugars.

Which conditions will inhibit the action of amylase?

1. High pH
2. Low temperatures
3. Presence of electrolytes

End of paper
### 2012 H2 Chemistry Prelim Paper 1 MCQ Key

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D</td>
<td>11</td>
<td>B</td>
<td>21</td>
<td>C</td>
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</tr>
<tr>
<td>2</td>
<td>B</td>
<td>12</td>
<td>D</td>
<td>22</td>
<td>B</td>
<td>32</td>
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<tr>
<td>3</td>
<td>D</td>
<td>13</td>
<td>B</td>
<td>23</td>
<td>A</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>14</td>
<td>C</td>
<td>24</td>
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<td>34</td>
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<td>5</td>
<td>B</td>
<td>15</td>
<td>B</td>
<td>25</td>
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<td>6</td>
<td>D</td>
<td>16</td>
<td>D</td>
<td>26</td>
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<td>D</td>
<td>17</td>
<td>D</td>
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<td>D</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td>A</td>
<td>18</td>
<td>A</td>
<td>28</td>
<td>B</td>
<td>38</td>
</tr>
<tr>
<td>9</td>
<td>B</td>
<td>19</td>
<td>D</td>
<td>29</td>
<td>D</td>
<td>39</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>20</td>
<td>A</td>
<td>30</td>
<td>B</td>
<td>40</td>
</tr>
</tbody>
</table>
Chemistry 9647

Paper 2 Structured Questions

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page. Write your calculator brand and model/number in the box provided above.

Answer all questions in the spaces provided on the question paper. All working must be shown clearly.

INFORMATION FOR CANDIDATES

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

You are reminded of the need for good English and clear presentation in your answers.

This document consists of 21 printed pages and 1 blank page.
1 Planning (P)

(a) The ‘solubility’ of a substance in aqueous solution is defined as the mass of anhydrous solid that will dissolve in and just saturate 100 g of water at a fixed temperature.

\[
\text{‘solubility’} = \frac{\text{mass of solid in a saturated solution}}{\text{mass of water in the saturated solution}} \times 100
\]

- A solution that is saturated at a particular temperature is one in which no more solid may be dissolved.
- A saturated solution can be recognised by undissolved solid in equilibrium with aqueous solution.
- For example, a saturated solution of potassium chlorate(V) can be represented by the equilibrium:

\[
\text{KClO}_3(s) \rightleftharpoons \text{KClO}_3(aq)
\]

You are provided with solid potassium chlorate(V), KClO_3, and distilled water. In addition to the standard apparatus present in a laboratory you are provided with the following materials:

- evaporating basin
- measuring cylinders

(i) Use the information given above to plan an experiment to describe how you would prepare a saturated solution of potassium chlorate(V) at room temperature.
(ii) Hence, describe an experiment to determine the ‘solubility’ of the potassium chlorate(V) prepared in (a)(i).

(iii) Create specimen results for your experiment and show how you would use these results to calculate the ‘solubility’ of potassium chlorate(V) at room temperature.

(iv) Identify a potential safety hazard in the experiment and state how you would minimise this risk.
(b) Sodium bromide crystallises as NaBr₂H₂O at low temperatures and as NaBr at higher temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility of sodium bromide /g per 100g H₂O</td>
<td>84.2</td>
<td>90.5</td>
<td>97.2</td>
<td>105.8</td>
<td>116.0</td>
<td>116.9</td>
<td>117.4</td>
<td>118.3</td>
<td>119.8</td>
<td>121.2</td>
</tr>
</tbody>
</table>

Plot the ‘solubility’ temperature data for sodium bromide and draw one line for the ‘solubility’ of NaBr₂H₂O and another line for the ‘solubility’ of NaBr. Draw two separate lines and extrapolate them to a point of intersection. The line at higher temperatures represents the ‘solubility’ of NaBr. The line at lower temperatures represents the ‘solubility’ of NaBr₂H₂O.
(i) Read from the graph the temperature where the two lines intersect. This is the transition temperature.

Estimated transition temperature = ______________________

(ii) Describe the difference in the variation of 'solubility' with temperature

• above the transition temperature,

• below the transition temperature.

The 'solubility' curve represents equilibrium conditions between solid sodium bromide and dissolved sodium bromide.

The position of equilibrium can be influenced by temperature change and whether a change is exothermic or endothermic.

From the shape of your graph, comment on the likely enthalpy change for solid sodium bromide dissolving under equilibrium conditions. Explain your answer.
2 A ketene is an organic compound of the form RR'C=C=O.

Ketenes can be prepared from acyl chlorides.

\[
\text{base} \quad \text{RR'CHCOCl} \rightarrow \text{RR'C=O} + \text{HC/}
\]

(a) Suggest the type of reaction that might occur during the preparation of ketenes from acyl chlorides.

Ketene is a reactive compound which readily undergoes addition reaction, for example

\[
\text{RR'C}=\text{C}=\text{O} + \text{H}_2\text{O} \rightarrow \text{RR'CHCOOH}
\]

Ketenes also undergo cycloaddition reaction with unsaturated compounds to form four-membered or larger rings.

(b) (i) Describe the mechanism for the reaction between ethenone and water.
(ii) Ethenone reacts with ethanoic acid to give compound \( R, \text{C}_4\text{H}_6\text{O}_3 \), which reacts with phenylamine to give compound \( S, \text{C}_8\text{H}_9\text{NO} \). Compound \( S \) yields phenylamine and sodium ethanoate with hot aqueous sodium hydroxide.

Suggest the structures of \( R \) and \( S \).

![Structure of R and S](image)

(iii) Compound \( T \), an ester, is formed when two molecules of ethenone react with one molecule of hydrogen cyanide.

\[
2\text{CH}_2=\text{C}=\text{O} + \text{HCN} \rightarrow \text{C}_5\text{H}_5\text{NO}_2
\]

\( T \)

Suggest a structure for the compound \( T \) using the given information on the addition and cycloaddition reactions of ketenes.

(iv) State the type of hybridisation and sketch the hybrid orbitals present at C-1 in ethenone.

\[
\overset{1}{\text{CH}_2=\text{C}=\text{O}}
\]

[Total: 8]
(a) Identify compounds A to E in the following reaction scheme.

\[ \text{a-terpineol, } \text{C}_{10}\text{H}_{18}\text{O}, \text{ contains an alcoholic group which is not easily oxidised.} \]

\[ \text{A} \quad \text{B} \quad \text{C} \quad \text{D} \quad \text{E} \]

\[ \text{warm alkaline aqueous iodine} \quad \text{acidified KMnO}_4 \quad \text{heat} \quad \text{H}_2, \text{Ni, 10 atm} \quad \text{yellow ppt} \]

\[ \text{excess conc. } \text{H}_2\text{SO}_4 \quad 170^\circ\text{C} \]

\[ \text{F} \]

\[ \text{A} \quad \text{B} \quad \text{C} \]

\[ \text{D} \quad \text{E} \]

\[ \text{[3]} \]
(b) The conversion of $\alpha$-terpineol to compound D uses HCl as the reagent.

(i) Suggest how you prepare gaseous HCl in the laboratory using sodium chloride as one of the reactants.

(ii) Explain, with aid of balanced equations, why small amounts of gaseous HI is produced when sodium iodide is used instead of sodium chloride in (b)(i).

(iii) Gaseous HI can also be prepared by another two-step method. Firstly, iodine is directly combined with red phosphorous to form phosphorus triiodide. In the next step, water is added to phosphorus triiodide to form gaseous HI and H$_3$PO$_3$ as a by-product.

Write balanced equations for the reactions above.
(c) Compound F can also be formed by using compound G.

![Chemical Reaction Diagram]

Suggest why compound B undergoes reduction with hydrogen over a nickel catalyst at room temperature and slight pressure, but compound G requires elevated temperature and pressure to form compound F.

(d) Compound G is oxidised by hot potassium manganate(VII) to form compound H, C₈H₆O₄.

(i) Draw the displayed formula of compound H.

(ii) Two isomers of compound G undergo oxidation with hot potassium manganate(VII) to give compound H in (d)(i).

Suggest the structures of the two isomers.
Electrophoresis can be used to separate amino acids produced by hydrolysing proteins. The amino acids are placed in a buffered solution in an electric field.

In an experiment, a spot of a solution containing a mixture of the 4 amino acids (tyr, lys, asp and phe) was placed in the middle of the plate in a buffered solution of pH 7. Following electrophoresis, the amino acids move to a new position under the influence of the electric charge.

**Table 1**: Amino acid data. This data is repeated on page 12.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Tyrosine (tyr)</th>
<th>Lysine (lys)</th>
<th>Aspartic Acid (asp)</th>
<th>Phenylalanine (phe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoelectric point</td>
<td>5.66</td>
<td>9.74</td>
<td>2.77</td>
<td>5.48</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="structure1.png" alt="Tyrosine Structure" /></td>
<td><img src="structure2.png" alt="Lysine Structure" /></td>
<td><img src="structure3.png" alt="Aspartic Acid Structure" /></td>
<td><img src="structure4.png" alt="Phenylalanine Structure" /></td>
</tr>
</tbody>
</table>

(i) Draw the structure of tyrosine formed in the buffered solution of pH 7.
This data is repeated from page 11.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Tyrosine (tyr)</th>
<th>Lysine (lys)</th>
<th>Aspartic Acid (asp)</th>
<th>Phenylalanine (phe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoelectric point</td>
<td>5.66</td>
<td>9.74</td>
<td>2.77</td>
<td>5.48</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="image" alt="tyrosine structure" /></td>
<td><img src="image" alt="lysine structure" /></td>
<td><img src="image" alt="aspartic acid structure" /></td>
<td><img src="image" alt="phenylalanine structure" /></td>
</tr>
</tbody>
</table>

(ii) Using the information provided, indicate on the diagram below the new position of the 4 amino acids when an electric current is applied.

Before electric current is applied

![Before diagram](image)

After electric current is applied

![After diagram](image)

(iii) Explain the relative position of the tyrosine and aspartic acid after the electric current is applied.
(b) Aspartame is an artificial sweetener which is about 200 times sweeter than sucrose.

Aspartame

(i) Aspartame is a high melting point crystalline white solid.

Explain the bonding in this solid that accounts for the high melting point.

(ii) A disadvantage of using aspartame as a sweetener is that it undergoes a chemical reaction and breaks up at a fast rate in acidic soft drinks.

1 Suggest a possible reason for the breaking up of aspartame in soft drinks.
2 Hence, suggest the structure of all the organic products formed in the reaction.
One possible synthesis route of aspartic acid is shown below.

Identify structures X and Y, and suggest the reagent(s) and conditions for steps I, II and III.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reagent(s) and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td></td>
</tr>
</tbody>
</table>

[5]

[Total: 12]
Tris is an abbreviation for tris(hydroxymethyl)aminomethane with the formula \((\text{HOCH}_2)_3\text{CNH}_2\). In biochemistry, Tris is widely used as a component of buffer solutions especially for solutions of nucleic acids.

(a) Describe and explain why the basicity of Tris differs from that of tert-butylamine, \((\text{CH}_3)_3\text{CNH}_2\).

(b) A solution containing Tris and Tris-Hydrochloride, \((\text{HOCH}_2)_3\text{CNH}_3^+\text{Cl}^-\) can resist pH changes on addition of small amounts of acid and base.

Write two relevant equations to illustrate how this occurs.
(c) Calculate the final pH, at 298 K, after a 5.00 cm³ portion of 1.00 mol dm⁻³ hydrochloric acid is added separately to

(i) 100 cm³ of 1.00 × 10⁻⁴ mol dm⁻³ sodium hydroxide solution.

(ii) 100 cm³ of solution X that contains 0.200 mol dm⁻³ Tris, (HOCH₂)₃CNH₂, and 0.200 mol dm⁻³ Tris-Hydrochloride, (HOCH₂)₃CNH₂⁺Cl⁻. (Given that pK₆ for Tris is 5.93 at 298 K)

(d) Solution Y contains 1.00 mol dm⁻³ Tris, (HOCH₂)₃CNH₂, and 1.00 mol dm⁻³ Tris-Hydrochloride, (HOCH₂)₃CNH₂⁺Cl⁻.

State which solution, X or Y, has a larger buffering capacity and explain why.
Iron is the most common element (by mass) on Earth. It exists in a wide range of oxidation states, although +2 and +3 are the most common states.

The chemical equation below shows the reaction of chlorine gas and iron(II) ion.

\[ \text{Cl}_2(g) + 2\text{Fe}^{2+}(aq) \rightarrow 2\text{Cl}^-(aq) + 2\text{Fe}^{3+}(aq) \]

(a) (i) Draw a diagram to show the apparatus needed to measure the \( E_{\text{cell}} \) for the above reaction. Label the chemicals and concentration of the chemicals used in the diagram. Indicate the direction of the electron flow.

(ii) Use the *Data Booklet* to calculate the \( E_{\text{cell}} \) for this reaction.
(b) On the other hand, ruthenium is a rare transition metal with oxidation states ranging from 0 to +8. The most common oxidation states are also +2 and +3.

The standard electrode potentials for Ru(III)/Ru(II) and Fe(III)/Fe(II) are given below.

\[
\begin{align*}
[\text{Ru(H}_2\text{O)}_6]^{3+} + e^- & \rightleftharpoons [\text{Ru(H}_2\text{O)}_6]^{2+} & E^\circ = +0.23 \text{ V} \\
[\text{Fe(H}_2\text{O)}_6]^{3+} + e^- & \rightleftharpoons [\text{Fe(H}_2\text{O)}_6]^{2+} & E^\circ = +0.77 \text{ V}
\end{align*}
\]

Comment on the relative stability of the +2 and +3 oxidation state of ruthenium compared to that of iron using the data above.

(c) When ruthenium(III) ions are treated with aqueous ammonia, an aqueous complex A is formed. Zinc is added to complex A and the resulting solution is treated with NaCl. Orange crystals of compound B are formed which contains 37% of ruthenium by mass.

(i) Suggest a formula for complex A and compound B.

Complex A …………………………  Compound B ……………………………

(ii) Aqueous ammonia is added to iron(III) chloride solution. The resulting mixture is treated with Zn metal to form compound C. Using the Data Booklet, suggest with reasoning the identity of compound C.
The following table lists some iron complexes together with their colours and their equilibrium constants, $K_c$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>$K_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(SCN)(H}_2\text{O)}_5]^{2+}(\text{aq})$</td>
<td>Deep red</td>
<td>$1 \times 10^2$</td>
</tr>
<tr>
<td>$[\text{FeF}_6]^{3-}(\text{aq})$</td>
<td>Colourless</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>$[\text{Fe(CN)}_6]^{4-}(\text{aq})$</td>
<td>Pale yellow</td>
<td>$1 \times 10^{24}$</td>
</tr>
<tr>
<td>$[\text{Fe(CN)}_6]^{3-}(\text{aq})$</td>
<td>Orange</td>
<td>$1 \times 10^{31}$</td>
</tr>
<tr>
<td>$[\text{Fe(edta)}]^{2-}(\text{aq})$</td>
<td>Colourless</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>$[\text{Fe(edta)}]^-(\text{aq})$</td>
<td>Yellow</td>
<td>$1 \times 10^{25}$</td>
</tr>
</tbody>
</table>

$[\text{edta} = (\text{-O}_2\text{CCH}_2\text{NCH}_2\text{CH}_2\text{N(CH}_2\text{COO}^-)\text{)}_2]$  

(d) Write down the equation for the formation of the complex ion formed when Fe$^{3+}$ is mixed with F$^-$ ions.

(e) Write an expression for the equilibrium constant, $K_c$, of $[\text{FeF}_6]^{3-}$.

(f) Use the data in the table to predict and explain:

(i) the effect of adding edta on the colour of a solution containing $[\text{Fe(SCN)(H}_2\text{O)}_5]^{2+}$,
(ii) the effect of adding EDTA on the $E^\circ$ value for the $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$ system.

(g) Explain why $[\text{Fe(CN)}_6]^{3-}$ is orange in colour.
1. (ai)
   1. Using a measuring cylinder, measure 100 cm$^3$ of water and place it in a 250 cm$^3$ beaker.
   2. Add solid KCIO$_3$ to water and stir with a glass rod to dissolve the solids.
   3. Add more solid KCIO$_3$ to the water until excess solids remains / no more solid dissolves.
   4. Allow the mixture to stand for a period of time (eg. 30 min) to establish equilibrium.
   5. Filter the solution to mixture to obtain the saturated solution as a filtrate.

(ii)
   1. Weigh an empty evaporating basin using a mass balance.
   2. Using a measuring cylinder, transfer 20 cm$^3$ of the saturated solution from (b)(i) into the weighed evaporating basin. (Any volume from 20 – 50 cm$^3$)
   3. Weigh the evaporating basin and saturated solution.
   4. Evaporate the water from the solution by placing the evaporating basin on top of a beaker of boiling water.
   5. Cool and reweigh the evaporating basin.
   6. Repeat the heating, cooling and weighing until a constant mass is obtained.

(iii) Mass of evaporating basin = $m_1$ g
     Mass of evaporating basin and 20 cm$^3$ saturated solution = $m_2$ g
     Final mass of solid KCIO$_3$ and evaporating basin = $m_3$ g
     Mass of water in saturated KCIO$_3$ solution = $m_2 - m_3$ g
     Mass of solid KCIO$_3$ in saturated solution = $m_3 - m_1$ g
     Solubility of KCIO$_3$ = \( \frac{m_3 - m_1}{m_2 - m_3} \times 100 \)

(iv) KCIO$_3$ solid is corrosive or caustic.
     Wear gloves when handling the reagent.
(i) 52.0 °C

(ii) above the transition temperature.
The solubility of NaBr increases gradually with temperature.

below the transition temperature.
The gradient of the graph is steeper, hence the solubility of NaBr.2H₂O increases more rapidly with temperature.

Dissolving sodium bromide under equilibrium conditions is endothermic.
2 (a) Elimination

(b) (i) Electrophilic addition

\[
\text{CH}_2=\text{C}=\text{O} \xrightarrow{\text{slow}} \text{CH}_3\text{C}=\text{O} + \text{:OH}^- \xrightarrow{} \text{CH}_3\text{COOH}
\]

(ii) \[\text{R} \quad \text{S}\]

(iii) \[\text{Diagram}
\]

(iv) \[\text{Diagram}
\]

3 (a)
(b) (i) Add concentrated sulfuric acid to sodium chloride.

(ii) \( I^- \) is a stronger reducing agent than \( Cl^- \)
Most of the HI can be oxidised by concentrated \( H_2SO_4 \) to form violet fumes of \( I_2 \) gas.

\[
NaI (s) \quad + \quad H_2SO_4 (l) \quad \rightarrow \quad HI (g) \quad + \quad NaHSO_4 (s)
\]

\[
8 HI (g) \quad + \quad H_2SO_4 (l) \quad \rightarrow \quad 4 I_2 (g) \quad + \quad H_2S (g) \quad + \quad 4 H_2O (l)
\]

(iii) \( P (s) \quad + \quad \frac{3}{2} I_2 (s) \quad \rightarrow \quad PI_3 (s) \)

or

\( P_4 (s) \quad + \quad 6 I_2 (s) \quad \rightarrow \quad 4 PI_3 (s) \)

\[
PI_3 (s) \quad + \quad 3 H_2O (l) \quad \rightarrow \quad H_3PO_3 (aq) \quad + \quad 3 HI (g)
\]

(c) Benzene in G is more resonance stabilized than alkene in B

(d) (i)

(ii)

4 (a) (i)
(iii) Aspartic acid and tyrosine formed negative ions and they migrate towards the positive terminal.

Aspartic acid is nearer to the positive terminal than tyrosine as the aspartic acid has a negative charge (-2) and a lower molecular mass than tyrosine.

(b) (i) Aspartame exist as zwitterions. A large amount of energy needed to break the ionic bonds between the oppositely charged ions

(ii) 1 acidic hydrolysis

2

CH₃OH
5 (a) The electron withdrawing hydroxyl grp decreases the electron density on the lone pair of N atom. Hence, the lone pair on N atom is less available to accept a proton.

Hence, Tris is less basic than tert-butylamine.

(b) \[(\text{HOCH}_2)_3\text{CNH}_2 \ + \ H^+ \rightarrow (\text{HOCH}_2)_3\text{CNH}_3^+\]
\[(\text{HOCH}_2)_3\text{CNH}_3^+ \ + \ \text{OH}^- \rightarrow (\text{HOCH}_2)_3\text{CNH}_2 \ + \ \text{H}_2\text{O}\]

(c) (i) No. of mole of (unreacted) HC\(\text{l}\) in 105 cm\(^3\) = 4.99 \times 10^{-3}
\[\text{[H}^+] = 4.99 \times 10^{-3}/0.105 = 0.04752 \text{ mol dm}^{-3}\]
\[\text{pH} = 1.32\]

(ii) \[\text{pOH} = 5.93 + \log \left( \frac{0.025/V}{0.015/V} \right) \text{ where V = total volume}\]
\[= 6.15\]
\[\text{pH} = 7.85\]

(d) Solution Y has a larger buffering capacity and will much better resist changes in pH upon the addition of a strong acid or base as the concentrations of its buffer components are much larger than that of solution X.
(a)  

\[
E_{\text{cell}} = +1.36 - (+0.77) = +0.59 \text{ V}
\]

(b) \(E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}}\) is more positive than \(E^0_{\text{Ru}^{3+}/\text{Ru}^{2+}}\), the relative stability of +2 oxidation state compared to +3 oxidation state is larger for iron than ruthenium.

(c)  

(i) Complex A \([\text{Ru(NH}_3\text{)}_6]^{3+}\)  

Compound B \([\text{Ru[(NH}_3\text{)}_6]^{2+}\cdot2\text{Cl}^{-}\) or \([\text{Ru[(NH}_3\text{)}_6]\cdot2\text{Cl}\) or \([\text{Ru(NH}_3\text{)}_6\text{Cl}_2\)  

(ii) \(E_{\text{cell}} = -0.56 - (-0.76) = +0.20\text{ V}\)  

Since \(\text{Fe(OH)}_3\) can be reduced by \(\text{Zn}\), the compound C is \(\text{Fe(OH)}_2\)

(d) \(\text{Fe}^{3+} + 6\text{F}^- \leftrightarrow \text{[FeF}_6]^{3-}\) or \([\text{Fe(H}_2\text{O)}_6]^{3+} + 6\text{F}^- \leftrightarrow \text{[FeF}_6]^{3-} + 6\text{H}_2\text{O}\)

(e)  

\[
K_c = \frac{[\text{FeF}_6]^{3-}}{[\text{Fe}^{3+}][\text{F}]^6}
\]

\[
K_c = \frac{[[\text{FeF}_6]^{3-}]}{[[\text{Fe(H}_2\text{O)}_6]^{3+}][\text{F}]^6}
\]

(f)  

(i) \(K_c\) of \([\text{Fe(edta})]^-\) is larger than \(K_c\) of \([\text{Fe(SCN)(H}_2\text{O)}_5]^{2+}\). Edta is a stronger ligand than \(\text{H}_2\text{O}\) and \(\text{SCN}^-\) and the deep red \([\text{Fe(SCN)(H}_2\text{O)}_5]^{2+}\) solution changes to yellow \([\text{Fe(edta})]^-\)

(ii) Addition of edta results in forming \([\text{Fe(edta})]^{2-}\) and \([\text{Fe(edta})]^-\).  

Since \(K_c\) of \([\text{Fe(edta})]^-\) is greater \(K_c\) of \([\text{Fe(edta})]^{2-}\), edta ligand stabilises \(\text{Fe(III)}\) relative to \(\text{Fe(II)}\) to a larger extent than water ligand. Hence \(E^\circ\) value is less than +0.77V/decreases.

(g) \([\text{Fe(CN)}_6]^{3-}\) has a partially-filled d orbitals; undergoes d-orbital splitting. During the transition, the d electron absorbs the blue wavelength of light from the visible region of the electromagnetic spectrum and emits the remaining wavelengths which appear as the orange colour of \([\text{Fe(CN)}_6]^{3-}\) observed.
H2 Chemistry

Paper 3 Free Response

Additional Materials: Data Booklet
Writing paper

INSTRUCTIONS TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer 4 out of 5 questions in this paper.

Begin each question on a fresh page of writing paper.

Fasten the writing papers behind the given Cover Page for Questions 1 & 2 and Cover Page for Questions 3, 4 & 5 respectively.

Hand in Questions 1 & 2, 3, 4 & 5 separately.

You are advised to spend about 30 min per question only.

INFORMATION FOR CANDIDATES

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

You are reminded of the need for good English and clear presentation in your answers.
Answer any 4 out of 5 questions in this paper. 
Begin each question on a fresh sheet of writing paper.

1 Sugars, or saccharides, are the most abundant bio-molecules found on the planet and play many important biological roles. A simple sugar, a derivative of a straight chain polyhydroxyl alcohol and glycerol, is considered to be the parent of all sugars.

(a) 2-chloropropane-1,3-diol can be synthesised from glycerol via the reaction scheme below.

\[
\begin{align*}
\text{glycerol} & \quad \xrightarrow{\text{KMnO}_4, \text{dilute H}_2\text{SO}_4, \text{heat}} \quad \text{HOOC} - & \text{C} - & \text{COOH} \\
\text{Step I} & & & & \\
\text{B} & \quad \xrightarrow{\text{Step II}} \quad \text{A} \\
\text{H}_2\text{O} & \quad \text{Step III} & \quad \text{2-chloropropane-1,3-diol} \\
\end{align*}
\]

Suggest reagents and conditions for steps I to III, and draw the structural formula of intermediates A and B. 

[5]
Glucose, an important simple sugar or monosaccharide, is required by the cells in our body as a source of energy and metabolic intermediate.

A common source of glucose is sucrose or table sugar. In humans and other mammals, sucrose is broken down into its constituent monosaccharides, glucose and fructose as shown below.

(i) Name the functional group, other than ether (R-O-R), present in sucrose.

(ii) Suggest the type of reaction undergone by sucrose.

(c) Glucose undergoes complete combustion to form carbon dioxide and water.

(i) Write a balanced equation for the complete combustion of glucose.

(ii) The standard enthalpy change of formation of CO₂, H₂O and glucose is -394 kJ mol⁻¹, -286 kJ mol⁻¹ and -1275 kJ mol⁻¹ respectively.

Use your answer in (c)(i) and the data given to calculate the energy released when 9.0 g of glucose undergoes complete combustion.

(iii) In a calometric experiment, 9.0 g of glucose was burnt completely and the energy released raised the temperature of 650 cm³ of water by 44°C.

Calculate the energy released by the combustion of 9.0 g of glucose in the experiment.

(iv) Suggest a reason for the discrepancy between the answers in (c)(ii) and (c)(iii).
(d) Group II nitrates and sugars undergo decomposition when heated.

(i) Write an equation for the thermal decomposition of Group II nitrates.

(ii) Suggest why the numerical value of the entropy change is very similar for the decomposition reaction of all the Group II nitrates.

(iii) Predict, with reasoning, whether magnesium nitrate or barium nitrate has a higher decomposition temperature.

(e) Chlorophyll is an extremely important bio-molecule which allows plants to absorb energy from light. It consists of a chlorin ring with a magnesium ion, Mg$^{2+}$, at the centre of the ring.

With the aid of an energy cycle, calculate the enthalpy change of hydration of Mg$^{2+}$ using the following data and appropriate data from the Data Booklet.

- enthalpy change of solution of MgCl$_2$  = $-153$ kJ mol$^{-1}$
- enthalpy change of hydration of Cl$^-$  = $-362$ kJ mol$^{-1}$
- enthalpy change of formation of MgCl$_2$  = $-642$ kJ mol$^{-1}$
- enthalpy change of atomization of Mg  = $+148$ kJ mol$^{-1}$
- first electron affinity of Cl  = $-364$ kJ mol$^{-1}$

[4]

[Total: 20]
2(a) Halogens react readily with hydrogen.

\[ \text{X}_2(g) + \text{H}_2(g) \rightarrow 2\text{HX}(g) \quad (\text{where } \text{X} = \text{Cl}, \text{Br} \text{ or I}) \]

(i) Describe how you could carry out this reaction using chlorine.

(ii) Describe **two** observations you would make if this reaction was carried out with bromine.

(iii) Describe and explain the trend observed in the reactions of the elements chlorine, bromine and iodine with hydrogen.

(b) Some halogens also react readily with alkanes. Consider the following sequence of reactions.

\[
\text{C}_6\text{H}_{14} \quad \xrightarrow{\text{Reaction 1}} \quad \text{C}_6\text{H}_{13}\text{X} \quad \xrightarrow{\text{Reaction 2}} \quad \text{C}_6\text{H}_{13}\text{OH}
\]

alkane **W**

(i) State the reagent and conditions needed for **reaction 1** when \( \text{X} \) is bromine, Br.

(ii) Use bond energy data from the *Data Booklet* to calculate the \( \Delta H^\circ \) of **reaction 1** when \( \text{X} \) is iodine, I.

(iii) Hence, suggest why it is not possible to synthesise iodoalkane by **reaction 1**.

(iv) In another separate experiment using **reaction 1**, alkane **W**, \( \text{C}_6\text{H}_{14} \), produced **only two** isomeric monobromo compounds **Y** and **Z**, with the molecular formula \( \text{C}_6\text{H}_{13}\text{Br} \). Compound **Z** is chiral.

Suggest the structures of **W**, **Y** and **Z**.

[6]
(c) Both isomers $Y$ and $Z$ with formula $C_6H_{13}Br$ can undergo reaction 2 with aqueous sodium hydroxide solution to form alcohols. When the reaction of one of these isomers with aqueous sodium hydroxide was investigated, the following kinetic data was obtained.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial $[C_6H_{13}Br]$ / mol dm$^{-3}$</th>
<th>Initial $[OH^-]$ / mol dm$^{-3}$</th>
<th>Initial rate of reaction / mol dm$^{-3}$ min$^{-1}$</th>
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<tbody>
<tr>
<td>1</td>
<td>1.30</td>
<td>2.60</td>
<td>13.0</td>
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<tr>
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<td>7.80</td>
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(i) Use these data to deduce the order of reaction with respect to each of the reagents, showing how you arrive at your answers. Hence, write the rate equation for the above reaction.

(ii) Suggest which isomer $Y$ or $Z$ was being investigated in the above reaction and explain your choice.

(iii) Hence, using the isomer you have suggested in (c)(ii), describe a mechanism that is consistent with your rate equation, and indicate which step in the mechanism is the rate determining step.

(iv) Draw a labeled energy profile diagram of the mechanism you described in (c)(iii).

[8]
[Total: 20]
3(a) Iron metal has traditionally been extracted from its ore using a Blast furnace. The process uses coke (carbon) and haematite (Fe$_2$O$_3$) in three stages, whereby

- coke is first oxidised by air to form carbon dioxide;
- the carbon dioxide formed further reacts with more coke to form carbon monoxide;
- the haematite is reduced to obtain the iron metal

New research proposes that iron could be recovered via electrolysis. This involves passing current via inert platinum electrodes into a mixture of molten Fe$_2$O$_3$. This new process is thought to be more advantageous than using the current Blast furnace method.

(i) Draw a diagram to illustrate the electrolysis set-up, showing clearly the polarity of the electrodes and the species attracted to and formed at each electrode.

(ii) Give the equations, including state symbols, for the reactions occurring at each electrode.

(iii) An initial pilot production plant using the new method yields 5 kg of iron per day. Calculate the current to be supplied per day if the pilot plant runs continuously for 24 hours each day.

(iv) Construct the equations for the reactions occurring at each stage of the Blast furnace extraction of iron.

(v) Suggest an advantage of the new electrolysis method over the Blast furnace method.

8

(b) Solutions of iron(II) compounds are commonly prepared in the laboratory.

(i) By selecting two appropriate half-equations from the Data Booklet, explain why iron(II) solutions are normally made up and stored in the presence of acids instead of bases.

(ii) With the aid of suitable equations, explain why iron(II) solutions can catalyse the reaction involving iodide ions with peroxodisulfate(VI) ions.

\[ 2I^- (aq) + S_2O_8^{2-} (aq) \xrightarrow{\text{f}} I_2 (aq) + 2SO_4^{2-} (aq) \]

5
Iron compounds can be used to catalyse a number of organic reactions. One such organic reaction is the Michael reaction as shown below.

\[
\begin{align*}
R'' & \quad + \\
\text{base / catalyst} & \\
H & \quad R' \quad R
\end{align*}
\]

E.g. of R or R' groups

E.g. of R'' groups

The reaction can also be carried out using sodium ethoxide (CH₃CH₂O⁻Na⁺) as a catalyst, whereby the labelled hydrogen \( H \) reacts with the ethoxide ion as a proton and is eventually transferred to its new position on the product.

(i) Explain how the ethoxide ion is able to remove the proton in the Michael reaction.

(ii) State the type of reaction which occurs in the Michael reaction.

The Michael reaction can be used to synthesise a useful blood anticoagulant known as Warfarin. The synthesis of Warfarin can give rise to two possible isomers.

(iii) Suggest the structure of compound \( A \) used to form Warfarin.

(iv) State the type of isomerism present in Warfarin and sketch the structures of these two isomers. [You may use R to represent a part of the molecule in your answer]

(v) Draw the structure of the product formed when 2,4-DNPH is reacted with Warfarin.
4 Oxygen reacts with various Period III elements to produce compounds of numerous uses. Examples are \( \text{Al}_2\text{O}_3 \) which is often used as a refractory material and chlorine oxides which act as oxidising agents used in water treatments and in bleaching.

(a) Element \( X \) forms a white oxide that is soluble in cold water. Its chloride dissolves in water to form a neutral solution.

Element \( Y \) forms two oxides. 0.09 mol of one of the two oxides produces 12.3 g of white precipitate when shaken with excess calcium hydroxide solution. A solution containing 1 mol of the oxide of element \( Y \) forms a neutral solution when the same amount of the oxide of element \( X \) is added to it.

Given that \( X \) and \( Y \) are Period III elements, identify the element \( X \) and the oxide of \( Y \) in the above reactions. Explain the observations with the help of relevant equations.

(b) When a sample of an oxide of chlorine, \( \text{Cl}_m\text{O}_n \), was vapourised in a suitable apparatus at 250 °C and 101 kPa, the density of the gas was found to be 1.60 g dm\(^{-3}\).

(i) Calculate the molar mass of the gas and hence suggest the value of \( m \) and \( n \).

(ii) Explain why the molar mass obtained in (b)(i) is different from the theoretical value.

(c) \( A \) to \( F \) are consecutive elements having atomic numbers between 10 to 20.

(i) Write an equation that represents the third ionisation energy of aluminium.

(ii) From the graph below, identify which element, \( A \) to \( F \), is aluminium. Explain your answer.
Other than its use as a refractory material, \( \text{Al}_2\text{O}_3 \) is also used in chemical reactions involving organic compounds. In the reaction scheme below, \( \text{Al}_2\text{O}_3 \) is used to dehydrate chloramphenicol-X to form compound D.

(ii) Identify the lettered compounds A to D.

(ii) Suggest the reagent and condition used in step II. State the type of reaction occurring in step II.

(iii) Describe a simple chemical test to distinguish between chloramphenicol-X and its isomer shown below.

---

[Total: 20]
Fluoxetine is an anti-depressant drug or mood elevator commonly used to treat depression and other mental illness like obsessive compulsive behaviour.

The structure of Fluoxetine is shown below:

```
  \text{NH} \quad \text{O} \quad \text{H} \\
\quad \text{N} \quad \text{H} \quad \text{O} \\
\text{O} \quad \text{H} \quad \text{N} \\
\text{O} \quad \text{H} \quad \text{N} \\
\text{O} \quad \text{H} \quad \text{N} \\ 
```

Fluoxetine

(a) (i) Draw a diagram to show how hydrogen bonding occurs between one molecule of Fluoxetine and two molecules of water.

(ii) Suggest why Fluoxetine is insoluble in water despite the formation of hydrogen bonding between Fluoxetine and water molecules.

(iii) Fluoxetine is manufactured and merchandised as Fluoxetine hydrochloride. Explain, in terms of structure and bonding, why this is so.

[5]

(b) Bupropion is another type of anti-depressant. It is synthesised from 3-chloropropiophenone as shown in the pathway below.

```
\text{Cl} \quad \text{O} \quad \text{Cl} \quad \text{O} \quad \text{Br} \quad \text{NH} \quad \text{O} \\
\text{C(CH_3)_3} \quad \text{C(CH_3)_3} \\
```

3-chloropropiophenone intermediate X Bupropion

(i) State the type of reaction that occurs in step I.

(ii) Suggest the reagents and conditions for step II.

(iii) Draw the structure of the product obtained by heating intermediate X with aqueous potassium hydroxide.

[3]
(c) Compound A, C_{11}H_{15}NO_3, has potential to treat certain mental disorders. Compound A reacts with aqueous bromine to form compound B, C_{11}H_{13}NO_3Br_2. 1 mole of compound A reacts with 2 mole of aqueous sodium hydroxide at room temperature. No decolourisation is observed upon heating compound A with acidified potassium manganate(VII). Compound A reacts with iodomethane to form compound C, C_{12}H_{16}NO_3I, which yields a yellow precipitate with aqueous silver nitrate at room temperature.

Suggest the structure of each lettered compound and explain the reactions involved.

[8]

(d) In some cases of mental illness, lithium ion, Li^+, can also be administered in the form of lithium salt as a mood-stabilizing drug.

(i) Explain why Li has the lowest first ionisation energy among the Period 2 elements.

(ii) All Group I halides dissolve in water to give neutral solutions containing hydrated ions.

Suggest why lithium forms Li(H_2O)_4^+ ions, whereas the other Group I halides form mainly M(H_2O)_6^+ ions.

[4]

[Total: 20]
INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer any 4 out of 5 questions in Paper 3.

Begin each question on a fresh page of writing paper.

Fasten your answers for Question 1 and 2 behind this Cover Page.

You are advised to spend about 30 min per question.

Circle the questions that you attempted.

INFORMATION FOR CANDIDATES

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

You are reminded the need for good English and clear presentation in your answers.

FOR EXAMINER’S USE

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<th>/ 20</th>
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18 September 2012

INSTRUCTION TO CANDIDATES

Write your name, class and register number in the spaces provided at the top of this page.

Answer any 4 out of 5 questions in Paper 3.

Begin each question on a fresh page of writing paper.

Fasten your answers for Question 3, 4 and 5 behind this Cover Page.

You are advised to spend about 30 min per question.

Circle the questions that you attempted.

INFORMATION FOR CANDIDATES

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

You are reminded the need for good English and clear presentation in your answers.
1 (a) Reaction I: NaBH₄ in ethanol, rtp  
Reaction II: PCl₅, rtp  
Reaction III: LiAlH₄ in dry ether, rtp

(b) (i) 1° and 2° alcohols
(ii) Hydrolysis

(c) (i) C₆H₁₂O₆ + 6O₂ ⇌ 6CO₂ + 6H₂O
(ii) ΔH_rxn = [6(-394) + 6(-286)] - [-1275] = - 2805 kJ mol⁻¹  
Energy released = 2801 x 0.0500 = 140 kJ
(iii) Energy released by combustion = 650 x 4.18 x 44 = 120 kJ
(iv) Some heat was lost to the surrounding.

(d) (i) M(NO₃)₂ ⇌ MO + 2NO₂ + ½O₂
(ii) Each mole of Group II nitrates release the same amount of gaseous molecules.
(iii) Ionic size of cation: Mg²⁺ < Ba²⁺  
Charge density hence polarizing effect of cation: Mg²⁺ > Ba²⁺  
Therefore Ba(NO₃)₂ has a higher decomposition temperature.

(e) MgCl₂ (s) \[\Delta H_{\text{soln}}(\text{MgCl}_2)\] \[\text{Mg}^2+ (\text{aq}) + 2\text{Cl}^- (\text{aq})\] 
\[\text{Mg}(s) + \text{Cl}_2(g)\] 
\[\Delta H_{\text{f}}(\text{MgCl}_2)\] 
\[\text{BE}(\text{Cl}^- - \text{Cl})\] 
\[\Delta H_{\text{hyd}}(\text{Mg}^2+)\] 
\[2 \times \Delta H_{\text{hyd}}(\text{Cl}^-)\] 
\[\Delta H_{\text{f}}(\text{Mg})\] 
\[\Delta H_{\text{f}}(\text{Cl}_2)\] 
\[\text{Mg}(g) + 2\text{Cl}_2(g)\] 
\[1\text{st IE} + 2\text{nd IE}(\text{Mg})\] 
\[\text{Mg}^2+(g) + 2\text{Cl}_2(g) + 2e^-\] 
\[2 \times 1\text{st EA}(\text{Cl})\] 
\[\text{Mg}^2+(g) + 2\text{Cl}^- (g)\] 
\[\Delta H_{\text{hyd}}(\text{Mg}^2+) = -148 - 244 - 736 - 1450 - 2 \times (-364) - 2 \times (-362) + (-642) + (-153)\] 
\[\text{hence } \Delta H_{\text{hyd}}(\text{Mg}^2+) = -1921 \text{ kJ mol}^{-1}\]
2(a) (i) Shine uv light on the mixture of hydrogen and chlorine gas.
(ii) Decolorisation of reddish brown bromine; white fumes of HBr seen.
(iii) Reactivity of halogens with hydrogen decreases down the group.

The total bond energy released in forming H-X decreased down the group more significantly than the total bond energy absorbed in breaking X-X and H-H bonds. ΔHrxn becomes more endothermic down the group, reactivity decrease down the group.

(b) (i) Limited Br₂ gas and uv light
(ii) \( \Delta H = 410 + 151 - 240 - 299 = +22.0 \text{ kJ mol}^{-1} \)
(iii) Endothermic due to the weak C-I bond formed.
(iv) \[
\begin{align*}
W: & & \text{CH}_3 & \text{CH}_3 \\
\text{H} & \text{H} & \text{H} & \text{CH}_3 \\
Z: & & \text{CH}_3 & \text{CH}_3 & \text{CH}_2\text{Br} \\
\text{H} & \text{Br} & \text{H} & \text{H}
\end{align*}
\]

(c) (i) Comparing experiments 1 & 3, when \([C_6H_{13}Br]\) was tripled, the initial rate of reaction increased by 3 times, order of reaction wrt \(C_6H_{13}Br\) is 1.

Comparing experiments 1 & 2
\[
\frac{13.0}{26.0} = \frac{[1.30][2.60]^b}{[2.60][1.30]^b}
\]
\[
1 = \left( \frac{2.60}{1.30} \right)^b
\]
\[
b = 0
\]
Rate = \(k[C_6H_{13}Br]\)

(ii) It should be isomer Y since it is a tertiary bromoalkane, it will form a stable carbocation in the slow step of the mechanism due to the presence of three electron donating alkyl group.
(iii) Mechanism: SN1

\[
(CH_3)_2CH-C(CH_3)_2Br + OH^- \rightarrow (CH_3)_2CH-C(CH_3)_2OH + Br^-
\]

(iv) Marking points:
- Axes are correctly labeled

3(a) (i)

(ii) Cathode: \( Fe^{3+} (l) + 3e^- \rightarrow Fe (s) \); Anode: \( 2O^2- (l) + O_2 (g) + 4e^- \)

(iii) \[
\frac{5 \times 1000}{55.8} = \frac{I \times 24 \times 60 \times 60}{3 \times 96500}; I = 300 \text{ A}.
\]
(iv) \[ \text{C} + \text{O}_2 \uparrow \rightarrow \text{CO}_2; \text{CO}_2 + \text{C} \uparrow \rightarrow 2\text{CO}; \text{Fe}_2\text{O}_3 + 3\text{CO} \uparrow \rightarrow 2\text{Fe} + 3\text{CO}_2 \]

(v) Less / no pollutants of CO or CO\(_2\) are formed.

(b)(i) Fe(II) is stabilised with respect to Fe(III) in acidic medium compared to basic medium. Fe\(^{2+}\) in acidic medium is a weaker reducing agent compared to Fe(OH)\(_2\) in basic medium.

(ii) Fe\(^{2+}\) acts as a homogeneous catalyst

\[
\text{Step 1: } 2\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}
\]

\[
\text{Step 2: } 2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2
\]

(c) (i) Ethoxide ion acts as a base

(ii) (Nucleophilic) Addition

(iii) 

(iv) Optical isomerism

(v)

4(a) Element X : Sodium / Na

\[ \text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]
Formula of the oxide of Element Y: SO₃

Upon addition of Ca(OH)₂, white ppt formed could be CaSO₄

No of mol of CaSO₄ = = 0.09 mol

SO₃ + Ca(OH)₂ → CaSO₄ + H₂O
white ppt

SO₃ + H₂O → H₂SO₄

H₂SO₄ + Na₂O → Na₂SO₄ + H₂O

(b) (i) \[101 \times 1000 \times M = \frac{134.5 - 0.298}{\text{average } M_r} \times 1.60 \times 10^3 \times 8.31 \times (250 + 273)\]

Molar mass of gas = 68.8 g mol⁻¹ = 67.5 g mol⁻¹

Hence m = 1, n = 2

(ii) There is significant van der Waals forces of attraction between the C/O₂ molecules.

(c) (i) \[\text{A}^{2+} (g) + \text{A}^{3+} (g) + e\]

(ii) C is aluminium, as it has the lowest 3rd IE. The removal of the third electron will lead to the formation of the stable noble gas configuration hence a small amount of energy is required to remove the valence electron.

(d) (i) A:

B, C:

D:

(ii) H₂O (g) or steam, conc. H₃PO₄, 65 atm, 300°C

Electrophilic Addition
(iii) Add 2,4-DNPH to each compound separately and heat. Chloramphenicol-X will not produce orange ppt of hydrazine; its isomer will produce orange ppt of hydrazone.

5(a) (i) Due to the presence of a large hydrophobic benzene rings.
(ii) Formation of ion-dipole interaction with water molecules causes solvation hence drug is better absorbed.

(b) (i) Free radical substitution
(ii) excess (CH₃)₃CNH₂, heat
(iii)

(c) A:

Or A can also be 1, 2 di-substituted isomer
(d)(i) Effective nuclear charge increases. The electrostatic force of attraction between nucleus and valence electrons increases hence energy required to remove the valence electrons increases.

(ii) Li$^+$ has the smallest ionic radius among the group I metal ion. Less H$_2$O ligands can be datively bonded to Li$^+$ cation, thus the coordination number is 4 and Li(H$_2$O)$_4^+$ ions is formed.
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

There are 40 questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D.

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

This paper consists of 18 printed pages and 0 blank page.
Section A

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

1. Which atom has the highest ratio of unpaired electrons to paired electrons in its ground state?
   - A boron
   - B carbon
   - C nitrogen
   - D oxygen

2. Bombardment of $^{14}$N with $\alpha$-particles (helium nuclei) produces a hydrogen nucleus and another nucleus. This other nucleus is
   - A $^{14}$C$_6$
   - B $^{14}$N$_7$
   - C $^{17}$O$_8$
   - D $^{18}$Ne$_{10}$

3. The successive ionisation energies (kJ mol$^{-1}$) of two elements are given below:

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<th>X</th>
<th>Y</th>
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<td>33604</td>
</tr>
<tr>
<td>9</td>
<td>35905</td>
<td>38860</td>
</tr>
</tbody>
</table>

Which of the following statements is false?
   - A The formula of the compound formed between X and Y is XY$_3$.
   - B The compound formed between X and Y is covalent.
   - C X has a giant covalent structure.
   - D Y exists as diatomic molecules.

4. When the N$_2^+$ ion is formed from N$_2$, a $\sigma$ bonding electron is removed. Which statement is correct?
   - A The bond order decreases so N$_2^+$ has a stronger, shorter bond than N$_2$.
   - B The bond order decreases so N$_2^+$ has a weaker, longer bond than N$_2$.
   - C The bond order increases so N$_2^+$ has a stronger, shorter bond than N$_2$.
   - D The bond order increases so N$_2^+$ has a weaker, longer bond than N$_2$. 
5 In which pair of species are the values of the bond angles the closest?

A BF₃ and NH₃  
B CH₃⁻ and BF₃  
C H₂O and C₂H₄  
D NH₄⁺ and SO₄²⁻

6 10 cm³ of hydrocarbon is burnt in 100 cm³ of excess oxygen at room temperature. The final volume of gas mixture is 85 cm³. When the gas mixture is bubbled through aqueous sodium hydroxide solution, the volume of gas mixture decreases to 55 cm³. What is the formula of the hydrocarbon?

A C₃H₆  
B C₃H₈  
C C₆H₁₂  
D C₆H₁₄

7 Use of the Data Booklet is relevant to this question. The graph represents the variation of a property of the Group II elements.

What is this property?

A ionic radius  
B ionisation energy  
C neutron / proton ratio  
D rate of reaction with water
The diagram shows bond energies in halogen molecules.

Why does the value for fluorine not follow the trend shown by chlorine, bromine and iodine?

A  Fluorine is more electronegative than the other halogens.
B  Lone electron pairs in fluorine repel more strongly than those in the other halogens.
C  The bonds in fluorine are more polar than those in the other halogens.
D  The bonds in fluorine have some $\pi$-character.

What is the pressure (in Pa) of a sample of hydrogen gas that has density of 8 g m$^{-3}$ at 300 °C?

A  $\frac{573 \times 4 \times 22.4 \times 101 \times 10^3}{273}$
B  $\frac{573 \times 8 \times 22.4 \times 101}{273}$
C  $\frac{273 \times 4 \times 11.2 \times 101 \times 10^3}{573}$
D  $\frac{573 \times 8 \times 11.2 \times 101}{273}$
10 The rate equation for the reaction

\[ \text{S}_2\text{O}_8^{2-} (aq) + 2 \text{I}^- (aq) \rightarrow 2\text{SO}_4^{2-} (aq) + \text{I}_2(aq) \]

is rate = \( k[S_2O_8^{2-}][I^-] \) where \( k \), the rate constant is found to be 0.2 mol\(^{-1}\) dm\(^3\) s\(^{-1}\) at temperature \( t \).

What is the half-life of the reaction when \( S_2O_8^{2-} \) is present in a large excess at a concentration of 0.5 mol dm\(^{-3}\) at the same temperature \( t \)?

A 0.7 s  
B 1.4 s  
C 3.5 s  
D 6.9 s

11 Hess’s Law can be used to calculate the average C–H bond energy in methane.

\[ \Delta H_{\text{at}}^o = \text{standard enthalpy change of atomisation} \]
\[ \Delta H_{\text{f}}^o = \text{standard enthalpy change of formation} \]
\[ \Delta H_{\text{c}}^o = \text{standard enthalpy change of combustion} \]

Which values of the following data are needed in order to perform the calculation?

A \( \Delta H_{\text{c}}^o (\text{C}) \), \( \Delta H_{\text{c}}^o (\text{H}_2) \), \( \Delta H_{\text{c}}^o (\text{CH}_4) \)  
B \( \Delta H_{\text{at}}^o (\text{C}) \), \( \Delta H_{\text{at}}^o (\text{H}_2) \), \( \Delta H_{\text{f}}^o (\text{CH}_4) \)  
C \( \Delta H_{\text{c}}^o (\text{C}) \), \( \Delta H_{\text{c}}^o (\text{H}_2) \), \( \Delta H_{\text{f}}^o (\text{CH}_4) \)  
D \( \Delta H_{\text{f}}^o (\text{CH}_4) \) only as \( \Delta H_{\text{f}}^o (\text{C}) \) and \( \Delta H_{\text{f}}^o (\text{H}_2) \) are defined as zero.

12 In a car engine, non-metallic element \( X \) forms a pollutant oxide \( Y \). Further oxidation of \( Y \) to \( Z \) occurs spontaneously in the atmosphere. In this further oxidation, 2 mol of \( Y \) reacts with 1 mol of gaseous oxygen. \( Z \) can dimerise at specific conditions.

Which statement about \( X \), \( Y \) and \( Z \) is **incorrect**?

A \( X \) forms a basic hydride.  
B \( Y \) is a diatomic molecule.  
C \( Z \) is a polar molecule.  
D \( Z \) contributes to global warming.
13 The diagram below represents the reaction profile of the monomer-dimer system:

\[ 2\text{NO}_2 (g) \xrightleftharpoons[k_f]{k_b} \text{N}_2\text{O}_4 (g) \]

brown \hspace{1cm} \text{colourless}

Which statement about the equilibrium is correct?

A The equilibrium constant \( K_c \) will be larger at higher temperatures.
B \( k_f \) increases and \( k_b \) decreases when the equilibrium mixture is heated.
C Doubling the total pressure of the system reduces the percentage dissociation to half.
D At higher temperature, the colour intensity of the mixture increases.

14 Which of the following statements about the spontaneity of the gas-phase reaction shown is true at 25 °C?

\[ 2\text{O=NCI(g)} \rightarrow 2\text{N=O(g)} + \text{Cl}_2(g) \]

A The reaction cannot be spontaneous.
B The reaction will be spontaneous regardless of the magnitude of \( \Delta H \) and \( \Delta S \).
C The reaction will be spontaneous only if the magnitude of \( \Delta H \) is large enough to overcome the unfavorable entropy change.
D The reaction will be spontaneous only if the magnitude of \( \Delta S \) is large enough to overcome the unfavorable enthalpy change.
When a mineral was heated in a Bunsen flame to constant mass, a colourless gas that turned limewater milky was evolved. The remaining solid was cooled and then added to aqueous hydrochloric acid. Vigorous effervescence was seen.

What was the mineral?

A  Dolomite, CaCO₃, MgCO₃
B  Barytocalcite, BaCO₃, CaCO₃
C  Aragonite, CaCO₃
D  Artinite, MgCO₃, Mg(OH)₂·3H₂O

The following two experiments are carried out with anhydrous potassium chloride and observations X and Y are made at the end of each experiment.

Concentrated sulfuric acid is added to the potassium chloride and the fumes produced are bubbled into aqueous potassium iodide solution - observation X.

The potassium chloride is dissolved in aqueous ammonia and this is then added to aqueous silver nitrate - observation Y.

What are the observations X and Y?

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Brown solution</td>
<td>Colourless solution</td>
</tr>
<tr>
<td>B</td>
<td>Brown solution</td>
<td>White precipitate</td>
</tr>
<tr>
<td>C</td>
<td>Colourless solution</td>
<td>Colourless solution</td>
</tr>
<tr>
<td>D</td>
<td>Colourless solution</td>
<td>White precipitate</td>
</tr>
</tbody>
</table>

The unbalanced equation below involves manganese species in acid medium.

\[ \text{MnO}_4^{2-} \rightarrow \text{Mn}^{2+} + \text{MnO}_4^- \]

Which of the following statements is false?

A  This is a disproportionation reaction.
B  MnO₄⁻ ions are purple due to the presence of d–d electronic transition.
C  Unequal amounts of Mn²⁺ and MnO₄⁻ ions are formed.
D  The 3d electrons in Mn²⁺ ions are unpaired.
18 The oxide and chloride of an element \( X \) are separately mixed with water. The two resulting solutions have the same effect on litmus. What is element \( X \)?

A  Sodium
B  Magnesium
C  Aluminum
D  Phosphorus

19 Under similar conditions, carbon monoxide competes 200 times more effectively than oxygen for haemoglobin available in blood. The effects in the body of carboxyhaemoglobin are detectable when it reaches 5% of the concentration of oxyhaemoglobin in the blood. Air contains 20% of oxygen by volume.

By using these data, it can be deduced that the minimum concentration (parts per million, ppm) of carbon monoxide in the atmosphere that will result in detectable effects in the body is

A  10 ppm
B  50 ppm
C  250 ppm
D  500 ppm

20 Which of the following compounds is not made up of 6.90% and 51.7% by mass of hydrogen and carbon respectively?

A  \( \text{O} \equiv \text{S} \)
B  \( \text{O} - \text{O} - \text{O} \)
C  \( \text{CH}_3\text{CSCH(CH}_3\text{)CHO} \)
D  \( \text{CH}_3\text{CO(}\text{CH}_2\text{)}_2\text{CO}_2\text{H} \)
21 A halogenoalkane is reacted with NH₃ in the following reaction. Which of the statements is correct?

\[
\begin{align*}
\text{NH}_3 & \quad \text{RX} \quad \text{Step 1} \\
\text{R-NH}_2 & \quad \text{RX} \quad \text{Step 2} \\
\text{NH-R} & \quad \text{RX} \quad \text{Step 3} \\
\text{N}^+\text{R-R} & \quad \text{RX} \quad \text{Step 4}
\end{align*}
\]

A  Rate of reaction of step 2 is faster than step 3 as RNH₂ is a stronger nucleophile.
B  Rate of reaction of step 3 is faster than step 2 as RNH₂ is a stronger nucleophile.
C  R₄N⁺ will be the major product when excess RX is used.
D  R₄N⁺ will be the major product when excess NH₃ is used.

22 Aspartic acid, HO₂CCH₂CH(NH₂)CO₂H, is an essential amino acid. Its anion, aspartate, is an important metabolite in the urea cycle. Aspartic acid can be used to make polymers.

Which of the following statements is true?

A  A white precipitate is formed when aqueous silver nitrate is added to compound B.
B  Reagent A is aqueous thionyl bromide.
C  One mole of hot aqueous KOH is required to react with one mole of polymer X in reaction III.
D  The imide (the –CONR₂ group present in the polymer X) has a higher pKₐ value than an average amide.

23 Which of the following gives the compounds in order of decreasing Kₐ?

A  CH₃CH₂OH > C₆H₅OH > CH₃CO₂H
B  CH₃CF₂CO₂H > FCH₂CHFCO₂H > F₂CHCH₂CO₂H
C  CH₃CH₂CO₂H > CH₂(OH)CH₂COOH > CH₃CH(OH)CO₂H
D  CH₃CH₂CO₂H > CH₃CH(OH)CO₂H > CH₂(OH)CH₂COOH
A chloroalkane \( G \) with molecular formula \( C_5H_{11}Cl \) exhibits optical activity. On warming \( G \) with alcoholic \( \text{NaOH} \), two alkenes \( E \) and \( F \) are formed, \( E \) being the major product. One of the products of the reaction between \( E \) and hot acidified potassium manganate(VII) gives a yellow precipitate with alkaline aqueous iodine.

Which of the following could be \( G \)?

A  \( \text{CH}_3\text{CHC}/\text{CH}_2\text{CH}_2\text{CH}_3 \)

B  \( \text{CH}_3\text{CH}_2\text{CHC}/\text{CH}_2\text{CH}_3 \)

C  \( \text{CH}_3\text{CH(CH}_3\text{)}\text{CHC}/\text{CH}_3 \)

D  \( \text{CH}_3\text{CC}/(\text{CH}_3)\text{CH}_2\text{CH}_3 \)

Which of the following compounds can be prepared by the apparatus shown?

A  1,2-dibromoethane by using bromine and ethene.

B  Ethanoic acid by using ethanol, sodium dichromate(VI) and sulfuric acid.

C  Bromoethane by using ethanol, sodium bromide and concentrated sulfuric acid.

D  Phenyl ethanoate by using phenol and ethanoyl chloride.
26 It has been estimated that for every atom of chlorine or bromine generated from a halogenoalkane in the stratosphere, one hundred thousand molecules of ozone may be destroyed.

Which of the following organic compounds is most destructive to ozone?

A CF₂C/CH₂CF₂C/
B CC₂BrCH₂Br
C CHC₂CBr₃
D CCl₄

27 What is the total number of stereoisomers that can be obtained from the major product of the reaction between compound H and NaOH in ethanol?

\[
\begin{align*}
\text{Br} & \quad \text{CH₃} \quad \text{C} \quad \text{CH₂CH₂CH=CHCH₃} \\
& \quad \text{compound H}
\end{align*}
\]

A 2
B 4
C 8
D 12
When a nonapeptide (containing nine amino acid residues) isolated from rat brains was hydrolysed, it gave the following smaller peptides as identifiable products:

- Gly-Ala-Phe
- Ala-Leu-Val
- Gly-Ala-Leu
- Phe-Glu-His
- His-Gly-Ala

What is the amino acid sequence in the nonapeptide?

A. Gly-Ala-Leu-Val-Phe-Glu-His-Gly-Ala
B. Phe-Glu-His-Gly-Ala-Leu-Val-Gly-Ala
C. Gly-Ala-Phe-Glu-His-Gly-Ala-Leu-Val
D. His-Gly-Ala-Phe-Glu-His-Leu-Val-Gly

A tripeptide, cysteine-alanine-histidine, was analysed using electrophoresis. The tripeptide was hydrolysed and the resulting solution was then placed at the centre of the plate in a buffer solution of pH 6.5. A potential difference was then applied across the plate.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Isoelectric point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cysteine (cys)</td>
<td>5.05</td>
</tr>
<tr>
<td>Alanine (ala)</td>
<td>6.00</td>
</tr>
<tr>
<td>Histidine (his)</td>
<td>7.60</td>
</tr>
</tbody>
</table>

With reference to the above table, which of the following statements is correct?

A. Alanine would remain at the centre of the plate.
B. Cysteine would migrate towards the cathode.
C. Histidine would migrate towards the anode.
D. Alanine would migrate towards anode.
The sequence below is the repeat unit of a polypeptide chain in egg albumin.

\[
\begin{array}{c}
 N \text{CH}_3 \\
 C \text{CH}_2C_6H_5 \\
 C \text{CH}_2OH \\
\end{array}
\begin{array}{c}
 H \\
 O \\
 O \\
\end{array}
\begin{array}{c}
 N \\
 C \\
 C \\
\end{array}
\begin{array}{c}
 N \\
 C \\
 C \\
\end{array}
\begin{array}{c}
 H \\
 O \\
 O \\
\end{array}
\begin{array}{c}
 N \\
 C \\
 C \\
\end{array}
\begin{array}{c}
 H \\
 O \\
 O \\
\end{array}
\begin{array}{c}
 N \\
 C \\
 C \\
\end{array}
\begin{array}{c}
 H \\
 O \\
 O \\
\end{array}
\begin{array}{c}
 N \\
 C \\
 C \\
\end{array}
\begin{array}{c}
 H \\
 O \\
 O \\
\end{array}
\begin{array}{c}
 N \\
 C \\
 C \\
\end{array}
\]

Which of the following will cause this part of the protein to coagulate?

I. Addition of Pb(NO_3)_2(aq)
II. Heating in a frying pan
III. Addition of H_2SO_4(aq)
IV. Whisking with an egg beater

A. II and IV only
B. I, II and III only
C. II, III and IV only
D. I, II, III and IV
Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct.)

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

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2, and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 The table below gives the percentage of HX dissociated into H₂ and X₂ at different temperatures.

<table>
<thead>
<tr>
<th>Temperature/ °C</th>
<th>HF</th>
<th>HC/</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13</td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>-</td>
<td>4 x 10⁻²</td>
<td>22</td>
</tr>
<tr>
<td>2000</td>
<td>6 x 10⁻⁵</td>
<td>4 x 10⁻¹</td>
<td>4</td>
<td>30</td>
</tr>
</tbody>
</table>

Which of the following statements explain the data given?

1 The polarity of the H–X bond becomes weaker on going down the group.
2 The s-p overlap in the H–X bond is less efficient on going down the group.
3 The dissociation of HX is an endothermic reaction.

32 All the statements below are true.

Which of these can be explained, at least in part, by reference to hydrogen bonding?

1 Ice floats on water.
2 The boiling point of propan-2-ol is 82 °C. The boiling point of propanone is 56 °C.
3 At a specific temperature, the apparent relative molecular mass of ethanoic acid is 90.
33 In which of the following does statement II give a correct explanation for statement I?

<table>
<thead>
<tr>
<th>Statement I</th>
<th>Statement II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  Ethanamide, CH₃CONH₂ is a weaker base than methylamine, CH₃NH₂.</td>
<td>The electronegativity of the oxygen atom of the carbonyl group reduces the availability of the lone pair of electrons on the nitrogen atom in ethanamide.</td>
</tr>
<tr>
<td>2  The boiling point of ethanol is higher than that of ethanethiol, C₂H₅SH.</td>
<td>The ethanethiol molecule has a larger electron cloud than ethanol.</td>
</tr>
<tr>
<td>3  The ionic product of water, Kᵢ, increases with increasing temperature.</td>
<td>H⁺(aq) and OH⁻(aq) ions react exothermically.</td>
</tr>
</tbody>
</table>

34 Use of the Data Booklet is relevant to this question.

The graph below shows the variation in electromotive force (emf) of the electrochemical cell with \( \lg [ \text{M}^+(\text{aq}) ] \) at 298 K.

\[
\text{Cu(s) } \mid \text{Cu}^{2+} (\text{aq}, 1 \text{ mol dm}^{-3}) \parallel \text{M}^+ (\text{aq}) \mid \text{M(s)}
\]

Which of the following statements are true?

1. The Cu^{2+}(aq) | Cu(s) half cell is the negative pole.
2. The emf of the given cell under standard conditions will be +0.46V.
3. The standard electrode potential of the half cell M⁺(aq) | M(s) is +0.80V.
The responses A to D should be selected on the basis of

<table>
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<th>A</th>
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<td></td>
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</tbody>
</table>

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

35 The following two equations show two different partial ligand substitution reactions of the hexaaquacopper(II) ion. (en represents 1,2-diaminoethane, H₂NCH₂CH₂NH₂)

\[
\begin{align*}
\text{I: } & [\text{Cu(H}_2\text{O)_6}^2+]^{\text{aq}} + \text{en}^{\text{aq}} \rightarrow [\text{Cu(en)(H}_2\text{O)_4}]^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)} & \Delta H = -54 \text{ kJ mol}^{-1} \\
\text{II: } & [\text{Cu(H}_2\text{O)_6}^2+]^{\text{aq}} + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Cu(NH}_3)_2(\text{H}_2\text{O)_4}]^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)} & \Delta H = -46 \text{ kJ mol}^{-1}
\end{align*}
\]

Which of the following statements are correct?

1. The entropy change, \(\Delta S^0\), for reaction I is more positive than that for reaction II.
2. The stability constant of \([\text{Cu(en)(H}_2\text{O)_4}]^{2+}\) is larger than that of \([\text{Cu(NH}_3)_2(\text{H}_2\text{O)_4}]^{2+}\).
3. The cation formed in reaction II exhibits geometric isomerism.

36 Use of the Data Booklet is relevant to this question.

The cell shown in the diagram below is set up under standard conditions.

Which of the following statements are correct?

1. Electrons will flow from Y to X through the meter.
2. The voltmeter reading will increase when aqueous KCN is added to beaker R.
3. The voltmeter reading will decrease when water is added to beaker Q.
Use of the Data Booklet is relevant to this question.

The methanoate anion and carbon dioxide can be simultaneously reduced to the tartrate anion in alkaline medium. The standard electrode potential of this half-cell is +0.20 V.

\[
2 \text{methanoate} + 2\text{CO}_2 + 4\text{H}_2\text{O} + 6\text{e}^{-} \rightarrow 2\text{OH}^{-} + \text{tartrate}
\]

Which of the following statements are true?

1. The oxidation states of carbon are +4 and +2 in carbon dioxide and methanoate respectively.
2. Tartrate can be oxidised to methanoate and carbon dioxide using aqueous iodine.
3. When \(^{14}\text{CO}_2\) is used in place of \(\text{CO}_2\), the asterisked carbon atoms (\(\text{C}^{*}\)) in the tartrate will be replaced with \(^{14}\text{C}\).

Deuterium, D, is an isotope of hydrogen.

Which mixtures, on heating, produce an alkaline gas containing deuterium?

1. \(\text{CH}_3\text{CH}_2\text{CONHCH}_3\) and \(\text{NaOD}\) in \(\text{D}_2\text{O}\)
2. \((\text{ND}_2\text{H}_2)_2\text{SO}_4\) and \(\text{NaOD}\) in \(\text{D}_2\text{O}\)
3. \(\text{C}_6\text{H}_5\text{CH}_2\text{CN}\) and \(\text{DCI}\) in \(\text{D}_2\text{O}\)
The responses A to D should be selected on the basis of

<table>
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</tr>
</tbody>
</table>

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

39 *Pravastatin* is a drug used to lower cholesterol in the blood.

1 It reacts with liquid bromine in tetrachloromethane to form a compound with 12 chiral centres.

2 It reacts with acidified potassium manganate(VII) under reflux to form one organic product.

3 It reacts with 3 moles of hydrogen gas in the presence of nickel catalyst and heat.

40 Which of the following groups of compounds show an increasing rate of hydrolysis?

1 CH₃CH₂Cl, CH₃CH₂Br, CH₃CH₂I
2 CH₃COONa, C₆H₅ONa, CH₃CH₂ONa
3 CH₃CONH₂, CH₃COOCH₃, CH₃COC₁
<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>11</td>
<td>B</td>
<td>21</td>
<td>C</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>12</td>
<td>D</td>
<td>22</td>
<td>D</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>13</td>
<td>D</td>
<td>23</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td>14</td>
<td>D</td>
<td>24</td>
<td>C</td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>15</td>
<td>B</td>
<td>25</td>
<td>C</td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>16</td>
<td>C</td>
<td>26</td>
<td>C</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>17</td>
<td>B</td>
<td>27</td>
<td>A</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>18</td>
<td>D</td>
<td>28</td>
<td>C</td>
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<td>9</td>
<td>D</td>
<td>19</td>
<td>B</td>
<td>29</td>
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<tr>
<td>10</td>
<td>D</td>
<td>20</td>
<td>B</td>
<td>30</td>
<td>A</td>
</tr>
</tbody>
</table>
READ THE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in. Write in dark blue or black ink in the spaces provided. You may use a soft pencil for any diagrams, graphs or rough working. Do not use paper clips, highlighters, glue or correction fluid.

Answers all questions.

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

<table>
<thead>
<tr>
<th>Question</th>
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<tr>
<td>1</td>
<td>12</td>
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<td>Total</td>
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For Examiner’s Use

This document consists of 17 printed pages and 1 blank page.
Planning (P)
The hydroxides of Group I metals (LiOH, NaOH, KOH, RbOH, CsOH) are highly corrosive white solids which rapidly absorb water vapour on exposure to the atmosphere.

All of these solids dissolve exothermically in water.
The enthalpy change of solution, $\Delta H_{\text{soln}}$, is the energy change associated with the following reaction.

$$MOH(s) + (aq) \rightarrow M^+(aq) + OH^-(aq)$$

where $M$ represents the Group I metal.

Both lattice energy and hydration enthalpy play an important part in determining the magnitude of $\Delta H_{\text{soln}}$.

Lattice energy and hydration enthalpy are both more exothermic when ions carry higher charges and/or ions have smaller radii.

When comparing Group I hydroxides, changes in $\Delta H_{\text{hydration}}$ are more significant than changes in lattice energy.

(a) Sketch the likely trend in $\Delta H_{\text{soln}}$ from LiOH to CsOH and explain your answer.

Explaination:

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[2]
(b) Without considering heat loss, based on the information given, identify one possible source of error in the experiment to determine \( \Delta H_{\text{soln}} \) of the hydroxides of Group I metals. State how you would minimise the effect of this source of error.

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

(c) Identify a safety risk in the experiment and suggest how you would minimise it when carrying out the experiment.

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(d) Given the enthalpy change of solution of lithium hydroxide is approximately \(-21 \text{ kJ mol}^{-1}\), describe the procedure you would carry out to find its enthalpy change of solution.

Your plan should give a step-by-step description of the method, including appropriate masses and volumes of reagents. You may use the apparatus normally found in a school or college laboratory.

The following data may be of use in planning the details of your experiment.

\[
\begin{align*}
\text{Ar: Li, 6.9; O, 16.0; H, 1.0} \\
4.3 \text{ J are required to raise the temperature of 1.0 cm}^3 \text{ of any solution by 1°C.}
\end{align*}
\]
(e) A student was interested to investigate how the enthalpy change of neutralisation, \( \Delta H_{\text{neutralisation}} \), varies when acids such as hydrochloric acid, HCl and ethanedioic acid, \((\text{CO}_2\text{H})_2\) are neutralised with aqueous solutions of a Group I hydroxide such as RbOH.

The student proposed measuring the temperature change when each of the given acids reacts with 30.0 cm\(^3\) of 2.0 mol dm\(^{-3}\) rubidium hydroxide.

Identify one aspect of the experimental procedure that must be kept the same to ensure comparable results.
(f) (i) In each experiment, 30.0 cm³ of 2.0 mol dm⁻³ RbOH is to be used. There is to be an excess of rubidium hydroxide, RbOH.

Suggest appropriate volumes and concentrations for each of the acids to be used in the individual experiments such that the experiments are equivalent. Justify your answer with respect to ethanedioic acid with relevant working. Complete the table below.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Volume / cm³</th>
<th>Concentration / mol dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td></td>
</tr>
<tr>
<td>Ethanedioic acid</td>
<td>(CO₂H)₂</td>
<td></td>
</tr>
</tbody>
</table>

(ii) Show the mathematical expression for the enthalpy change of neutralisation of rubidium hydroxide with ethanedioic acid, using the volume and concentration from (f) (i) and ΔT to represent the temperature change.
The Dissolved Oxygen Concentration (DOC) in rivers and lakes is important for aquatic life. If DOC falls below 5 mg dm$^{-3}$, most species of fish cannot survive.

Environmental chemists can determine the DOC in water using the procedure below.

A sample of water is shaken with aqueous Mn$^{2+}$ and aqueous alkali. The dissolved oxygen oxidises the Mn$^{2+}$ to Mn$^{3+}$, forming a pale brown precipitate of Mn(OH)$_3$.

\[
\text{O}_2(\text{aq}) + \text{Mn}^{2+} (\text{aq}) + 8 \text{OH}^-(\text{aq}) + 2 \text{H}_2\text{O}(l) \rightarrow 4 \text{Mn(OH)}_3 (s)
\]

The Mn(OH)$_3$ precipitate is then reacted with an excess of aqueous potassium iodide, which is oxidised to iodine, I$_2$.

\[
2 \text{Mn(OH)}_3 (s) + 2\text{I}^- \rightarrow \text{I}_2(\text{aq}) + 2 \text{Mn(OH)}_2 (s) + 2 \text{OH}^- (\text{aq})
\]

The iodine formed is then determined by titration using aqueous sodium thiosulfate, Na$_2$S$_2$O$_3$ (aq).

(a) A student decided to analyse the National Junior College’s pond water using the above procedure. The student found that a 20.0 cm$^3$ sample of the pond water required 18.60 cm$^3$ of 0.00100 mol dm$^{-3}$ of Na$_2$S$_2$O$_3$ (aq) for titration.

(i) Calculate the DOC of the sample of pond water, in mg dm$^{-3}$.

\[
\text{DOC} = \text{................................. mg dm}^{-3}
\]

(ii) Comment on whether there is enough dissolved oxygen in the pond water for the carps to survive.

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

........................................................................................................................................ [4]
(b) Another d-block element, rhenium is similar in many ways to manganese. The standard electrode potential $E^\circ$ for the change between 2 oxidation states of rhenium is +0.3V.

$$\text{ReO}_4^- (aq) + 4H^+(aq) + 3e^- \rightleftharpoons \text{ReO}_2(s) + 2H_2O(l)$$

ReO$_4^-$ (aq) is colourless while ReO$_2$ is a dark solid.

(i) Draw a fully labelled diagram for the apparatus that can be used to determine this standard electrode potential.

(ii) Using the *Data Booklet*, show that a reaction occurs when an aqueous solution containing sodium sulfite, Na$_2$SO$_3$ is added to aqueous ammonium perrhenate, NH$_4$ReO$_4$.

Describe the observation(s) and write a balanced equation for the reaction.

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[3]

[Total: 10]
Copper, silver and gold share certain attributes: they have one s-orbital electron in addition to a filled d-shell. The filled d-shells in these elements do not contribute much to the interatomic interactions, which are dominated by the s-electrons through metallic bonds. Contrary to metals with incomplete d-shells, metallic bonds in copper are relatively weak. Thus pure copper is soft and malleable.

Alloys are made to alter the mechanical properties of copper, to induce hardness and ductility. Brass and bronze are typical substitutional alloys in which some of the copper atoms are substituted by zinc in the former, and by tin in the latter.

The table below gives the hardness of copper and these two alloys as measured on the Brinell Scale.

<table>
<thead>
<tr>
<th></th>
<th>copper</th>
<th>brass</th>
<th>bronze</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>42</td>
<td>114</td>
<td>241</td>
</tr>
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(a) Using relevant information from the Data Booklet, account for the difference in the hardness of copper, brass and bronze.

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(c) Copper forms compounds with variable oxidation states. Copper(I) compounds are unstable in water. The following flow scheme shows the reactions between different compounds of copper.

(i) State the type of reaction between copper(I) sulfate and water. Using relevant data from the Data Booklet, explain why this reaction occurs.

(ii) Give the formulae of the complex ions in F and G.

F: ...........................................

G: ...........................................

(iii) When solution G was diluted with water, it changed from yellow to green and finally blue. Explain the colour changes.

[7]
(iv) Describe what you would observe when potassium iodide solution is added to solution E. Write an equation for the reaction that occurs.

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(v) Explain why solution E is blue.

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[5]

(d) Copper has remarkable resistance to corrosion. However, many well-known architectural structures built with copper, such as the Statue of Liberty in the United States and the Royal Observatory in Edinburgh, on centuries of exposure to the elements, appear green due to the formation of the basic carbonate, Cu(OH)$_2$.CuCO$_3$.

Explain the formation of the basic copper carbonate.

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

[2]

[Total:18]
Aspartic acid, HO$_2$CCH$_2$CH(NH$_2$)CO$_2$H, is one of the two acidic essential amino acids. A 25.0 cm$^3$ solution of fully protonated aspartic acid, HO$_2$CCH$_2$CH(NH$_3^+$)CO$_2$H, is titrated with 0.500 mol dm$^{-3}$ NaOH (aq). The titration curve is shown below. The label ‘E1’, ‘E2’ and ‘E3’ denotes equivalence point 1, 2 and 3 respectively.

(i) The species present at E1 is HO$_2$CCH$_2$CH(NH$_3^+$)CO$_2$–. Identify the species present at E2 and E3.

(ii) The equation for the first acid dissociation constant, $K_{a1}$, of the fully protonated aspartic acid can be written as follows:

\[
\text{HO}_2\text{CCH}_2\text{CH(NH}_3^+)\text{CO}_2\text{H} \rightleftharpoons \text{HO}_2\text{CCH}_2\text{CH(NH}_3^+)\text{CO}_2^- + \text{H}^+
\]

Using the titration curve, determine $K_{a1}$.

\[
K_{a1} = \text{………………..} \text{ mol dm}^{-3}
\]
(iii) Explain why the shape of the graph at \( E_3 \) differs from that at \( E_1 \).

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(iv) At pH = 4.0, the mixture can act as a buffer. Identify the two species present in this buffer and calculate the ratio of the concentrations of these two species at this pH.
(b) Papain, an enzyme in fresh papaya juice is used as a meat tenderiser. It is responsible for catalysing the hydrolysis of certain proteins in muscle tissues, causing the tough meats to soften during the cooking process.

Papain is a relatively heat resistant enzyme, with an optimal temperature range of 60-70 °C. The three main amino acids involved in the catalytic activity of papain are His48, Asp102 and Ser185.

The first stage in the mechanism of the action of papain is illustrated in the figure below.

(i) Name the region of the papain enzyme that is illustrated above.

(ii) With reference to the figure above, explain why the action of this enzyme would be inhibited if the pH was too low.

[Total: 11]
(i) Name the four functional groups in compound Q, other than the phenyl group.

1) .........................................................................................
2) .........................................................................................
3) .........................................................................................
4) .........................................................................................

(ii) Draw the structural formulae of the compound(s) when compound Q is treated with

- Cold HCl(aq)

- Hot NaOH (aq)
6 (a) 2-methylpropane reacts with Br\textsubscript{2} to give a mixture in which the major products are two monobrominated alkanes.

\[
\begin{align*}
\text{CH}_3\text{C}-\text{CH}_3 & \rightarrow \text{CH}_3\text{C}-\text{CH}_2\text{Br} + \text{CH}_3\text{C}-\text{CH}_3 \\
\text{H} & \hspace{2cm} \text{H} \\
63\% & \hspace{2cm} \hspace{2cm} \hspace{2cm} 37\%
\end{align*}
\]

(i) State the conditions required for this reaction.

(ii) Outline the mechanism for the formation of 1-bromo-2-methylpropane from 2-methylpropane under the conditions stated in (i).

(iii) Discuss two factors which are responsible for the observed percentages of the two monobrominated alkanes.
(b) 1-bromo-2-methylpropane undergoes a series of reactions as shown by the given flow scheme.

(i) State the conditions needed for step 1.
................................................................................................................................................

(ii) Explain as fully as you can why the conditions you stated in (i) are required.
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(iii) Draw the structures of compounds S, T and U in the boxes provided below.

<p>| | | |</p>
<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S</strong></td>
<td><strong>T</strong></td>
<td><strong>U</strong></td>
</tr>
</tbody>
</table>
(iii) When an alkaline solution of complexed Cu$^{2+}$(aq) is added to compound V, a reddish-brown precipitate is observed.

Propose a 2-step synthesis for compound V from 1-bromo-2-methylpropane.
Solutions to Paper 2

1. (a) (i)

![Graph showing the size of cations increasing down Group II, heat of hydration of cation less exothermic.

- $\Delta H_{(soln)} = -LE + \Sigma \Delta nH_{(hyd)}^{[1/2]}$
- Size of cations increases down Group II, heat of hydration of cation less exothermic $^{[1/2]}$

Most students can score these two marks. The students who drew an increasing line above the x-axis were awarded one upon two.

Common mistakes

- It is clearly stated in the question that all of the heats of solution are exothermic. Many students did not seem to notice that, judging from their answers. Their lines were above the x-axis.
- It is $\Sigma n\Delta H_{(hyd)}$, not just $n\Delta H_{(hyd)}$!
- A lot of students, while getting the full credit for the graph, failed to include the equation in their explanation.

(b) The Group I hydroxides are all hygroscopic. $^{[1/2]}$ Weigh the solid out promptly so as to minimise its exposure to air. $^{[1/2]}$

(c) Wear gloves. $^{[1/2]}$ The chemicals are corrosive. $^{[1/2]}$

Common mistakes

- Toxicity is not the same as corrosiveness!
- Grammar! A pair of gloves, not just a glove! If you were to use just one glove, won’t your other hand get corroded? A pair of goggles, not just a goggle! If you were to use just one goggle, how are you going to wear it? Hold it over your eye?

(d) Procedure

Major points $^{[1/2]}$ each, maximum 2

- Measure the initial temperature of the water.
- Measure the highest/maximum temperature reached. (No marks if temperature is lowest/minimum; ECF according to answer to (a)).
- Measuring cylinder to measure out the water.
- Weigh mass of the residue and weighing bottle after adding the LiOH into the cup.

Minor points $^{[1/2]}$ each, maximum 1

- Weigh out LiOH using a weighing bottle.
- Cup to be supported with a beaker.
- Repeat the experiment until two $\Delta_{m}T$ values are within 5% of each other. ‘m’ has to be specified as the mass of the solid.
**Preliminary calculations [1]**

- **Justify** mass of LiOH weighed out. [NOTE: The capacity of the cup must be stated, otherwise at most half a mark will be awarded.]

\[
\frac{3mc}{\Delta H} \leq n \leq \frac{10mc}{\Delta H}
\]

where \( m \) is between 50 to 90% of the stated capacity of cup.

Simplifying,

\[6.14 \times 10^{-4}m \leq \text{amount of LiOH} \leq 2.05 \times 10^{-3}m\]

If the capacity of the cup is 100 cm\(^3\) and filling 90% of it, then

\[1.32 \, g \leq \text{mass of LiOH} \leq 4.40 \, g\]

(e) Volumes of the two solutions are the same/same setup/same apparatus [1]

(f) (i)

- \( 3 ^\circ C \leq \Delta T \leq 10 ^\circ C \) for both experiments.

\[
\Delta T_1 = \frac{57.3C_1V_1}{4.3(30+V_2)} \quad \text{and} \quad \Delta T_2 = \frac{2 \times 57.3C_2V_2}{4.3(30+V_2)} = \frac{25.7C_2V_2}{30+V_2}
\]

- no. of moles of H\(_2\)SO\(_4\) half that of CH\(_3\)COOH.

- total volume not more than 90% of capacity of cup and not less than 50% of capacity of cup.

- acids are the limiting reagents i.e. \( C_1V_1 < 60 \) and \( C_2V_2 < 30 \).

2 (a)(i) \( n(O_2) = \frac{1}{4} n(S_2O_3^{2-}) = \frac{1}{4} \left( \frac{18.60 \times 0.301}{1000} \right) = 4.65 \times 10^{-6} \) [2]

\[ [O_2] = (4.65 \times 10^{-6}) \times \frac{1600}{20} = 2.325 \times 10^{-4} \text{moldm}^{-3} \] [1/2]

\[ [O_2] = (2.325 \times 10^{-4}) \times 32000 = 7.44 \text{mgdm}^{-3} \] [1/2]

(a)(ii) The carps will be able to survive. (Justification).
(b)(i)  

\[
2H^+ + 3SO_3^{2-} + 2ReO_4^- \rightarrow H_2O + 3SO_4^{2-} + 2ReO_2 \quad [1]
\]

\[E_{cell}^0 = (0.3 - 0.17) \text{ V} = 0.13 \text{ V} > 0 \quad [1]\]

Dark solid forms. [1]

3(a) Copper, brass and bronze all have metallic bonds. Copper is a pure metal made up of Cu^{2+} ions (0.069nm) arranged in a orderly metallic lattice. Brass and bronze are alloys and the presence of metal ions of different sizes disrupts the orderly metallic lattice. Ionic radius of Sn^{2+} ion (0.112nm) is bigger than ionic radius of Zn^{2+} ions (0.074nm) and the bigger ions Sn^{2+} will disrupt the orderly metallic lattice more significantly. The greater extent of disruption of the orderly lattice makes it more difficult for the layers of atoms to slide over each other, leading to greater hardness.

Or

Copper gives out 1 electron to the sea of electron, zinc gives out 2 while tin gives out 4. Ionic radius of Cu^{+} is approximately 0.069nm, Zn^{2+} is 0.074nm and Sn^{4+} is approximately 0.112nm. Charge/size of Cu^{+} is lowest, followed by Zn^{2+} and Sn^{4+}. The metallic bond is weakest in Cu followed by Zn and Sn. Therefore, greater force is needed for the layers of atom to slide over each other in Brass and bronze.

3(b) Zinc does not form any ions that have partially filled 3d orbital.

3(c) (i) Type of reaction: Disproportionation

\[
\begin{align*}
\text{Cu}^+ & \rightarrow \text{Cu}^{2+} + e \quad E^{\text{ox}} = -0.15 \text{V} \\
\text{Cu}^+ + e & \rightarrow \text{Cu} \quad E^{\text{red}} = +0.52 \text{V}
\end{align*}
\]

\[E^{\text{cell}} = +0.52 - 0.15 = 0.37 \text{V} > 0, \text{ reaction is feasible.}\]
(ii) \[\text{F: } [\text{Cu(RNH}_2\text{)}_4]^{2+} \quad \text{G: } [\text{CuCl}_4]^{2-}\]

(iii) \[\text{[CuCl}_4]^{2-} + 6\text{H}_2\text{O} \rightleftharpoons [\text{Cu(H}_2\text{O)}_6]^{2+} + 4\text{Cl}^{-}\]

(iv) Cream precipitate in brown solution.
\[
2\text{Cu}^{2+} + 4\text{I}^{-} \rightarrow 2\text{CuI} + \text{I}_2
\]

(v) \([\text{Cu}^{2+}\text{] has partially filled 3d orbitals. When ligands approach, the 3d orbitals of } \text{Cu}^{2+} \text{ are split into 2 different energy levels. When an electron is promoted from lower energy 3d orbital to higher energy 3d orbital, an energy corresponding to the wavelength in the visible region is absorbed. The complementary colour of the wavelength absorbed is blue.}\]

(d) When copper is exposed to air, it is oxidized to \(\text{CuO}\). When \(\text{CuO}\) reacts with the moisture in the air, \(\text{Cu(OH)}_2\) is formed. Some of the \(\text{Cu(OH)}_2\) reacts with \(\text{CO}_2\) in the air to form \(\text{CuCO}_3\). This leads to the formation of \(\text{Cu(OH)}_2.\text{CuCO}_3\).

4(a) (i) \(\text{E}_2: -\text{O}_2\text{CCH}_2\text{CH(NH}_3^+\text{)}\text{CO}_2^- \quad \text{E}_3: -\text{O}_2\text{CCH}_2\text{CH(NH}_2\text{)}\text{CO}_2^-\)

(ii) \(\text{pKa}_1 = 2.11\)
\[
\text{Ka}_1 = 10^{-2.11} = 7.76 \times 10^{-3}
\]

(iii) \(\text{E}_1: \) The solution present at \(\text{E}_1\) can act as a buffer and the pH change is relatively small when small amount of \(\text{NaOH(aq)}\) is added.
\(\text{E}_3: \) The solution present at \(\text{E}_3\) is a salt and when small amount of \(\text{NaOH(aq)}\) is added, there is a large increase in pH due to \(\text{OH}^-\) from \(\text{NaOH}\).

Or
\(\text{E}_1: \) At \(\text{E}_1\), the species still have \(\text{H}^+\) available to neutralize \(\text{OH}^-\), however, at \(\text{E}_3\), the species present does not have any \(\text{H}^+\) to neutralize \(\text{OH}^-\) from \(\text{NaOH}\), hence, the large increase in pH is due to the \(\text{OH}^-\) from \(\text{NaOH}\).

(iv) the two species present are \(\text{HO}_2\text{CCH}_2\text{CH(NH}_3^+\text{)}\text{CO}_2^-\) and \(\text{-O}_2\text{CCH}_2\text{CH(NH}_3^+\text{)}\text{CO}_2^-\)
\(\text{Salt: } -\text{O}_2\text{CCH}_2\text{CH(NH}_3^+\text{)}\text{CO}_2^-\)
\(\text{Acid: } \text{HO}_2\text{CCH}_2\text{CH(NH}_3^+\text{)}\text{CO}_2^-\)
\[
\text{pH} = \text{pKa} - \log\left(\frac{[\text{salt}]}{[\text{acid}]\right)}
\]
\[
4 = 3.86 - \log\left(\frac{[\text{salt}]}{[\text{acid}]\right)} = 1.38
\]

(b) (i) Active site

(ii) When pH is low, the concentration of \(\text{H}^+\) from the solution is high, \(-\text{COO}^-\) of asp will be protonated to form \(-\text{COOH}\). Therefore, no lone pair is available to abstract \(\text{H}^+\) from his and subsequent electron
transfer cannot happen. The will not be –O:– on ser to act as a nucleophile to attack the δ+ C of the peptide bond to bring about hydrolysis.

5(i)
1. Primary amine
2. Tertiary alcohol
3. amide
4. ester

(ii) cold HCl(aq)

\[
\begin{align*}
\text{CH}_3	ext{CO}_2\text{Na} & \quad \text{CH}_3\text{CH}_2\text{CO}_2\text{Na} \\
\text{CH}_2\text{NH}_2 & \quad \text{CH}_2\text{NH}_3^+ \\
\end{align*}
\]

Hot NaOH(aq)

\[
\begin{align*}
\text{NaO} & \quad \text{CH}_2\text{NH}_2 \\
\text{CH}_2\text{NH}_2 & \quad \text{CH}_2\text{NH}_3^+ \\
\end{align*}
\]

6 (a) (i) Limited Br₂ or excess alkane and ultraviolet light/ sunlight/ heat

(ii) Free radical substitution [1]

\[
\begin{align*}
\text{Initiation} & \quad \text{Br} + \text{Br} \xrightarrow{\text{UV}} 2 \text{Br} \cdot \\
\text{Propagation} & \quad \text{CH}_3\text{CH}_2\text{CH}_3 + \text{Br} \cdot \xrightarrow{} \text{CH}_3\text{CH}_2\text{CH}_3 + \text{HBr} \\
& \quad \text{CH}_3\text{CH}_2\text{CH}_3 + \text{Br}_2 \xrightarrow{} \text{CH}_3\text{CH}_2\text{CH}_3 + \text{Br} \cdot \\
\text{Termination} & \\
\end{align*}
\]
(iii) There are 9 primary H atoms available for substitution to form 1-bromo-2-methylpropane compared to 4 secondary H atoms to form 2-bromo-2-methylpropane. By equal probability of substitution, expected ratio of 1-bromo-2-methylpropane : 2-bromo-2-methylpropane is 9 : 1.

However, a tertiary radical, $\cdot$C(CH$_3$)$_3$, is more stable than a primary radical, $\cdot$CH$_2$CH(CH$_3$)$_2$ due to the electro-donating effects of the alkyl groups. More tertiary radicals are formed, giving rise to more 2-bromo-2-methylpropane formed. Thus the observed percentages.

(b) (i) AlBr$_3$ or FeBr$_3$ or AlCl$_3$ or FeCl$_3$, anhydrous

(ii) The Lewis acid catalyst is required to form a strong electrophile $\text{(CH}_3\text{)}_2\text{CHCH}_2^+ [1]$ to react with the aromatic/resonance stabilised benzene.

$$\text{AlBr}_3 \text{ use a vacant orbital of Al to accept/extract a lone pair/ Br}^-. [1]$$

OR $\text{AlBr}_3 + \text{R-Br} \Leftrightarrow \text{AlBr}_4^- + \text{R}^+ [1]$

OR AlCl$_3$ or AlBr$_3$ will dissolve in water and be hydrolysed, hence unable to act as a Lewis acid catalyst.

(iii)

(iv) $\text{CH}_3\text{C}\text{CH}_3\text{H}\text{C}\text{H}_2\text{Br} \xrightarrow{\text{NaOH(aq), heat}} \text{CH}_3\text{C}\text{CH}_2\text{OH}$

$\text{CH}_3\text{C}\text{CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7, \text{dil H}_2\text{SO}_4 \text{ heat with immediate distillation}} \text{CH}_3\text{C}\text{CH}_2\text{Br}$
READ THESE INSTRUCTIONS FIRST

Answer any four questions.

Start your answer to each question on a fresh piece of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

At the end of the examination, fasten all your work securely behind the cover page.

This paper consists of 13 printed pages including 1 blank page.
Answer any **four** questions.

1 (a) The graph below shows the variation of pV versus p for NH₃, which exists as a gas under normal room conditions.

![Graph showing pV versus p for NH₃](image)

Explain the shape of the graph, commenting on the behaviour of NH₃ gas as an ideal gas at **A, B, C and D**.

2

(b) Ammonia is manufactured by the Haber Process, using gaseous nitrogen and hydrogen.

\[
3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta H = -92.4 \text{ kJ mol}^{-1}
\]

In an experiment starting with a 3:1 ratio of H₂ and N₂ mixture at 400 °C and a constant total pressure of 200 atm in the presence of iron catalyst, the equilibrium mixture was found to contain 36.3 % by volume of ammonia.

(i) Justify the conditions of temperature and pressure used.

(ii) Write an expression for K_p of this reaction.

(iii) Calculate the partial pressures of each of these three gases at equilibrium, and hence calculate K_p at this temperature, stating its units.

3

(c) Hydrazine, \( \text{NH}_2\text{NH}_2 \), is a flammable liquid with ammonia-like odour. It has basic chemical properties like ammonia.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{NH}_2\text{NH}_2 )</th>
<th>( \text{NH}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_b ) / mol dm(^{-3} )</td>
<td>( 1.3 \times 10^{-6} )</td>
<td>( 1.8 \times 10^{-6} )</td>
</tr>
</tbody>
</table>

Explain the difference in the \( K_b \) values of these two compounds.
1 (d) Hydrazine is miscible with water but immiscible with trichloromethane.

(i) Explain, in terms of bonding, and with appropriate diagrams to illustrate, the difference in the miscibilities of hydrazine with the two stated solvents.

(ii) Hydrazine hydrate, made from hydrazine, takes part in the following reaction:

\[ \text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O} + \text{IO}_3^- + 2\text{H}^+ + \text{Cl}^- \rightarrow \text{N}_2 + \text{IC}^- + 4\text{H}_2\text{O} \]

Calculate the change in the oxidation states of the species oxidised. \[4\]

(e) Hydrazines are part of many organic syntheses and undergo condensation reactions with carbonyl compounds. Below is a scheme showing some reactions of phenylethanone, which includes the reaction mentioned.

(i) Draw the structural formulae of Compounds E, F and G.

(ii) State what Reagent X is, and give the conditions under which the reaction will take place. \[4\]

(f) Hydrazine reacts in a similar way with an isomer of phenylethanone, H. H is also a monosubstituted benzene like phenylethanone. Suggest the identity of H. \[1\]

[Total: 20]
The Group II element, barium, was first isolated by Sir Humphry Davy, a British chemist and inventor in the nineteenth century. Besides being used widely in pyrotechnics, barium is also used in the production of hydrogen peroxide, a colourless liquid with a boiling point of 150 °C.

Hydrogen peroxide was originally produced commercially in a two-stage process. In the first stage, barium was heated in air to form barium peroxide. In the second stage, barium peroxide was added to aqueous nitric acid. The equations for the reactions are shown below.

Stage 1: \( \text{Ba}(s) + \text{O}_2(g) \rightarrow \text{BaO}_2(s) \)

Stage 2: \( \text{BaO}_2(s) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{Ba(NO}_3)_2(\text{aq}) \)

(a) (i) Suggest one method of separating hydrogen peroxide from the reaction mixture in Stage 2.

(ii) Suggest one reason why nitric acid was eventually replaced by sulfuric acid in Stage 2 to lower the cost of this commercial production.

(iii) Draw the dot-and-cross diagram for barium peroxide.

(b) (i) Write an equation for the reaction of barium with water.

(ii) Would the reaction in (i) occur more or less vigorously than that for magnesium? Justify your answer by quoting relevant data from the Data Booklet.

(c) Although Group II elements can form many compounds, the standard enthalpy of formation of solid barium chloride cannot be obtained directly.

(i) Define the term standard enthalpy of formation of barium chloride.

(ii) Given the standard enthalpy change of solution of barium chloride is \(-13.2\ \text{kJ mol}^{-1}\), write a thermochemical equation to represent the standard enthalpy change of solution of barium chloride.
2 (c) (iii) Using the information from (ii) and the following data:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H^0 / \text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba(OH)}_2(\text{aq}) + 2\text{HCl(}\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + 2\text{H}_2\text{O(}l))</td>
<td>(-114.4)</td>
</tr>
<tr>
<td>(\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(}l))</td>
<td>(-285.9)</td>
</tr>
<tr>
<td>(\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{HCl(}g))</td>
<td>(-92.3)</td>
</tr>
<tr>
<td>(\text{HCl(}g) + \text{aq} \rightarrow \text{HCl(}aq))</td>
<td>(-71.9)</td>
</tr>
<tr>
<td>(\text{Ba(s)} + \text{O}_2(\text{g}) + \text{H}_2(\text{g}) + \text{aq} \rightarrow \text{Ba(OH)}_2(\text{aq}))</td>
<td>(-1002)</td>
</tr>
</tbody>
</table>

draw an appropriate energy cycle and use it to calculate the enthalpy change of formation of solid barium chloride.

(iv) Use the following entropy data and your answer to (iii),

<table>
<thead>
<tr>
<th>(S^0 / \text{J K}^{-1} \text{ mol}^{-1})</th>
<th>(\text{BaCl}_2(\text{s}))</th>
<th>(\text{Ba(s)})</th>
<th>(\text{Cl}_2(\text{g}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>124</td>
<td>63</td>
<td>223</td>
</tr>
</tbody>
</table>

calculate the lowest temperature at which the following reaction becomes feasible.

\[
\text{BaCl}_2(\text{s}) \rightarrow \text{Ba(s)} + \text{Cl}_2(\text{g})
\]

[9]

(d) Catalytic poisoning is normally undesirable as it results in a loss of the usefulness of expensive metals like platinum and palladium. However, poisoning of a catalyst can be used to enhance selectivities of some reactions.

An example of such practice is seen in the Rosenmund reduction where carbonyl compounds are produced. The palladium catalyst required for this reduction reaction is poisoned with barium sulfate.

The scheme below shows a 4–step synthesis of compound **G** which has the molecular formula \(\text{C}_3\text{H}_9\text{ON}\). One of the steps involves the Rosenmund reduction.

\[
\text{CH}_3\text{COOH} \xrightarrow{\text{SOCI}_2} \text{D} \xrightarrow{\text{H}_2 / \text{Pd}} \text{BaSO}_4 \xrightarrow{\text{HCN}} \text{E} \xrightarrow{\text{Step (i)}} \text{F} \xrightarrow{\text{HCN}} \text{G} \xrightarrow{\text{BaSO}_4} \text{C}_3\text{H}_9\text{ON}
\]

Give the structural formulae of compounds **D** – **G** and the reagent(s) and conditions required for Step (i).

[5]

[Total: 20]
3 (a) In the Clemmensen reaction, zinc is used, along with hydrochloric acid, for the reduction of a carbonyl compound into an alkane.

\[
\begin{align*}
\text{R-C=O} & \quad \xrightarrow{\text{Zn, HCl}} \quad \text{R-C-H} \\
\text{Clemmensen reaction}
\end{align*}
\]

\(W\) and \(X\) are carbonyl compounds which undergo Clemmensen reaction to form the same alkane, \(Y\). \(W\) is an optically active compound but \(X\) and \(Y\) are not. Only \(W\) forms a silver mirror with Tollens’s reagent. 0.3 mol of \(Y\) burns in excess oxygen to produce 33.6 dm\(^3\) of CO\(_2\) at standard temperature and pressure.

Calculate the number of moles of CO\(_2\) produced, and hence deduce the possible structures of \(W\), \(X\) and \(Y\).

(b) Compound \(J\) has molecular formula of C\(_4\)H\(_7\)Cl and exhibits the following properties:

- \(J\) reacts with acidified potassium manganate(VII), giving effervescence of a colourless gas.
- \(J\) reacts with ethanolic potassium cyanide to produce compound \(K\) with molecular formula C\(_5\)H\(_7\)N.
- \(J\) rotates plane-polarised light.

Draw the displayed formula for \(J\). Explain how the identity you suggest for \(J\) fits in with the reactions described above.

(c) A number of experiments were carried out at constant pressure and temperature in which compound \(J\) was reacted with ethanolic potassium cyanide. The concentrations of compound \(J\) and ethanolic potassium cyanide were varied and the results are as shown below:

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>[J] / mol dm(^{-3})</th>
<th>[KCN] / mol dm(^{-3})</th>
<th>Initial rate of formation of product / mol dm(^{-3}) min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.015</td>
</tr>
<tr>
<td>2</td>
<td>0.30</td>
<td>0.10</td>
<td>0.045</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.20</td>
<td>0.030</td>
</tr>
</tbody>
</table>
3 (c) (i) Deduce the rate equation for the reaction between $J$ and potassium cyanide. Hence, describe the mechanism for this reaction, showing any relevant charges, lone pairs of electrons and movement of electrons.

(ii) It is common to plot a graph of concentration against time to determine the rate law for a reaction. This approach works well for simple systems with numerically exact data. However, in practice, experimental data suffers from random errors, making it difficult to determine the gradient or slope accurately.

A better approach is to make characteristic kinetics plots based on the integrated rate law:

<table>
<thead>
<tr>
<th>Reaction order</th>
<th>Integrated rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero</td>
<td>$[A] = [A]_0 - kt$</td>
</tr>
<tr>
<td>first</td>
<td>$\ln [A] = \ln [A]_0 - kt$</td>
</tr>
<tr>
<td>second</td>
<td>$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$</td>
</tr>
</tbody>
</table>

Note:

- $[A]$ = conc of a reactant at any moment of time
- $[A]_0$ = initial concentration of that reactant
- $t$ = time since reaction started

Based on the information given and your answer to c(i), sketch a graph for the reaction of $J$ with potassium cyanide and show how the rate constant for the reaction could be determined from it.

(d) In the above reaction between $J$ and potassium cyanide, ethanol was used as the solvent. Another similar reaction was carried out using propanone as the solvent and the rate constant, $k$, for this experiment was found to be $1.50 \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$.

(i) State the overall order of reaction when propanone is used as the solvent.

(ii) Explain why the mechanism described in c(i) was favoured when ethanol was used as the solvent instead of propanone.

(e) With the aid of a suitable diagram, state and explain how the rate of a reaction will change when temperature is decreased.

[Total: 20]
4 This question describes two methods for the syntheses of organic compounds which have one carbon atom fewer than the starting material.

(a) One method is the Hoffmann degradation whereby treating a primary amide with aqueous alkaline bromine produces a primary amine.

\[ R-\text{CONH}_2 + \text{Br}_2 + \text{OH}^- \rightarrow R-\text{NH}_2 \]

The Hoffmann degradation can be used as the last step in the following synthesis of phenylamine from benzoyl chloride.

\[ \text{COC} + \text{P} \rightarrow \text{NH}_2 \]

(i) Suggest reagents and conditions for Step I and the structure of compound P.

(ii) Suggest a route to prepare phenylamine from benzene.

(iii) Give a test (stating reagents and observations) that would enable you to distinguish phenol from phenylamine.

(b) Another method is decarboxylation whereby a carboxylic acid loses CO₂.

In 1849, the German chemist Kolbe first published a method describing the preparation of an alkane from the electrolysis of the sodium or potassium salt of a carboxylic acid. The reaction occurs via the formation of radicals.

The following steps summarise the preparation of ethane using an aqueous solution of potassium ethanoate:

Step 1 \[ \text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{COO} + e \quad \text{Anode reaction} \]

Step 2 \[ \text{CH}_3\text{COO} \rightarrow \text{CH}_3 + \text{CO}_2 \quad \text{Decarboxylation} \]

Step 3 \[ 2 \text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3 \quad \text{Dimerization} \]

(i) What do you understand by the term ‘radical’?

(ii) Draw the dot-and-cross diagram of the radical in Step 1, and predict the OCO bond angle.

(iii) Write the half equation for the cathode reaction.
(b) (iv) In the electrolysis of an aqueous solution containing 2.43 g of potassium ethanoate at 1 atm pressure and 28 °C, 200 cm³ of ethane gas was collected. Calculate

(I) the percentage yield of ethane in this electrolysis.
(II) the time for this electrolysis if a current of 0.5 A was used.

(c) In the electrolysis of potassium butanoate solution, hexane (b.p. 63 °C) was formed together with its isomer P (b.p. 58 °C). Account for

(i) the identity of P and its formation.
(ii) the difference in the boiling points of the isomers.

(d) Another electrolysis was carried out using a mixture of potassium ethanoate and potassium methanoate solution.

Draw the structure(s) of the organic product(s) formed.
5 (a) The typical oxides of tin and lead are SnO, SnO₂, PbO and PbO₂.

The following two generalisations can be made about the oxides of the elements in Group IV of the Periodic Table.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

(i) Use these generalisations to suggest which of the above oxides of tin or lead is the most acidic
   - acidic
   - basic

(ii) PbO is found to be amphoteric. Write a balanced equation, with state symbols, for its reaction with aqueous NaOH.

(b) 0.00425g of lead(II) sulfate can dissolve in 100 cm³ of deionised water at 25 °C.

(i) What is the solubility, in mol dm⁻³, of lead(II) sulfate in deionised water at 25 °C?

(ii) Determine the solubility product of lead(II) sulfate at 25 °C.

(iii) How would you expect the solubility of lead(II) sulfate to differ from the calculated value in (i) when it is dissolved in potassium sulfate solution? Explain your answer.

(c) The table below gives the melting points of CO₂, SiO₂ and PbO.

<table>
<thead>
<tr>
<th></th>
<th>Melting point/ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>-78</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1610</td>
</tr>
<tr>
<td>PbO</td>
<td>888</td>
</tr>
</tbody>
</table>

In terms of structure and bonding, explain the difference in the melting points of

(i) CO₂ and SiO₂

(ii) SiO₂ and PbO
(d) Styrene is used for making polystyrene, a common plastic material.

The pathway below shows the production of styrene from compound R.

(i) Suggest reagents and conditions for steps I and II and the structures of compounds S and T.

(ii) Give the structural formula for U. Explain clearly why you placed the new functional group in its particular position.

(iii) Suggest how styrene will react with cold alkaline KMnO₄, giving the observations and the organic product(s) formed.

(iv) What is the major product formed when styrene reacts with iodine monochloride, ICl? [9]

[Total: 20]
Cover page for Paper 3

Staple this cover page in front of your writing paper.
Please circle the question numbers which you have attempted.

<table>
<thead>
<tr>
<th>Question</th>
<th>For Examiner’s Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>
NJC SH2 Preliminary Examinations Paper 3 Solutions

1(a) Pressure is approximately zero at A
Volume occupied by gas particles is small compared to the volume of the container
\[ \therefore \text{NH}_3 \text{ is almost an ideal gas.} \]

Low pressure at B, intermolecular attractions are dominant, thus NH\(_3\) molecules are pulled closer together. This reduces the impact on wall collisions and makes them softer. \[ P_{\text{NH}_3} < P_{\text{ideal}} \], hence the negative deviation. Volume occupied by gas particles is still relatively small compared to container.

High pressure at D, mainly repulsion between particles. The volume of the molecules becomes a significant fraction of the volume of the container, and thus is no longer negligible. \[ V_{\text{NH}_3} > V_{\text{ideal}} \], hence the positive deviation.

At C, NH\(_3\) appears to follow the ideal gas equation, because the two deviations balance out.

1(b)(i) A relatively low temperature of 400 °C is used to increase the yield of the exothermic reaction. Iron catalyst is used to compensate for any reduction in rate due to the low temperature used.
A high pressure of 200 atm caters to the forward reaction, which is accompanied by a reduction in volume. Pressure exceeding 200 atm would increase the cost of production.

1(b)(iii) \[ P_{\text{NH}_3} = 0.363 \times 200 = 72.6 \text{ atm} \]
\[ P_{\text{H}_2} = 0.47775 \times 200 = 95.55 \text{ atm} \]
\[ P_{\text{N}_2} = 0.15925 \times 200 = 31.85 \text{ atm} \]

\[ K_p = = 1.90 \times 10^{-4} \text{ atm}^{-2} \]

1(c) The - NH\(_2\) in hydrazine has a stronger electron-withdrawing effect than the – H in ammonia
\[ \therefore \text{the lone pair of electrons in ammonia is more available for donation to a proton} \]
\[ \therefore \text{the stronger base & the bigger K}_b \text{ value} \]

1(d)(i) Hydrazine and water form a miscible mixture
Free intermingling of the molecules of hydrazine & water through mutual H-bonding
\[ \therefore \text{Exists as a homogeneous phase} \]
Hydrazine and trichloromethane are immiscible

Segregation between the molecules of hydrazine & trichloromethane into 2 distinct layers

• NH₂NH₂ have strong H-bond with one another
• CHCl₃ have van der Waals attraction for one another

Each cannot establish any significant attraction for the other and will be squeezed out from one another’s layer

--- H-bond

--- H-bond

Phase boundary

Van der Waals forces
1(d)(ii) -2 oxidation state in N of hydrazine is oxidized to 0 in N₂

1(e)(i) 
\[
\begin{align*}
    &\text{H₂NN=C-CH₃} & \text{CH₃} \\
    &\text{CH(OH)CH₃} \\
\end{align*}
\]

Compound E  Compound F  Compound G

1(e)(ii) Reagent X is I₂(aq) with NaOH(aq); and the reaction mixture is warmed.

1(f)

\[
\text{CH₂CHO}
\]

Compound H

2  a  (i) Distillation and collect the distillate that boils over at 150 °C.
   (ii) Solid BaSO₄ will be formed and it can be removed by filtration.
   (iii) 

\[
\begin{align*}
    &\text{Ba}^{2⁺} \cdot \left[ \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \cdot \text{O} \right]^{2⁻} \\
\end{align*}
\]

b  (i) Ba + 2H₂O → Ba(OH)$_₂$ + H₂
   (ii) Reaction in b(i) involves the reduction of water by the group II metals. Reaction is more vigorous with barium as barium is a stronger reducing agent than magnesium as evidenced by the following data:

\[
\begin{align*}
    &\text{Mg} \rightarrow \text{Mg}^{2⁺} + 2e & E^{\text{oxid}} = +2.38V \\
    &\text{Ba} \rightarrow \text{Ba}^{2⁺} + 2e & E^{\text{oxid}} = +2.90V \\
\end{align*}
\]

c  (i) Standard enthalpy of formation of barium chloride is the heat change or enthalpy change when 1 mole of solid barium chloride is formed from its elements in their standard states (25°C and 1 atmosphere) i.e, formed from barium solid and chlorine gas.
(ii) \( \text{BaCl}_2(s) + \text{aq} \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \quad \Delta H = -13.2 \text{ kJ mol}^{-1} \)

(iii) \( \begin{align*} \text{Ba(s)} + \text{Cl}_2(g) + O_2(g) + 2H_2(g) & \xrightarrow{\Delta H_f} \text{BaCl}_2(s) + O_2(g) + 2H_2(g) \\
\text{Ba(OH)}_2(\text{aq}) + \text{Cl}_2(g) + H_2(\alpha) & \xrightarrow{\text{aq}} \text{BaCl}_2(\text{s}) + 2\text{H}_2\text{O}(l) \\
\text{Ba(OH)}_2(\text{aq}) + 2\text{HCl}(g) & \xrightarrow{\text{aq}} \text{BaCl}_2(\text{aq}) + 2\text{H}_2\text{O}(l) \end{align*} \)

Using Hess’ Law,
\[ \Delta H_f + 2(-285.9) + (-13.2) = (-1002) + 2(-92.3) + 2(-71.9) + (-114.4) \]
\[ \Delta H_f = -859.8 \text{ kJ mol}^{-1} \]
\[ = -860 \text{ kJ mol}^{-1} \]

(iii) \( \text{BaCl}_2(s) \rightarrow \text{Ba(s)} + \text{Cl}_2(g) \)

Using \( \Delta S = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}} \)
\[ = (63 + 223) - (124) = +162 \text{ JK}^{-1} \text{ mol}^{-1} \]

For the reaction to be feasible, \( \Delta G = \Delta H - T\Delta S \) must be less than zero.
\[ T = \frac{\Delta H}{\Delta S} = \frac{+859.8}{+162 \times 10^{-3}} = 5307\text{K} \]

Lowest temp for the reaction to be feasible is 5307K.
d  D: CH₃COCl  E: CH₃CHO

F: CH₃C–CN  G: CH₃C–CH₂NH₂

H

OH

Reagents and conditions for step (i):
LiAlH₄ in dry ether  or  H₂ with Pt as catalyst

3  (a)  •  W contains chiral carbon.
•  W is an aldehyde.

No of moles of CO₂ = \( \frac{33.6}{22.4} \) = 1.50 mol

n₢ : n CO₂
0.3 : 1.50
1:5

•  Y contains 5 carbon atoms.

Structure of W:

```
\[\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{C}--\text{C}--\text{C}--\text{C}--\text{H} \\
\text{H} \\
\text{H} \\
\text{CH₃} \\
\end{array}\]
```

Structure of Y:

```
\[\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{C}--\text{C}--\text{C}--\text{C}--\text{H} \\
\text{H} \\
\text{H} \\
\text{CH₃} \\
\end{array}\]
```
Structure of X:

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{CH}_3 \\
\text{O} \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}
\]

(b) | Observations                                                                 | Deductions                      |
---|-------------------------------------------------------------------------------|---------------------------------|
J  | has molecular formula of C\(_4\)H\(_7\)Cl.                                    | J is a halogenoalkane.          |
J  | reacts with ethanolic potassium cyanide to produce compound K with molecular formula C\(_5\)H\(_7\)N. | J undergoes nucleophilic substitution of Cl with CN. |

Displayed formula of J:
(c) (i) Comparing Expt 1 & 2, when [J] triples while [KCN] is kept constant, initial rate of formation of product triples. Hence, reaction is first order wrt J.

Comparing Expt 1 & 3, when [J] doubles and [KCN] doubles, initial rate of formation of product only doubles. Hence, reaction is zero order wrt KCN.

Rate = k[J]

Mechanism:
Nucleophilic Substitution (SN1)

Step 1:

Step 2:
(ii) \[ \ln[J] = \ln[J]_o - kt \]
\[ \ln[J] = -kt + \ln[J]_o \quad [y = mx + c] \]

Hence, rate constant = – gradient

(d) (i) overall order = 2

(ii) Ethanol is more polar than propanone, stabilizes carbocation to a greater extent through formation of stronger ion-dipole interactions. Hence SN1 mechanism is favoured when ethanol is used as the solvent.

(e) Fraction of molecules

\[ \text{where } T_2 < T_1 \]

Legend:
- \[ \text{fraction of molecules having energy } \geq \text{Ea at } T_1 \]
- \[ \text{fraction of molecules having energy } \geq \text{Ea at } T_2 \]

At a lower temperature \( T_2 \), the fraction of molecules having energy greater than or equal to \( \text{Ea} \) decreases, from \( \text{ } \) to \( \text{ } \)

Hence, the number of effective collisions decreases and rate of reaction decreases.
4. (i) NH₃ in ethanol, in sealed tube

\[
P : \quad \text{CONH}_2
\]

(ii) Sn, c.HCl, reflux followed by NaOH(aq)

\[
\text{c. HNO}_3 \\
\text{c. H}_2\text{SO}_4 \\
55\degree C
\]

\[
\text{NO}_2 \\
\text{Sn, c.HCl , reflux} \\
\text{followed by NaOH(aq)} \\
\ammonia
\]

(iii) Add neutral aqueous iron(III) chloride to both.

An intense violet complex will be observed for phenol.
No violet complex for phenylamine.

Or Add sodium metal to both.

Effervescence will be observed for phenol. Gas evolved extinguished burning splinter with a “pop” sound.
No gas evolved for phenylamine.

(b) (i) a “radical” contains a lone/unpaired electron or odd number of electrons.
(ii) 

\[
\text{\begin{tabular}{c}
 H \\
\Hline
 C & C & O \\
\Hline
 H
\end{tabular}}
\]

OCO bond angle = 120°

(iii) \(2 \text{H}_2\text{O} + 2e \rightarrow \text{H}_2 + 2\text{OH}^-\)

(b) (iv) (I) Mr of CH₃COOK = 98.1

Amt of CH₃COOK in 2.43g = 0.02477 mol

1 mol of CH₃COOK gives rise to 1 mol of CH₃ radical.
2 mol of CH₃ gives rise to 1 mol of CH₃CH₃ molecule.

Step 1 \(\text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{COO} + e \) \ldots Anode reaction

Step 2 \(\text{CH}_3\text{COO} \rightarrow \text{CH}_3 + \text{CO}_2 \) \ldots Decarboxylation

Step 3 \(2 \text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3 \) \ldots Dimerization

Theoretical amt of CH₃CH₃ to be produced = \(\frac{0.02477}{2} = 0.01238\) mol

Theoretical volume of CH₃CH₃ to be produced:

\[
pV = nRT \\
(101000)V = (0.01238)(8.31)(28 + 273) \\
V = 3.065 \times 10^{-4} \text{ m}^3
\]

Percentage yield of CH₃CH₃ = \(\frac{200 \times 10^{-6}}{3.065 \times 10^{-3}} \times 100\% = 65.2\%\)

OR

\[
pV=nRT \\
(101000)(200 \times 10^{-6}) = n (8.31)(28 + 273) \\
n = 8.075 \times 10^{-3}
\]

8.075 \times 10^{-3} mol of CH₃CH₃ produced.
Percentage yield of CH₃CH₃ = \( \frac{8.075 \times 10^{-3}}{0.01238} \times 100\% = 65.2\% \)

(II) \hspace{1cm} \text{electron : CH₃COO}^–

\begin{align*}
\text{1} & : \text{1} \\
\text{Amt of electrons required} = 0.02477 \text{ mol}
\end{align*}

Q = It

\begin{align*}
(0.02477)(96500) \text{ = 0.5 t} \\
t = \text{4778s} \\
= \text{79.6 min}
\end{align*}

(c) (i)

\begin{align*}
P & : \\
\begin{array}{c}
\text{CH}_3 - \text{C} - \text{C} - \text{CH}_3 \\
\text{CH}_3 - \text{C} - \text{CH}_2\text{CH}_2\text{CH}_3
\end{array}
\end{align*}

\text{or}

\text{Step 1} \hspace{0.5cm} \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^– \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}• + e

\text{Step 2} \hspace{0.5cm} \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}• \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2 + \text{CO}_2

\text{Step 3} \hspace{0.5cm} 2 \text{CH}_3\text{CH}_2\text{CH}_2\text{•} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3

\text{In step 2, once the primary radical is formed, it immediately forms a more stable secondary radical by rearrangement of radical/ hydride shift.}

\begin{align*}
\text{1}\text{o radical} & \hspace{2cm} \text{2}\text{o radical}
\end{align*}

\text{Collision of 2 secondary radicals give rise to P.}

(ii)

\text{Hexane has a higher boiling point than P as hexane is straight-chain with a higher surface area of contact between its molecules compared to P which is branched.}

\text{More energy is required to overcome the stronger temporary dipole induced dipole between hexane molecules.}
Potassium methanoate:

**Step 1**  
HCOO$^-$ → HCOO$^+$ + e

**Step 2**  
HCOO$^+$ → H$^+$ + CO$_2$

**Step 3**  
H$^+$ → H$_2$

---

5  
(a)  
(i) SnO$_2$  
PbO

(ii) PbO(s) + 2NaOH(aq) + H$_2$O(l) → Na$_2$Pb(OH)$_4$(aq)

(b)  
(i) Amount of PbSO$_4$ dissolved in 100 cm$^3$= \(\frac{0.00425}{207 + 32.1 + 4(16.0)}\)  
= 1.402 x 10$^{-5}$ mol

Solubility = 1.402 x 10$^{-5}$ mol x \(\frac{1000}{100}\) = 1.402 x 10$^{-4}$ mol dm$^{-3}$

(ii) \(K_{sp} = [Pb^{2+}][SO_4^{2-}] = (1.402 x 10^{-4})^2\)  
= 1.97 x 10$^{-8}$ mol$^2$dm$^{-6}$

(iii) PbSO$_4$(s) $\rightleftharpoons$ Pb$^{2+}$(aq) + SO$_4^{2-}$(aq)

The solubility will be lower due to common ion effect. By LCP, equilibrium above shifts to LHS due to a higher concentration of SO$_4^{2-}$ ion.

(c)  
(i) CO$_2$ has a simple covalent structure whereas SiO$_2$ has a giant covalent structure. A greater amount of energy is required to break the strong covalent bonds between Si and O atoms as compared to the weak van der Waals forces between CO$_2$ molecules.

(ii) SiO$_2$ has a giant covalent structure and PbO has a giant ionic structure. Both
covalent and ionic bonds are strong. The covalent bonds between Si and O atom is stronger than the ionic bonds between the Pb\(^{2+}\) and O\(^{2-}\) ions in this case. Hence a greater amount of energy is required to break the covalent bonds in SiO\(_2\).

(d) (i) Step I: excess conc.H\(_2\)SO\(_4\), 170°C  
Step II: conc.H\(_2\)SO\(_4\), conc.HNO\(_3\), 55°C

\[
\begin{align*}
S: & \quad \text{CH}_2\text{CHO} \\
T: & \quad \text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]

(ii) U:

\[
\begin{align*}
\text{CH}_2\text{CHCl}_2 & \quad \text{CH}_3 \\
\text{NO}_2
\end{align*}
\]

The –CH\(_2\)CHCl\(_2\) group is 2,4-directing whereas the –NO\(_2\) group is 3-directing. Hence the next substitution will occur on position 2 relative to the –CH\(_2\)CHCl\(_2\) group or the 3\(^{rd}\) position relative to the –NO\(_2\) group. Both are essentially the same position.

(iii) Mild oxidation occurs. KMnO\(_4\) decolourised with the formation of brown MnO\(_2\) ppt.

\[
\begin{align*}
\text{CH(OH)CH}_2\text{OH}
\end{align*}
\]

(iv)
READ THESE INSTRUCTIONS FIRST

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

There are forty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D.
Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.
Section A

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

1. The mass percentage of magnesium in a mixture of magnesium chloride and magnesium nitrate was found to be 21.25%. What mass of magnesium chloride is present in 100 g of the mixture?

   A 47 g  
   B 51 g  
   C 53 g  
   D 56 g

2. The use of the Data Booklet is relevant to this question.

   The successive ionisation energies, in kJ mol\(^{-1}\), of an element \(X\) are given below.

   870 1800 3000 3600 5800 7000 13200

   What is \(X\)?

   A \(8\text{O}\)  
   B \(33\text{As}\)  
   C \(52\text{Te}\)  
   D \(53\text{I}\)

3. Iodine and phosphorus each form a trifluoride. What are the shapes of these two molecules?

   \(\text{IF}_3\)  
   \(\text{PF}_3\)

   A trigonal planar  trigonal planar
   B T-shaped  trigonal pyramidal
   C trigonal pyramidal  trigonal planar
   D T-shaped  trigonal planar
4 Which of the following diagrams correctly describes the behavior of a fixed mass of an ideal gas? (\(T\) is measured in K.)

A

\[ p \quad \text{constant } T \]

\[ 0 \quad V \]

B

\[ p \quad \text{constant } T \]

\[ 0 \quad p \]

C

\[ pV \quad \text{constant } T \]

\[ 0 \quad p \]

D

\[ V \quad \text{constant } p \]

\[ 0 \quad T \]
Questions 5 and 6 refer to the “OXO” reaction shown below.

The “OXO” reaction shown below is industrially important for making alcohols, aldehydes and carboxylic acids. For example, butanal can be synthesised from propene, \(\text{C}_3\text{H}_6\), according to the following scheme. It can then be converted to butan-1-ol and butanoic acid.

\[
\text{CH}_3\text{CH} = \text{CH}_2(\text{g}) + \text{CO}(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO(}\text{g})
\]

\text{propene} \hspace{2cm} \text{butanal}

5 The value of \(\Delta G\) for this reaction is negative. What is the sign of \(\Delta S\) and \(\Delta H\) for the above reaction?

<table>
<thead>
<tr>
<th>(\Delta S)</th>
<th>(\Delta H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>+</td>
</tr>
<tr>
<td>B</td>
<td>+</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>-</td>
</tr>
</tbody>
</table>

6 Use of the Data Booklet is relevant to this question.

Taking the bond energy for the \(\text{C}=\text{O}\) bond in carbon monoxide to be 1077 kJ mol\(^{-1}\) and using other appropriate bond energies, what is the numerical value of \(\Delta H\) for the above “OXO” reaction?

- A 137 kJ mol\(^{-1}\)
- B 213 kJ mol\(^{-1}\)
- C 573 kJ mol\(^{-1}\)
- D 623 kJ mol\(^{-1}\)

7 The radioactive decay is a first order reaction. If the rate of decay of a radioactive isotope decreases from 200 counts per minute to 25 counts per minute after 21.6 hours, what is its half-life?

- A 2.4 hours
- B 6.5 hours
- C 7.2 hours
- D 7.8 hours
8 Which of the following statements correctly explains why a small increase in temperature leads to a significant increase in the rate of a gaseous reaction?

A The average kinetic energy of the molecules is slightly greater at a higher temperature.
B The proportion of molecules with any given energy increases.
C The frequency of collisions between molecules is greater at a higher temperature.
D The frequency of collisions between molecules with kinetic energy greater than the activation energy is greater at a higher temperature.

9 An equilibrium can be represented by the following equation:

\[ P(aq) + Q(aq) \rightleftharpoons 2R(aq) + S(aq) \]

In a certain mixture, the equilibrium concentration of \( Q \) is 10 mol dm\(^{-3} \).
What will be the new equilibrium concentration of \( Q \) if 5 mol of pure \( Q \) is dissolved in the mixture?

A 15 mol dm\(^{-3} \)
B between 10 mol dm\(^{-3} \) and 15 mol dm\(^{-3} \)
C 10 mol dm\(^{-3} \)
D between 5 mol dm\(^{-3} \) and 10 mol dm\(^{-3} \)

10 Which of the following correctly lists 0.10 mol dm\(^{-3} \) solutions of HCl, KCl, NH\(_4\)Cl, KOH and KCN in order of increasing pH?

A HCl, KCl, KCN, NH\(_4\)Cl, KOH
B HCl, NH\(_4\)Cl, KCl, KCN, KOH
C HCl, KCl, NH\(_4\)Cl, KCN, KOH
D KCl, KCN, KOH, HCl, NH\(_4\)Cl

11 Thorium hydroxide, Th(OH)\(_4\), is a sparingly soluble salt. Which of the following shows the correct expression of its molar solubility \( s \) (mol dm\(^{-3} \)) in terms of its solubility product \( K_{sp} \)?

A \( s = (K_{sp})^{1/5} \)
B \( s = (K_{sp}/4)^{1/2} \)
C \( s = (K_{sp})^{1/5}/256 \)
D \( s = (K_{sp}/256)^{1/5} \)
12 Use of the Data Booklet is relevant to this question.

Using inert electrodes, a current was passed through two beakers containing aqueous silver sulfate and aqueous copper(II) nitrate, connected in series under standard conditions.

![Diagram showing a circuit with two beakers, one containing 1.00 mol dm$^{-3}$ Cu(NO$_3$)$_2$(aq) and the other containing 0.50 mol dm$^{-3}$ Ag$_2$SO$_4$(aq).]

At 25°C, 1 atm

What is the ratio of the mass of silver to copper deposited after the current was passed for t minutes?

- A 0.59
- B 0.85
- C 1.70
- D 3.40

13 Use of the Data Booklet is relevant to this question.

The circuit shown in the diagram was set up.

![Diagram showing a circuit with a battery and a beaker containing 1.00 mol dm$^{-3}$ CuSO$_4$(aq).]

At 25°C, 1 atm

pure Cu

impure Cu containing Ag and Fe impurities

sludge

What are the products formed at the anode and cathode and what is the substance present in the sludge after some time?

<table>
<thead>
<tr>
<th>anode</th>
<th>cathode</th>
<th>sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Cu$^{2+}$</td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>B Fe$^{2+}$</td>
<td>Cu$^{2+}$</td>
<td>Ag</td>
</tr>
<tr>
<td>C Ag$^+$, Fe$^{2+}$</td>
<td>Cu$^{2+}$</td>
<td>Zn</td>
</tr>
<tr>
<td>D Cu$^{2+}$, Fe$^{2+}$</td>
<td>Cu</td>
<td>Ag</td>
</tr>
</tbody>
</table>
14 On descending Group II from magnesium to barium, which of the following
statements is true?

A The enthalpy change of hydration of the $\text{M}^{2+}$ ion becomes more exothermic.
B The first ionisation energy increases.
C The nitrates is less easily decomposed by heat to give brownish fumes.
D The solubility of the Group II oxides decreases.

15 What is observed when aluminium chloride is added to excess water?

<table>
<thead>
<tr>
<th>solubility in water</th>
<th>pH of resulting solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A insoluble</td>
<td>7.0</td>
</tr>
<tr>
<td>B very slightly soluble</td>
<td>6.5</td>
</tr>
<tr>
<td>C dissolves</td>
<td>5.0</td>
</tr>
<tr>
<td>D dissolves</td>
<td>3.0</td>
</tr>
</tbody>
</table>

16 Which of the following compounds has the highest melting point?

A NaCl
B MgCl$_2$
C AlCl$_3$
D SiCl$_4$

17 Both aqueous bromine and aqueous chlorine appear as yellow solutions. Which
of the following reagents can be used to distinguish the two solutions?

A aqueous chlorine
B aqueous sodium chloride
C aqueous sodium thiosulfate
D aqueous iron(II) sulfate, followed by aqueous sodium hydroxide
18 In the laboratory, there are three bottles labeled A, B and C. Each bottle contains one of the following reagents: CaCl$_2$(aq), FeCl$_2$(aq) and AgNO$_3$(aq). The tests were carried out using these reagents and the results were summarised in the table below:

<table>
<thead>
<tr>
<th>Tests</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing reagents A and B, followed by addition of NH$_3$(aq)</td>
<td>A white ppt soluble in NH$_3$(aq)</td>
</tr>
<tr>
<td>Mixing reagents A and C, followed by addition of NH$_3$(aq)</td>
<td>A grey precipitate insoluble in NH$_3$(aq)</td>
</tr>
</tbody>
</table>

What are the identities of the reagents A, B and C?

A | B | C |
---|---|---|
A | CaCl$_2$ | AgNO$_3$ | FeCl$_2$ |
B | FeCl$_2$ | AgNO$_3$ | CaCl$_2$ |
C | AgNO$_3$ | FeCl$_2$ | CaCl$_2$ |
D | AgNO$_3$ | CaCl$_2$ | FeCl$_2$ |

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

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

with aqueous ammonium thiocyanate with alkaline aqueous ammonium thiocyanate

A | Fe-NH$_3$ complex | Fe(OH)$_3$ |
B | Fe-CNS$^-\,$ complex | Fe-NH$_3$ complex |
C | Fe-CNS$^-\,$ complex | Fe(OH)$_3$ |
D | Fe-CNS$^-\,$ complex | Fe-OH$^-\,$ complex |
20 The table shows the possible oxidation states of five d-block elements in the Periodic Table. (The elements are represented by letters which are not their symbols.)

<table>
<thead>
<tr>
<th>element</th>
<th>possible oxidation numbers</th>
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<tbody>
<tr>
<td>P</td>
<td>- 3 - - - - - - - - - - -</td>
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<tr>
<td>Q</td>
<td>- 2 3 4 - - - - - - - - -</td>
</tr>
<tr>
<td>R</td>
<td>1 2 3 4 5 - - - - - - - -</td>
</tr>
<tr>
<td>S</td>
<td>- 2 - 4 5 6 7 - - - - - -</td>
</tr>
</tbody>
</table>

Which of the following ions is likely to exist?

A. $PO_2^+$
B. $QO_3^-$
C. $RO_4^{2+}$
D. $SO_2^{2+}$

21 Warfarin is used as a rat poison.

How many $sp^2$ hybridised carbon atoms are present in the Warfarin molecule?

A. 4
B. 12
C. 14
D. 16
22 The structure of vitamin D2 is shown below.

When it is completely reacted with hydrogen in the presence of a palladium catalyst at room temperature, how many chiral centres does the product molecule possess?

A 7  
B 8  
C 9  
D 10

23 Limonene is an oil formed in the peel of citrus fruits.

Which of the following is the major product formed when hydrogen bromide reacts with limonene at room temperature?

A  
B  
C  
D  

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24 A sample of ethylbenzene is quantitatively oxidised to the corresponding carboxylic acid.

What is the mass of product formed from 1.00 g of ethylbenzene?

A 1.15 g  
B 1.28 g  
C 1.32 g  
D 1.38 g

25 The Hofmann elimination is a process where an amine undergoes treatment with excess methyl iodide to form a tertiary amine intermediate followed by treatment with silver oxide, water and heat to form an alkene.

What is the structure of the alkene formed when a cyclic amine, piperidine, undergoes the Hofmann elimination?

A \( \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{N(CH}_3\text{)}_2 \)  
B \( \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3 \)  
C \( \text{N}--\text{CH}_3 \)  
D \( \text{H}_2\text{C}--\text{CHCH}_3 \)
26 When sodium iodide in propanone is added to an optically active sample of 2-bromobutane, a sodium bromide precipitate formed after 13 minutes upon heating.

\[
\text{NaI} + \text{CH}_3\text{CHBrCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CHICH}_2\text{CH}_3 + \text{NaBr(s)}
\]

The experiment was repeated several times and the rate equation was found to be

\[
\text{Rate} = k[\text{CH}_3\text{CHBrCH}_2\text{CH}_3][\text{NaI}]
\]

Which of the following statements is incorrect?

A A racemic mixture is formed.
B The reaction involves nucleophilic substitution.
C The reaction is bimolecular.
D A similar experiment, using 1-bromobutane, will produce precipitate in less than 13 minutes.

27 The following compound contains 4 chlorine atoms (labelled 1, 2, 3 and 4).

![Compound with 4 chlorine atoms]

What is the relative order of increasing ease of hydrolysis of the chlorine atoms?

A 1, 2, 3, 4
B 2, 1, 3, 4
C 1, 2, 4, 3
D 2, 1, 4, 3
28 Compound Z can be obtained via the 2-step synthesis from compound V.

\[
\begin{align*}
\text{CHO} & \quad \text{H}_2 \text{ gas} \quad \text{Pt} \\
\text{OH} & \quad \text{X} \quad \text{Na metal} \\
\text{CN} & \quad \rightarrow \\
\end{align*}
\]

What is the change in gas volume if 96 dm\(^3\) of \(\text{H}_2\) gas was reacted with one mole of compound V, followed by excess sodium metal, at room conditions?

A Gas volume contracted by 60 dm\(^3\)
B Gas volume contracted by 36 dm\(^3\)
C Gas volume expanded by 60 dm\(^3\)
D Gas volume expanded by 36 dm\(^3\)

29 Which of the following compound can be used, in a 1-step conversion, to produce the following cyclic structure?

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

A \(\text{HO}_2\text{CCH}_2\text{NH}_2\) and \(\text{HO}_2\text{CCH}_2\text{OH}\)
B \(\text{HO}_2\text{CCH}_2\text{CONHCH}_2\text{OH}\)
C \(\text{ClOCCH}_2\text{COCl}\) and \(\text{H}_2\text{NCH}_2\text{OH}\)
D \(\text{ClOCCH}_2\text{OH}\) and \(\text{H}_2\text{NCH}_2\text{CO}_2\text{H}\)
The thermal decomposition of calcium ethanoate produces its metal carbonate and a carbonyl compound.

\[(\text{CH}_3\text{CO}_2)_2\text{Ca} \rightarrow \text{CaCO}_3 + (\text{CH}_3\text{CO})_2\text{CO}\]

When a mixture of calcium ethanoate and calcium methanoate was heated, a mixture of three carbonyl compounds X, Y and Z were obtained. Both X and Y give a silver mirror with Tollens’s reagent but not Z. Both X and Z give yellow precipitate in aqueous alkaline iodine but not Y.

Based on the above, which of the following statements are incorrect?

A. Only X and Y can decolourise aqueous potassium manganate(VII).
B. The ratio of X to Y to Z formed is 2:1:1.
C. Only X reacts with HCN to produce an optically active product.
D. All three compounds can form an orange precipitate with 2,4-DNPH.
Section B

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

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

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

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<td>1, 2 and 3 are correct</td>
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<td>1 only is correct</td>
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</table>

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

31 10 cm$^3$ of a gaseous hydrocarbon X is mixed with 100 cm$^3$ oxygen and ignited. After the reaction the gases produced are shaken with aqueous KOH solution. The final volume of gases is 25 cm$^3$. Which of the following hydrocarbons could be X?
(All volumes are measured at room temperature and pressure.)

1 C$_4$H$_8$
2 C$_5$H$_{10}$
3 C$_6$H$_6$

32 1 dm$^3$ of gas X weighs 1 g and 1 dm$^3$ of gas Y weighs 5 g under the same conditions of temperature and pressure. Which of the following statements are correct?

1 The ratio of the M$_r$ of X to Y is 1:5.
2 The average velocity of the molecules in gas X and gas Y are the same at the same temperature.
3 The number of molecules of Y in 1 dm$^3$ is five times the number of molecules of X in 1 dm$^3$. 
The responses A to D should be selected on the basis of

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

33 In the reaction between iodide and peroxodisulfate, iron(III) is used as a catalyst. Which of the statements are incorrect?

1 The rate of both the forward and backward reaction increases to the same extent, but the rate constant remains the same.
2 One of the equations involve: \(2\text{Fe}^{3+} + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{Fe}^{2+} + \text{S}_4\text{O}_6^{2-}\).
3 This reaction is an example of a homogeneous catalysis.

34 Ammonia is manufactured in the Haber process.

\[\text{N}_2 (g) + 3\text{H}_2 (g) \rightleftharpoons 2\text{NH}_3 (g) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}\]

Given that \(K_p\) for the above reaction is 3.375 at \(T\) K, which of the following statements involving the reaction is correct?

1 The partial pressure of \(\text{H}_2\) (g) at equilibrium at \(T\) K can be expressed as \(\frac{2}{3}(P_{\text{NH}_3})^{\frac{2}{3}}(P_{\text{N}_2})^{\frac{1}{3}}\).
2 When equilibrium is established, temperature, \(T\) K, is given by \(T = \frac{\Delta H}{\Delta S}\).
3 When pressure is increased, the yield of ammonia and the equilibrium constant increases.
The responses A to D should be selected on the basis of

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

35 The Group II metals have higher melting points than the Group I metals. Which of the following factors could contribute towards the higher melting points?

1. There are smaller interatomic distances in the metallic lattices of the Group II metals.
2. Two valence electrons are available from each Group II metal atom for bonding the atom into the metallic lattice.
3. Group II metals have higher first ionization energies.

36 Chromium and its compounds undergo the following reactions.

\[ \text{CrK(SO}_4\text{)}_2 \rightarrow \text{A (green solution)} \rightarrow \text{B (yellow solution)} \rightarrow \text{C (orange solution)} \rightarrow \text{D} \]

D has the following composition by mass: Cr, 15.5%; S, 38.1%; N, 29.2%

Which of the following can be deduced from the above reaction scheme?

1. The values of \( x \) and \( y \) in D are 4 and 2 respectively.
2. The types of reactions that occur are ligand exchange and redox only.
3. The formula of A is Cr(OH)\(_2\)(H\(_2\)O)\(_6\).
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No other combination of statements is used as a correct response.

37 A hydrocarbon, on heating with an excess of hot concentrated acidic KMnO$_4$(aq), produces CH$_3$COCH$_3$ and (CH$_3$)$_2$CHCO$_2$H as the only organic products. What could the hydrocarbon be?

38 Which reagents can be used to distinguish between the following compounds?

1 PCl$_5$
2 Na$_2$Cr$_2$O$_7$
3 NaHCO$_3$
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No other combination of statements is used as a correct response.

39 The following are structures of 3 amino acids.

Which of the following represents dipeptides formed from these amino acids?
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No other combination of statements is used as a correct response.

40 Lysine is an essential amino acid found in the body. It has three pKₐ values associated with it: 2.2, 9.0 and 10.5

\[
\text{\begin{tabular}{c}
\text{CO}_2\text{H} \\
\text{H}_2\text{N} \\
\text{(CH}_2\text{)}_4\text{NH}_2
\end{tabular}}
\]

When one mole of protonated lysine was titrated against hydroxide ions, the following pH curve is obtained:

Which of the following statements are true with respect to the curve above?

1 Equal amounts of \(\text{H}_3\text{N}^+\text{CH(CO}_2\text{H})(\text{CH}_2)_4\text{NH}_3^+\) and \(\text{H}_3\text{N}^+\text{CH(CO}_2\text{H})(\text{CH}_2)_4\text{NH}_2\) are present at point A.
2 The major species present at point C has no net charge.
3 The major species present at point B will migrate towards the cathode of an electrolytic cell.
NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION 2012
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1 Planning (P)

Paracetamol (acetaminophen) is commonly used for the relief of headaches and is a major ingredient in numerous cold and flu medicine.

It is a white solid (m.p. = 169 °C) which can be prepared by a reaction between 4-aminophenol and ethanoic anhydride.

$$\text{HOC}_6\text{H}_4\text{NH}_2 \quad \text{(CH}_3\text{CO)}_2\text{O} \quad \text{CH}_3\text{CONHC}_6\text{H}_4\text{OH}$$

4-aminophenol \hspace{1cm} ethanoic anhydride \hspace{1cm} paracetamol

\( (M_r = 109) \quad (M_r = 102) \quad (M_r = 151) \)

A typical yield, based on 4-aminophenol, is 70%.

The crude product can be purified by recrystallisation from water.

The purity of the recrystallised product can be confirmed by determining its melting point.

Ethanoic anhydride can cause irritation of tissue, especially in nasal passages.

4-aminophenol is a skin irritant and is toxic.

(a) Using the information above:

(i) Write a balanced equation for the formation of paracetamol;

(ii) Calculate the minimum masses of reactants needed to prepare 5 g of pure paracetamol.
(b) Write a full description of the purification of the crude paracetamol. List the essential apparatus you would use in the process. You do not have to describe the preparation of paracetamol.

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2 Given the following thermochemical data:

<table>
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<tr>
<th>Reaction</th>
<th>$\Delta H^\circ$ / kJ mol$^{-1}$</th>
</tr>
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<tr>
<td>C(graphite) + 2H$_2$(g) $\rightarrow$ CH$_4$(g)</td>
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<tr>
<td>C(graphite) + O$_2$(g) $\rightarrow$ CO$_2$(g)</td>
<td>$-393.5$</td>
</tr>
<tr>
<td>H$_2$(g) + $\frac{1}{2}$O$_2$(g) $\rightarrow$ H$_2$O(l)</td>
<td>$-285.9$</td>
</tr>
</tbody>
</table>

(a) With the aid of an energy cycle, calculate the enthalpy change for the reaction

CH$_4$(g) + 2O$_2$(g) $\rightarrow$ 2H$_2$O(l) + CO$_2$(g)
(b) The experimental enthalpy change is \(-801.7\) kJ mol\(^{-1}\) for the following reaction

\[
\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) \quad \text{...............(I)}
\]

(i) Calculate the enthalpy change of vaporisation of water at 298K.

(ii) Using bond energy data from the *Data Booklet*, calculate another value for \(\Delta H\) for reaction (I) in (b). Account for any differences between your answer and the given experimental value in (b).

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[3]

[Total: 8]
Mixtures of citric acid, $\text{C}_5\text{H}_7\text{O}_4\text{CO}_2\text{H}$ ($K_a = 7.40 \times 10^{-4} \text{ mol dm}^{-3}$), and its sodium salt are often used as acidity regulators for food. The mixture regulates the pH of food by acting as a buffer.

(a) Prove that the pH of a mixture formed from 25.0 cm$^3$ of 0.200 mol dm$^{-3}$ citric acid and 2.48 g of sodium citrate ($M_r = 198$) is 3.53.

(b) When 0.059 g of an unknown solid was added to the mixture prepared in (a), the pH of the resultant solution is 3.73. Determine the molar mass of the solid and hence suggest its identity.
(c) Determine the volume of 0.100 mol dm$^{-3}$ of HCl(aq) that needs to be added to the solution in (a) to obtain a buffer at its maximum buffering capacity.

4 Cobalt and vanadium are transition metals.

(a) Give one characteristic chemical property of cobalt and vanadium which shows that they are transition metals.

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

[1]

(b) Aqueous cobalt(II) chloride, CoCl$_2$ is a pink solution. When a mixture of the pink solution and tartaric acid, HO$_2$CCH(OH)CH(OH)CO$_2$H, is added to aqueous hydrogen peroxide, the following changes take place.

The initially pink solution turns green and then oxygen is vigorously evolved. Finally, the solution turns pink again.

Suggest a role for the CoCl$_2$(aq) and for the tartaric acid. Write an equation for the overall reaction.

CoCl$_2$(aq): ..................................................................................................................................

Tartaric acid: ..................................................................................................................................

Equation: ..................................................................................................................................

[3]
(c) Aqueous CoCl₂ also undergoes the following reaction.

\[
\text{CoCl}_2(aq) + \text{NH}_4\text{Cl, NH}_3 \text{ and O}_2 \rightarrow \text{Crystals of salt K}
\]

(i) Crystals of salt, K has the following composition by mass:

Co, 22.0%; N, 31.4%; H, 6.7%; Cl, 39.8%

On adding an excess of AgNO₃(aq) to an aqueous solution containing 0.01 mol of K, 4.29 g of AgCl(s) is precipitated.

Calculate the empirical formula of K, and draw the structure of the cation present in K to show the geometry around the central ion.

(ii) State the types of reactions occurring in step I.

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(iii) $E^o$ data for some cobalt complex ions are given below.

$[\text{Co(C}_2\text{O}_4]_3^{3-}\text{(aq)} + e^- \rightleftharpoons [\text{Co(C}_2\text{O}_4]_3^{4-}\text{(aq)} \quad E^o = +0.57 \text{ V}$

$[\text{Co(NH}_3]_6^{3+}\text{(aq)} + e^- \rightleftharpoons [\text{Co(NH}_3]_6^{2+}\text{(aq)} \quad E^o = +0.11 \text{ V}$

Use the $E^o$ data given above to predict the reaction, if any, of adding $\text{C}_2\text{O}_4^{2-}$ to $K$. Explain your prediction.

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................................................................................................................................................................. [7]

(d) Some of the ions of vanadium and their corresponding colours are shown in the table below.

<table>
<thead>
<tr>
<th>formula of vanadium ion</th>
<th>$\text{VO}_3^{-}$</th>
<th>$\text{VO}^{2+}$</th>
<th>$\text{V}^{3+}$</th>
<th>$\text{V}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour of aqueous solution</td>
<td>yellow</td>
<td>blue</td>
<td>green</td>
<td>violet</td>
</tr>
</tbody>
</table>

The colour of the reaction mixture changes from yellow to green when a transition metal is added to an aqueous solution containing the salt of a vanadium ion.

By reference to the Data Booklet, suggest a possible identity of the transition metal and explain the colour change observed.

Identity of the transition metal: ..........................................................................................................................................

Explanation:

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[Total: 14]
5 The standard enthalpy change of fusion ($\Delta H_{\text{fus}}^\circ$) is the energy required to convert one mole of a substance in the solid state to the liquid state under standard pressure. The table below shows numerical values of standard enthalpy change of fusion for the respective elements:

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta H_{\text{fus}}^\circ$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2.60</td>
</tr>
<tr>
<td>Al</td>
<td>10.7</td>
</tr>
<tr>
<td>Si</td>
<td>50.2</td>
</tr>
<tr>
<td>Cl</td>
<td>6.41</td>
</tr>
</tbody>
</table>

(a) Explain, in terms of structure and bonding, the difference in the $\Delta H_{\text{fus}}^\circ$ between:

(i) Si and Cl

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(ii) Na and Al

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(b) Experimental results show that the first ionisation energies for the elements phosphorus and iodine are similar. Suggest an explanation for the observations.

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[Total: 6]
6 X₂ and Y₂ are halogens and they are known to be more soluble in organic solvents.

In an experiment, excess X₂ was mixed with Na₂S₂O₃(aq). When hexane was added, two immiscible layers were observed and was later separated using a separatory funnel. A reddish brown organic layer was obtained and the aqueous layer was divided into 2 portions.

To one portion of the aqueous layer, Y₂(aq) was added and shaken. When CCl₄ was added, a violet organic layer was obtained.

To another portion of the aqueous layer, AgNO₃(aq) was added. The precipitate formed does not dissolve in aqueous NH₃.

(a) Suggest a suitable identity of X₂ and Y₂.

X₂: ...................................................... Y₂: ...................................................... [1]

(b) Write a balanced ionic equation for the reaction between Na₂S₂O₃ and X₂.

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

(c) Explain in energy terms, why halogens are more soluble in organic solvent than in water.

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[Total: 4]
Keratin refers to a family of fibrous proteins which is the key component of hair and nails. The keratins in hair consist of α-helically coiled single protein strands, further twisted into superhelical ropes that may be further coiled. The presence of keratins determines the strength and structure of hair i.e. straight or wavy. Nails, which are less flexible and elastic, contains keratins which have β-pleated sheets twisted together, stabilised and hardened by R-group interactions.

The table below shows the amino acid composition of 2 samples of keratins. One sample was extracted from nails, the other sample from hair.

<table>
<thead>
<tr>
<th>Acid</th>
<th>R group</th>
<th>Amino acid composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Sample A</strong></td>
</tr>
<tr>
<td>asp</td>
<td>−CH₂CO₂H</td>
<td>3.0</td>
</tr>
<tr>
<td>asn</td>
<td>CH₃CONH₂</td>
<td>3.0</td>
</tr>
<tr>
<td>thr</td>
<td>−CH(OH)CH₃</td>
<td>6.9</td>
</tr>
<tr>
<td>ser</td>
<td>−CH₃OH</td>
<td>11.7</td>
</tr>
<tr>
<td>glu</td>
<td>−CH₂CH₂CO₂H</td>
<td>6.1</td>
</tr>
<tr>
<td>tyr</td>
<td>−CH₂−OH</td>
<td>1.9</td>
</tr>
<tr>
<td>pro</td>
<td>CH₂CH₂ (cyclic)</td>
<td>3.6</td>
</tr>
<tr>
<td>gly</td>
<td>−H</td>
<td>6.5</td>
</tr>
<tr>
<td>ala</td>
<td>−CH₃</td>
<td>4.8</td>
</tr>
<tr>
<td>cys</td>
<td>−CH₂SH</td>
<td>17.5</td>
</tr>
<tr>
<td>val</td>
<td>−CH(CH₃)₂</td>
<td>5.9</td>
</tr>
<tr>
<td>met</td>
<td>−CH₂CH₂SCH₃</td>
<td>0.5</td>
</tr>
<tr>
<td>ile</td>
<td>−CH(CH₃)CH₂CH₃</td>
<td>2.7</td>
</tr>
<tr>
<td>leu</td>
<td>−CH₂CH(CH₃)₂</td>
<td>6.1</td>
</tr>
<tr>
<td>gln</td>
<td>−CH₃CH₂CONH₂</td>
<td>6.0</td>
</tr>
<tr>
<td>phe</td>
<td>−CH₂−</td>
<td>1.4</td>
</tr>
<tr>
<td>trp</td>
<td>−CH₂−C−</td>
<td>3.7</td>
</tr>
<tr>
<td>lys</td>
<td>−CH₂CH₂CH₂CH₂NH₂</td>
<td>2.3</td>
</tr>
<tr>
<td>his</td>
<td>−CH₂−C−</td>
<td>0.8</td>
</tr>
<tr>
<td>arg</td>
<td>−CH₂CH₂NH(NH₂)=NH₂⁺</td>
<td>5.6</td>
</tr>
</tbody>
</table>
(a) Draw a diagram representing the secondary structure of keratins found in nails. In your diagram, show clearly the bonding that is involved in stabilising the secondary structure. You may represent the R groups using the symbol “R”.

(b) By referring to the amino acid composition data, answer the questions below:

(i) State the R group interaction that is mainly responsible for the stabilisation of the tertiary structure of keratins. Write an equation to support your answer.

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(ii) In order to straighten wavy hair permanently, using a heating iron is insufficient. Instead, one will need to go to the hairdresser to undergo a treatment of chemicals. Explain why.

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(iii) Which sample belongs to keratins extracted from a nail sample? Explain.

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[Total: 8]
8(a) There are four stereoisomers of compound P.

What is the type of stereoisomerism exhibited by P? Draw the stereoisomers of P.

Type of stereoisomerism: .................................................................
(b) Q is a structural isomer of P in (a).
Suggest the structures of Q, R, S, T and U in the reaction scheme below.

\[
\begin{align*}
Q & \quad \text{\(C_{11}H_{12}O_2\)} \\
\text{aqueous HCl} & \quad \rightarrow \\
\text{heat} & \\
R & \quad \text{\(C_3H_6O_2\)} \\
+ & \\
S & \\
\text{H}_2 & \\
\text{Ni catalyst} & \\
\text{heat} & \\
U & \quad \text{\(C_8H_7OBr_3\)} \\
\text{aqueous bromine} & \leftarrow \\
T & \\
\end{align*}
\]
When methylbenzene is nitrated by a mixture of concentrated nitric acid and concentrated sulfuric acid, the product consists largely of two isomers, V and W, of formula C\textsubscript{7}H\textsubscript{7}NO\textsubscript{2}. V has a plane of symmetry perpendicular to the plane of the benzene ring in its molecule, while W does not. The formation of V proceeds via an organic intermediate X.

(a) Draw the displayed formulae of V and X, showing clearly the geometry of the bonds around the carbon atom bonded to the nitrogen atom.

<table>
<thead>
<tr>
<th>isomer V</th>
<th>organic intermediate X</th>
</tr>
</thead>
</table>

(b) What is the name of the mechanism of the reaction for the formation of V? Briefly outline the mechanism of this reaction using equations.

Name of mechanism: .................................................................

Mechanism:
NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

INDEX NO.

TUTOR

CHEMISTRY

9647/02

Paper 2 Structured

10 September 2012

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

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 all questions in the spaces provided.
A Data Booklet is provided.

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

For Examiner’s Use

<table>
<thead>
<tr>
<th></th>
<th>P</th>
<th>/12</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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<td>2</td>
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<td>3</td>
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<td>/ 7</td>
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<tr>
<td>4</td>
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<td>/ 6</td>
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<td>8</td>
<td></td>
<td>/ 9</td>
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<td>9</td>
<td></td>
<td>/ 4</td>
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</tbody>
</table>

This document consists of 17 printed pages and 0 blank page.
1 Planning (P)

Paracetamol (acetaminophen) is commonly used for the relief of headaches and is a major ingredient in numerous cold and flu medicine.

It is a white solid (m.p. = 169 °C) which can be prepared by a reaction between 4-aminophenol and ethanoic anhydride.

\[
\text{HOCl}_2\text{H}_4\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{CONHC}_6\text{H}_4\text{OH} + \text{CH}_3\text{CO}_2\text{H}
\]

A typical yield, based on 4-aminophenol, is 70%.

The crude product can be purified by recrystallisation from water.

The purity of the recrystallised product can be confirmed by determining its melting point.

Ethanoic anhydride can cause irritation of tissue, especially in nasal passages.

4-aminophenol is a skin irritant and is toxic.

(a) Using the information above:

(i) Write a balanced equation for the formation of paracetamol:

\[
\text{HOCl}_2\text{H}_4\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{CH}_3\text{CONHC}_6\text{H}_4\text{OH} + \text{CH}_3\text{CO}_2\text{H}
\]

(ii) Calculate the minimum masses of reactants needed to prepare 5 g of pure paracetamol.

\[
\text{Mass of 4-aminophenol required} = \frac{5}{151} \times \frac{100}{70} \times 109 = 5.16 \text{ g}
\]

\[
\text{Mass of ethanoic anhydride required} = \frac{5}{151} \times \frac{100}{70} \times 102 = 4.82 \text{ g}
\]
(b) Write a full description of the purification of the crude paracetamol. List the essential apparatus you would use in the process. You do not have to describe the preparation of paracetamol.

**Apparatus:**
- Conical flask for dissolving crude solid (accept beaker)
- Hot plate for heating (accept oil bath but not water bath or heating mantle)
- Filter funnel/ conical flask for hot filtration
- Buchner apparatus for collecting pure crystals.

**Method:**
- Dissolve crude solid in minimum amount of hot water
- Filter solution while hot
- Cool hot solution (in ice bath)
- Collect crystals using vacuum filtration/ reduced pressure (using Buchner apparatus)
- Wash with small amounts of cold water
- Dries crystals between filter paper/ under IR lamp.

................................................................................................................................. [6]

(c) Write a brief description showing how you would use the melting point of the purified product to confirm its purity. You do not have to describe how you would obtain the melting point.

- Melts sharply/ over small temperature range
- Melting point agrees with data value (i.e. 169 °C)

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

(d) Identify two potential safety hazards in this experiment and the relevant safety precautions you would take.

<table>
<thead>
<tr>
<th>Hazard</th>
<th>Precaution</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-aminophenol is a skin irritant and is toxic. Ethanoic acid is corrosive</td>
<td>Avoid skin contact; wear personal protective equipment (gloves, goggles); flood affected areas if there is spillage.</td>
</tr>
<tr>
<td>Ethanoic anhydride can cause irritation of tissue, especially in nasal passages.</td>
<td>Perform experiment in fume cupboard.</td>
</tr>
<tr>
<td>Ethanoic anhydride is flammable</td>
<td>Do not use naked flames.</td>
</tr>
</tbody>
</table>

- Precautions must be relevant to the hazard
- Do not allow “use fume cupboard as a precaution for toxicity.”
- Do not allow “do not eat/ consume, do not breathe in” as precautions

................................................................................................................................. [2]

[Total: 12]
2 Given the following thermochemical data:

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<th>$\Delta H^\circ$ / kJ mol$^{-1}$</th>
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<tr>
<td>H$_2$(g) + ½O$_2$(g) → H$_2$O(l)</td>
<td>−285.9</td>
</tr>
</tbody>
</table>

(a) With the aid of an energy cycle, calculate the enthalpy change for the reaction

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) → 2\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$

By Hess’ Law:

$$\Delta H = 75.0 + \{2(-285.9) + (-393.5)\}$$

$$= -890.3 \text{ kJ mol}^{-1}$$
(b) The experimental enthalpy change is $-801.7 \text{ kJ mol}^{-1}$ for the following reaction:

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(g)} + \text{CO}_2(\text{g}) \quad \text{(I)}$$

(i) Calculate the enthalpy change of vaporisation of water at 298K.

\[
\begin{align*}
-890.3 & \\
\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(l)} + \text{CO}_2(\text{g}) & \\
-801.7 & \\
2\Delta H_{\text{vap}} & \\
2\text{H}_2\text{O(}l\text{)} + \text{CO}_2(\text{g}) & \\
2\Delta H_{\text{vap}} & = +890.3 + (-801.7) \\
2\Delta H_{\text{vap}} & = +88.6 \\
\Delta H_{\text{vap}} & = +44.3 \text{ kJ mol}^{-1}
\end{align*}
\]

(ii) Using bond energy data from the Data Booklet, calculate another value for $\Delta H$ for reaction (I) in (b). Account for any differences between your answer and the given experimental value in (b).

\[
\begin{align*}
\Delta H & = 4(410) + 2(496) - 4(460) - 2(740) \\
& = -688 \text{ kJ mol}^{-1}
\end{align*}
\]

The value obtained from bond energy calculations is different because bond energies are only average values obtained from different molecules. They may not be the actual values for the molecules used.
3 Mixtures of citric acid, $C_6H_7O_4CO_2H$ ($K_a = 7.40 \times 10^{-4} \text{ mol dm}^{-3}$), and its sodium salt are often used as acidity regulators for food. The mixture regulates the pH of food by acting as a buffer.

(a) Prove that the pH of a mixture formed from 25.0 cm$^3$ of 0.200 mol dm$^{-3}$ citric acid and 2.48 g of sodium citrate ($M_r = 198$) is 3.53.

$$\text{pH} = - \log (7.40 \times 10^{-4}) + \log \frac{2.48/198}{0.025 \times 0.200}$$

$$= 3.53$$

(b) When 0.059 g of an unknown solid was added to the mixture prepared in (a), the pH of the resultant solution is 3.73. Determine the molar mass of the solid and hence suggest its identity.

Since pH is raised on addition of the solid, the solid added must be a base.

$$C_6H_7O_4CO_2H + OH^- \rightarrow C_6H_7O_4CO_2^- + H_2O$$

$$3.73 = - \log (7.40 \times 10^{-4}) + \log \frac{[C_6H_7O_4CO_2Na][C_6H_7O_4CO_2H]}{[C_6H_7O_4CO_2Na][C_6H_7O_4CO_2H]} = 3.97$$

Let the molar mass of the solid be $M$

$$n_{\text{citric acid}} = 0.025 \times 0.200 - 0.059/M$$

$$n_{\text{citrate}} = 2.48/198 + 0.059/M$$

$$\frac{2.48/198 + 0.059/M}{0.025 \times 0.200 - 0.059/M} = 3.97 \quad \Rightarrow \quad M = 40.0$$

Solid is sodium hydroxide.
(c) Determine the volume of 0.100 mol dm\(^{-3}\) of HCl(aq) that needs to be added to the solution in (a) to obtain a buffer at its maximum buffering capacity.

\[ \text{pH at max. buffering capacity} = 3.13 \]
\[ \text{C}_5\text{H}_7\text{O}_4\text{CO}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{C}_5\text{H}_7\text{O}_4\text{CO}_2\text{H} + \text{H}_2\text{O} \]

Let the volume of 0.100 mol dm\(^{-3}\) HCl required be \( V \)

\[
\begin{align*}
\text{n}_{\text{citric acid}} &= 0.025 \times 0.200 + 0.100V \\
\text{n}_{\text{citrate}} &= 2.48/198 - 0.100V \\
\end{align*}
\]

At max. buffering capacity,

\[
\begin{align*}
[C_5H_7O_4CO_2H] &= [C_5H_7O_4CO_2^-] \\
0.025 \times 0.200 + 0.100V &= 2.48/198 - 0.100V \\
V &= 0.0376 \text{ dm}^3 = 37.6 \text{ cm}^3 \\
\end{align*}
\]

4 Cobalt and vanadium are transition metals.

(a) Give one characteristic chemical property of cobalt and vanadium which shows that they are transition metals.

- variable oxidation state or catalytic activity or complex ion formation or
- formation of coloured ions

(b) Aqueous cobalt(II) chloride, CoCl\(_2\) is a pink solution. When a mixture of the pink solution and tartaric acid, HO\(_2\)CCH(OH)CH(OH)CO\(_2\)H, is added to aqueous hydrogen peroxide, the following changes take place.

The initially pink solution turns green and then oxygen is vigorously evolved. Finally, the solution turns pink again.

Suggest a role for the CoCl\(_2\)(aq) and for the tartaric acid. Write an equation for the overall reaction.

\[
\begin{align*}
\text{CoCl}_2(\text{aq}): & \quad \text{catalyst} \\
\text{Tartaric acid:} & \quad \text{Ligand} \\
\text{Equation:} & \quad 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \\
\end{align*}
\]
(c) Aqueous CoCl₂ also undergoes the following reaction.

\[
\text{CoCl}_2(aq) + \text{NH}_4\text{Cl}, \text{NH}_3 \quad \text{and } \text{O}_2 \rightarrow \text{Crystals of salt } K
\]

(i) Crystals of salt, K has the following composition by mass:

Co, 22.0%; N, 31.4%; H, 6.7%; Cl, 39.8%

On adding an excess of AgNO₃(aq) to an aqueous solution containing 0.01 mol of K, 4.29 g of AgCl(s) is precipitated.

Calculate the empirical formula of K, and draw the structure of the cation present in K to show the geometry around the central ion.

\[
\text{ratio of Co:N:H:Cl} = \frac{22.0}{58.9} : \frac{31.4}{14.0} : \frac{6.7}{1.0} : \frac{39.8}{35.5} = 0.3735:2.243:6.7:1.121
\]

\[
= 1:6:18:3
\]

empirical formula of K ..........................................................

\[
\text{CoN}_6\text{H}_18\text{Cl}_3
\]

![Structure of the cation in K]

(ii) State the types of reactions occurring in step I.

Ligand exchange and redox

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

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

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

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

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

.....................................................................................................................
(iii) $E^\circ$ data for some cobalt complex ions are given below.

$$[\text{Co(C}_2\text{O}_4]_3^{3-}(aq) + e^- \rightleftharpoons [\text{Co(C}_2\text{O}_4]_4^{4-}(aq) \quad E^\circ = +0.57 \text{ V}$$
$$[\text{Co(NH}_3]_6^{3+}(aq) + e^- \rightleftharpoons [\text{Co(NH}_3]_6^{2+}(aq) \quad E^\circ = +0.11 \text{ V}$$

Use the $E^\circ$ data given above to predict the reaction, if any, of adding $\text{C}_2\text{O}_4^{2-}$ to $\text{K}$. Explain your prediction.

$\text{Co}^{3+}$ is more stable when $\text{NH}_3$ is the ligand as seen from the smaller $E^\circ$ value for the reduction of $[\text{Co(NH}_3]_6]^{3+}$ to $[\text{Co(NH}_3]_6]^{2+}$.

The ligand $\text{C}_2\text{O}_4^{2-}$ is unable to displace the ammonia ligands in $\text{K}$.

No ligand exchange reaction takes place when $\text{C}_2\text{O}_4^{2-}$ is added to $\text{K}$.

[7]

(d) Some of the ions of vanadium and their corresponding colours are shown in the table below.

<table>
<thead>
<tr>
<th>formula of vanadium ion</th>
<th>$\text{VO}_3^-$</th>
<th>$\text{VO}^{2+}$</th>
<th>$\text{V}^{3+}$</th>
<th>$\text{V}^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour of aqueous solution</td>
<td>yellow</td>
<td>blue</td>
<td>green</td>
<td>violet</td>
</tr>
</tbody>
</table>

The colour of the reaction mixture changes from yellow to green when a transition metal is added to an aqueous solution containing the salt of a vanadium ion.

By reference to the Data Booklet, suggest a possible identity of the transition metal and explain the colour change observed.

Identity of the transition metal: .................................................................

Explanation:

$$\text{VO}_3^- + 4\text{H}^+ + e^- \rightleftharpoons \text{VO}^{2+} + 2\text{H}_2\text{O} \quad E^\circ = +1.00 \text{ V}$$
$$\text{VO}^{2+} + 2\text{H}^+ + e^- \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O} \quad E^\circ = +0.32 \text{ V}$$
$$\text{V}^{3+} + e^- \rightleftharpoons \text{V}^{2+} \quad E^\circ = -0.26 \text{ V}$$
$$\text{Co}^{2+} + 2e^- \rightleftharpoons \text{Co} \quad E^\circ = -0.28 \text{ V}$$
$$\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe} \quad E^\circ = -0.04 \text{ V}$$
$$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni} \quad E^\circ = -0.25 \text{ V}$$

Co reducing $\text{V}(+5)$ to $\text{V}(+3)$

$$E^\circ_{\text{cell}} = +1.00 - (-0.28) = 1.28 \text{ V} > 0$$
$$E^\circ_{\text{cell}} = +0.32 - (-0.28) = 0.60 \text{ V} > 0$$
$$E^\circ_{\text{cell}} = -0.26 - (-0.28) = 0.02 \text{ V} > 0 \text{ but too small}$$

Fe reducing $\text{V}(+5)$ to $\text{V}(+3)$

$$E^\circ_{\text{cell}} = +1.00 - (-0.04) = 1.04 \text{ V} > 0$$
$$E^\circ_{\text{cell}} = +0.32 - (-0.04) = 0.36 \text{ V} > 0$$
$$E^\circ_{\text{cell}} = -0.26 - (-0.04) = -0.22 \text{ V} < 0$$
Ni reducing $V$(+5) to $V$(+3)
\[ E^{\circ}_{\text{cell}} = +1.00 - (-0.25) = 1.25 \, V > 0 \]
\[ E^{\circ}_{\text{cell}} = +0.32 - (-0.25) = 0.57 \, V > 0 \]
\[ E^{\circ}_{\text{cell}} = -0.26 - (-0.25) = 0.01 \, V > 0 \text{ but too small} \]
The $E^\circ$ potential for $Co^{2+}/Co$ ($Fe^{3+}/Fe$ or $Ni^{2+}/Ni$) is bigger (less negative/more positive) than that for $V^{3+}/V^{2+}$.
5 The standard enthalpy change of fusion ($\Delta H_{\text{fus}}^\circ$) is the energy required to convert one mole of a substance in the solid state to the liquid state under standard pressure. The table below shows numerical values of standard enthalpy change of fusion for the respective elements:

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta H_{\text{fus}}^\circ$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>2.60</td>
</tr>
<tr>
<td>Al</td>
<td>10.7</td>
</tr>
<tr>
<td>Si</td>
<td>50.2</td>
</tr>
<tr>
<td>Cl</td>
<td>6.41</td>
</tr>
</tbody>
</table>

(a) Explain, in terms of structure and bonding, the difference in the $\Delta H_{\text{fus}}^\circ$ between:

(i) Si and Cl

Silicon has a giant covalent structure while chlorine has a simple molecular structure.

Melting of silicon requires breaking the numerous strong covalent bonds between the atoms while melting of chlorine requires overcoming the weak dispersion forces between the molecules.

Hence, more energy is required for silicon.

........................................................................................................................................................................ [2]

(ii) Na and Al

Both aluminium and sodium have giant metallic structures with strong metallic bonds between the cations and delocalised sea of electrons.

Aluminium contributes more electrons for metallic bonding than sodium and the cation has smaller ionic radius. Hence the metallic bonds in aluminium are stronger and more energy is required for the fusion process.

........................................................................................................................................................................ [2]

(b) Experimental results show that the first ionisation energies for the elements phosphorus and iodine are similar. Suggest an explanation for the observations.

Iodine has more protons $\rightarrow$ has a higher nuclear charge.

However, valence electrons are further away from the nucleus $\rightarrow$ experiences greater screening effect.

As a result, the valence electron in I experiences similar effective nuclear effect as that in P $\rightarrow$ requires similar energies to remove the electron.

........................................................................................................................................................................ [2]

[Total: 6]
6 X₂ and Y₂ are halogens and they are known to be more soluble in organic solvents.

In an experiment, excess X₂ was mixed with Na₂S₂O₃(aq). When hexane was added, two immiscible layers were observed and was later separated using a separatory funnel. A reddish brown organic layer was obtained and the aqueous layer was divided into 2 portions.

To one portion of the aqueous layer, Y₂(aq) was added and shaken. When CCl₄ was added, a violet organic layer was obtained.

To another portion of the aqueous layer, AgNO₃(aq) was added. The precipitate formed does not dissolve in aqueous NH₃.

(a) Suggest a suitable identity of X₂ and Y₂.

X₂: Bromine 
Y₂: Iodine

(b) Write a balanced ionic equation for the reaction between Na₂S₂O₃ and X₂.

4Br₂(ℓ) + S₂O₃²⁻(aq) + 5H₂O(ℓ) → 2SO₄²⁻(aq) + 8Br⁻(aq) + 10H⁺(aq)

(c) Explain in energy terms, why halogens are more soluble in organic solvent than in water.

In order for halogens to be soluble in organic solvents,
- Interactions between the halogen molecules and the solvent molecules must be formed,
- Since the intermolecular forces are similar in both halogen molecules and the solvent molecules are similar (e.g. van der Waals’ forces),
- The energy evolved in bond formation is likely able to compensate the energy that is needed to break the interactions. Hence, it is energetically favourable.

.............................................................................................................................. [2]

[Total: 4]
Keratin refers to a family of fibrous proteins which is the key component of hair and nails. The keratins in hair consist of α-helically coiled single protein strands, further twisted into superhelical ropes that may be further coiled. The presence of keratins determines the strength and structure of hair i.e. straight or wavy. Nails, which are less flexible and elastic, contains keratins which have β-pleated sheets twisted together, stabilised and hardened by R-group interactions.

The table below shows the amino acid composition of 2 samples of keratins. One sample was extracted from nails, the other sample from hair.

<table>
<thead>
<tr>
<th>Acid</th>
<th>R group</th>
<th>Amino acid composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sample A</td>
</tr>
<tr>
<td>asp</td>
<td>$-\text{CH}_2\text{CO}_2\text{H}$</td>
<td>3.0</td>
</tr>
<tr>
<td>asn</td>
<td>$\text{CH}_3\text{CONH}_2$</td>
<td>3.0</td>
</tr>
<tr>
<td>thr</td>
<td>$-\text{CH(OH)}\text{CH}_3$</td>
<td>6.9</td>
</tr>
<tr>
<td>ser</td>
<td>$-\text{CH}_2\text{OH}$</td>
<td>11.7</td>
</tr>
<tr>
<td>glu</td>
<td>$-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$</td>
<td>6.1</td>
</tr>
<tr>
<td>tyr</td>
<td>$\text{CH}_2$&lt;br&gt;OH</td>
<td>1.9</td>
</tr>
<tr>
<td>pro</td>
<td>$\text{CH}_2$&lt;br&gt;$\text{CH}_2$ (cyclic)&lt;br&gt;$\text{CH}_2$</td>
<td>3.6</td>
</tr>
<tr>
<td>gly</td>
<td>$-\text{H}$</td>
<td>6.5</td>
</tr>
<tr>
<td>ala</td>
<td>$-\text{CH}_3$</td>
<td>4.8</td>
</tr>
<tr>
<td>cys</td>
<td>$-\text{CH}_2\text{SH}$</td>
<td>17.5</td>
</tr>
<tr>
<td>val</td>
<td>$-\text{CH}$(CH$_3$)$_2$</td>
<td>5.9</td>
</tr>
<tr>
<td>met</td>
<td>$-\text{CH}_2\text{CH}_2\text{SCH}_3$</td>
<td>0.5</td>
</tr>
<tr>
<td>ile</td>
<td>$-\text{CH}$(CH$_3$)CH$_2$CH$_3$</td>
<td>2.7</td>
</tr>
<tr>
<td>leu</td>
<td>$-\text{CH}_2\text{CH}$(CH$_3$)$_2$</td>
<td>6.1</td>
</tr>
<tr>
<td>gln</td>
<td>$-\text{CH}_2\text{CH}_2\text{CONH}_2$</td>
<td>6.0</td>
</tr>
<tr>
<td>phe</td>
<td>$\text{CH}_2$&lt;br&gt;</td>
<td>1.4</td>
</tr>
<tr>
<td>trp</td>
<td>$\text{CH}_2$&lt;br&gt;</td>
<td>3.7</td>
</tr>
<tr>
<td>lys</td>
<td>$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$</td>
<td>2.3</td>
</tr>
<tr>
<td>his</td>
<td>$\text{CH}_2$&lt;br&gt;</td>
<td>0.8</td>
</tr>
<tr>
<td>arg</td>
<td>$-\text{CH}_2\text{CH}_2\text{NH}$(NH$_2$)$=\text{NH}_2^+$</td>
<td>5.6</td>
</tr>
</tbody>
</table>
(a) Draw a diagram representing the secondary structure of keratins found in nails. In your diagram, show clearly the bonding that is involved in stabilising the secondary structure. You may represent the R groups using the symbol “R”.

(b) By referring to the amino acid composition data, answer the questions below:

(i) State the R group interaction that is mainly responsible for the stabilisation of the tertiary structure of keratins. Write an equation to support your answer.

Disulfide bonds

\[ \text{CH}_2\text{S-H + H-S-CH}_2^- + [O] \rightarrow \text{CH}_2\tilde{\text{S}}\text{S-CH}_2^- + \text{H}_2\tilde{\text{O}} \]

(ii) In order to straighten wavy hair permanently, using a heating iron is insufficient. Instead, one will need to go to the hairdresser to undergo a treatment of chemicals. Explain why.

Disulfide bonds are covalent and strong, hence not easily broken by heating. Treatment with chemicals is required.

(iii) Which sample belongs to keratins extracted from a nail sample? Explain.

Nails are less flexible implying that there are more disulfide bonds (i.e. cross linkages) formed between the R groups.

Hence the sample with greater amount of cys residues is probably keratins from nail.
There are four stereoisomers of compound P.

What is the type of stereoisomerism exhibited by P? Draw the stereoisomers of P.

Type of stereoisomerism: *cis-trans / geometric* ....................................................

![Stereoisomers of P](image)

[4]
(b) Q is a structural isomer of P in (a).
Suggest the structures of Q, R, S, T and U in the reaction scheme below.

Q \((\text{C}_{11}\text{H}_{12}\text{O}_{2})\)

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CO}_2\text{H} & \quad \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \\
R \,(\text{C}_3\text{H}_6\text{O}_2) & + \\
\text{aqueous HCl} & \quad \text{aqueous bromine} \\
\text{heat} & \quad \text{heat} \\
\text{S} & \quad \text{U} \,(\text{C}_8\text{H}_7\text{OBr}_3) \\
\end{align*}
\]

H\text{2} \text{Ni catalyst}
When methylbenzene is nitrated by a mixture of concentrated nitric acid and concentrated sulfuric acid, the product consists largely of two isomers, V and W, of formula C₇H₇NO₂. V has a plane of symmetry perpendicular to the plane of the benzene ring in its molecule, while W does not. The formation of V proceeds via an organic intermediate X.

(a) Draw the displayed formulae of V and X, showing clearly the geometry of the bonds around the carbon atom bonded to the nitrogen atom.

<table>
<thead>
<tr>
<th>isomer V</th>
<th>organic intermediate X</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Formula V" /></td>
<td><img src="image" alt="Formula X" /></td>
</tr>
</tbody>
</table>

(b) What is the name of the mechanism of the reaction for the formation of V? Briefly outline the mechanism of this reaction using equations.

Name of mechanism: **Electrophilic substitution**

Mechanism:

\[
\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-
\]

![Mechanism Diagram](image)
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.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [   ] at the end of each question or part question.
1 Aldehydes and ketones react with primary amines in slightly acidic solution to form imines which have the C=N functional group. For example, propanal reacts with methylamine to give N-methyl-1-propanimine.

\[
\begin{align*}
  \text{propanal} & \quad \xrightarrow{\text{CH}_3\text{NH}_2, \text{H}^+} \quad \text{CH}_3\text{CH}_2\text{C}=\text{N}\text{CH}_3 \quad \text{N-methyl-1-propanimine}
\end{align*}
\]

(a) Aldehydes and ketones also react with 2,4-dinitrophenylhydrazine (2,4-DNPH) to give compounds that are closely related to imines.

(i) Write a balanced equation for the reaction between benzaldehyde and 2,4-DNPH.

(ii) State what you would observe in the reaction with 2,4-DNPH. What is the type of reaction?

(b) The mechanism for the reaction between benzaldehyde and methylamine is shown below.
(i) What is the type of reaction in step I?

(ii) The positive charge on the iminium ion, G⁺, does not reside on a carbon atom. Suggest the structure of G⁺.

(iii) Write equations for step I and step IV to show the movement of electrons, using curved arrow notation. Show the lone pairs of electrons, if any, that are involved in each step.

(iv) The maximum rate of formation of imines occurs at a pH of about 4.5. Explain why the rate is slow under very acidic conditions and under alkaline conditions.

(c) Acrylamide is a carcinogen. It is formed when potato chips are heated to above 120 °C. Its formation has been linked to the presence of glucose (C₆H₁₂O₆) and an α-amino acid L found in relatively high amounts in potato.

Glucose reacts with L to form an imine M. At high cooking temperatures, M decomposes to produce only three compounds in equimolar amounts: acrylamide, carbon dioxide and compound N (C₆H₁₃NO₅).

(i) Name the functional groups in acrylamide.

(ii) Deduce the structure of L. Show clearly how you obtained your answer.

(d) Suggest the reagents and conditions required to synthesise the following imine derivative. Identify all the intermediate compounds.
2 (a) A container holds a gaseous mixture of nitrogen and propane. The pressure in the container at 200 °C is 4.5 atm. At −40 °C, the propane completely condenses and the pressure drops to 1.5 atm. Calculate the mole fraction of propane in the original gaseous mixture. [3]

(b) The graph below shows the variation in electromotive force (e.m.f.) of the following electrochemical cell with lg [Ag⁺(aq)] at 298 K.

\[
\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq}) \parallel \text{Ag}^{+}(\text{aq}) \parallel \text{Ag(s)}
\]

(i) Using the information from the graph, calculate the standard electrode potential of the half-cell, Ag⁺(aq) | Ag(s), at 298 K.

(ii) If the Ag⁺(aq) solution of the electrochemical cell is replaced by a saturated solution of silver bromate(V), AgBrO₃, in 0.1 mol dm⁻³ potassium bromate(V) and the e.m.f. of the cell measured at 298 K is +0.27 V, determine

(I) the concentration of Ag⁺(aq) ions in the saturated solution, and
(II) the solubility product of silver bromate(V) at 298 K. [5]
(c) Solid silver nitrate was slowly dissolved in a solution containing ethanedioate, \( \text{C}_2\text{O}_4^{2-} \), and chromate(VI), \( \text{CrO}_4^{2-} \), ions of concentrations 2.50 \( \times 10^{-2} \) mol dm\(^{-3} \) and 1.44 \( \times 10^{-5} \) mol dm\(^{-3} \) respectively.

(i) When a permanent precipitate of silver ethanedioate first appeared, the concentration of silver ions in the solution was 2.10 \( \times 10^{-5} \) mol dm\(^{-3} \). Calculate the solubility product of silver ethanedioate.

(ii) The dissolving of solid silver nitrate in was continued until a permanent red precipitate of silver chromate(VI) first appeared. Calculate the concentrations of silver ions and ethanedioate ions at that instant. (\( K_{sp} \) of silver chromate(VI) is 1.2 \( \times 10^{-12} \) mol\(^3\) dm\(^{-9} \).)

(iii) What is the amount of silver ethanedioate precipitated from 1.00 dm\(^3\) of the solution? [7]

(d) An electrochemical cell containing an oxygen cathode and a hydrogen anode is shown below. The pistons above the gas chambers are frictionless.

(i) Write balanced equations for the half reactions and for the overall reaction in the cell.

(ii) How does the concentration of sulfuric acid affect the equilibria of the half reactions?

(iii) If weights are added to the pistons of both chambers, how would the reading of the voltmeter change? Explain your answer. [5]

[Total: 20]
3 (a) (i) Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4 and K_2Cr_2O_7. Suggest a reason why these reagents do not attack an alkane such as CH_4.

(ii) It is found by experiment that, during free-radical substitution of alkane, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

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<th>type of hydrogen atom</th>
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<td>primary</td>
<td>RCH_3 → RCH_2Cl</td>
<td>1</td>
</tr>
<tr>
<td>secondary</td>
<td>R_2CH_2 → R_2CHCl</td>
<td>7</td>
</tr>
<tr>
<td>tertiary</td>
<td>R_3CH → R_3CCl</td>
<td>21</td>
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</table>

Using this information, and considering the number and type of hydrogen atoms within the molecule, predict the relative ratio of the two possible products J and K from the monochlorination of 2-methylpropane. Explain your answer.

(b) Compounds A and B are amines with the same molecular formula. Both have a molecular mass of 73.0 and the following composition by mass: C, 65.8 % and H, 15.1 %.

Compound A has a pK_b of 3.23 and contains a tri-substituted N atom.

The pH of an aqueous solution of 0.0100 mol dm^{-3} of compound B is 11.5. When B undergoes free-radical substitution reaction, it only gives one mono-substituted organic product.

(i) Calculate the molecular formulae of compounds A and B.

(ii) Calculate the pK_b of compound B.

(iii) Suggest the structural formulae of compounds A and B.

(iv) State and explain the relative basicity of compounds A and B.
(c) (i) The hydrolysis of 2-bromo-2-methylpropane takes place as follows.

\[(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+ + \text{Br}^-\]

An experiment was conducted to determine the order of reaction with respect to 2-bromo-2-methylpropane. The following results were obtained.

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It was found that the order of reaction with respect to 2-bromo-2-methylpropane is one and the half-life of the reaction is 34.5 s.

Using a non-graphical method, show that the concentration of 2-bromo-2-methylpropane at the start of the experiment is 0.0096 mol dm⁻³.

(ii) Hence, deduce how long the reaction has proceeded when concentration of (CH₃)₃COH obtained is 0.0084 mol dm⁻³.

(iii) The following two mechanisms are both consistent with the reaction being overall first order.

mechanism X: \[(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+ + \text{Br}^-\]

mechanism Y: \[(\text{CH}_3)_3\text{CBr} \rightleftharpoons (\text{CH}_3)_3\text{C}^+ + \text{Br}^-\] slow
\[(\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+\] fast

Explain why both mechanisms X and Y show overall first order kinetics.

(iv) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane increases when the temperature is increased. Explain this observation with the aid of a suitable diagram.

(v) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane is R at T °C. What is the new rate if temperature is increased to (T+50) °C?

Explain your answer.

[10]

[Total: 20]
4 This question is about thermal decomposition reactions of Group II compounds.

(a) A student investigates the thermal decomposition of some Group II nitrates. He separately heats equal amounts of the nitrates of magnesium, calcium and barium for one minute, passes the gases produced through aqueous sodium hydroxide and measures the volume of the remaining gas. The following table shows the results:

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<th>Element of nitrate</th>
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<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of remaining gas / cm$^3$</td>
<td>90</td>
<td>19</td>
<td>9</td>
</tr>
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</table>

(i) Explain the purpose of sodium hydroxide and identify the remaining gas.

(ii) Draw an appropriate experimental set-up that allows the student to perform the experiment and measure the volume of the remaining gas.

(iii) Using suitable data from the Data Booklet, explain the results obtained by the student.

(iv) Hence, estimate the volume of remaining gas produced after 1 min if the student were to heat zinc nitrate.

(v) The student heats a 10.0 g mixture of magnesium nitrate and calcium nitrate till no further changes. The volume of remaining gas produced was 780 cm$^3$ at room temperature. Calculate the mass of magnesium nitrate present.

(b) The decomposition of calcium carbonate is as follows.

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

In order to determine the enthalpy change of decomposition, two pieces of calcium carbonate were selected, each with a mass of 1.25 g. The first piece was placed in 20 cm$^3$ of excess dilute hydrochloric acid and the temperature rose by 2 °C. The second piece was heated strongly for ten minutes to decompose it thoroughly. It was then allowed to cool to room temperature before it was added to 20 cm$^3$ of dilute hydrochloric acid. The temperature rose by 26 °C. The two experiments were estimated to be 90% efficient.

(i) By using the information above and drawing a suitable energy cycle, calculate the enthalpy change of decomposition of calcium carbonate, in kJ mol$^{-1}$, to 3 significant figures.

When calcium carbonate is heated in a sealed tube at its thermal decomposition temperature, the reaction eventually reaches an equilibrium.

(ii) Given that $\Delta S = +161$ J mol$^{-1}$ K$^{-1}$ and your answer in part (i), calculate the thermal decomposition temperature, in K.

(iii) Hence sketch the graph of $\Delta G$ against $T$, labelling clearly the thermal decomposition temperature.
Iron is the sixth most abundant element in the Universe and the most common refractory element.

(a) Iron(III) oxide has a high melting point and is a good conductor of electricity when molten. Explain, in terms of its bonding and structure, why iron(III) oxide has these properties. [3]

(b) Samples of iron(III) oxide and iron(III) chloride are added, with stirring, to separate beakers of pure water. Suggest the pH value of the resulting solution in each beaker after stirring, giving a reason for your choice. Write equations for any reactions occurring. [4]

(c) Give the ion-electron equations for the electrode reactions in the electrolysis of aqueous iron(III) chloride using inert electrodes. [2]

(d) When water reacts with iron(III) ions, it acts as a ligand in the formation of the complex ion, \([\text{Fe(H}_2\text{O)}_6]^3+\) to give a coloured solution.

(i) Explain what is meant by the term ligand.

(ii) Explain why solutions containing iron(III) ions are coloured but those containing zinc ions are colourless. [5]

(e) A solution contains a mixture of iron(III) and zinc ions. You are provided with NaOH(aq) and HNO\(_3\)(aq). You are to propose a series of test-tube experiments to separate the two cations so that each cation is present as its aqueous ions.

(i) Give a description of your proposed sequence of steps to separate the two cations, numbering each step.

(ii) With the aid of appropriate equations, explain the reactions involved. [6]

[Total: 20]
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.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.
1 Aldehydes and ketones react with primary amines in slightly acidic solution to form imines which have the C=N functional group. For example, propanal reacts with methylamine to give N-methyl-1-propanimine.

\[
\text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{NH}_2 \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{C}==\text{N} \text{CH}_3
\]

\[\text{propanal} \quad \text{N-methyl-1-propanimine}\]

(a) Aldehydes and ketones also react with 2,4-dinitrophenylhydrazine (2,4-DNPH) to give compounds that are closely related to imines.

(i) Write a balanced equation for the reaction between benzaldehyde and 2,4-DNPH.

\[
\text{C}==\text{O} \quad + \quad \text{H}_2\text{N}==\text{N}==\text{NO}_2 \quad \rightarrow \quad \text{C}==\text{N}==\text{N}==\text{NO}_2
\]

\[\text{benzaldehyde} \quad \text{2,4-DNPH} \quad \text{2,4-dinitrophenylhydrazone}\]

(ii) State what you would observe in the reaction with 2,4-DNPH. What is the type of reaction?

orange precipitate condensation
(b) The mechanism for the reaction between benzaldehyde and methylamine is shown below.

\[ \text{Benzaldehyde} + \text{CH}_3\text{NH}_2 \rightarrow \text{Carbinolamine} \]

(i) What is the type of reaction in step I?  
**nucleophilic addition**

(ii) The positive charge on the iminium ion, \( G^+ \), does **not** reside on a carbon atom. Suggest the structure of \( G^+ \).

\[ \text{G imine} \xrightarrow{\text{step V}} \text{G}^+ \xleftarrow{\text{step IV}} \text{-iminium ion} \xrightarrow{\text{step III}} \text{Carbinolamine} \]

\[ \text{G}^+ \]

\[ \text{Benzaldehyde} + \text{CH}_3\text{NH}_2 \rightarrow \text{Imine} \]

\[ \text{Imine} \rightarrow \text{G}^+ \]

\[ \text{G}^+ \rightarrow \text{Carbinolamine} \]

\[ \text{Imine} \]
(iii) Write equations for step I and step IV to show the movement of electrons, using curved arrow notation. Show the lone pairs of electrons, if any, that are involved in each step.

\[
\text{amine} + \text{H}^+ \rightarrow \text{amine protonae} \\
\text{alkaline} \rightarrow \text{very low } \text{H}^+ \text{ conc; no catalyst (Step III)}
\]

(iv) The maximum rate of formation of imines occurs at a pH of about 4.5. Explain why the rate is slow under very acidic conditions and under alkaline conditions.

- acidic: amine protonated; no nucleophile (Step I)
- alkaline: very low H\(^+\) conc; no catalyst (Step III)

(c) Acrylamide is a carcinogen. It is formed when potato chips are heated to above 120 °C. Its formation has been linked to the presence of glucose (C\(_6\)H\(_{12}\)O\(_6\)) and an \(\alpha\)-amino acid L found in relatively high amounts in potato.

Glucose reacts with L to form an imine M. At high cooking temperatures, M decomposes to produce only three compounds in equimolar amounts: acrylamide, carbon dioxide and compound N (C\(_{6}\)H\(_{13}\)NO\(_5\)).

(i) Name the functional groups in acrylamide.

- alkene, amide
(ii) Deduce the structure of L. Show clearly how you obtained your answer.

\[ L : \text{H}_2\text{N} - \text{C} - \text{CO}_2\text{H} \ (\text{asparagine}). \]

Accept other possible alternatives.

(d) Suggest the reagents and conditions required to synthesise the following imine derivative. Identify all the intermediate compounds.

\[ \text{O} \]

\[ \text{OH} \] heat

\[ \text{Br} \] heat in sealed tube

\[ \text{H}^+ \] [Total: 20]
2 (a) A container holds a gaseous mixture of nitrogen and propane. The pressure in
the container at 200 °C is 4.5 atm. At −40 °C, the propane completely
condenses and the pressure drops to 1.5 atm. Calculate the mole fraction of
propane in the original gaseous mixture.

Let the amount of nitrogen and propane be \( n_1 \) and \( n_2 \) respectively. Since the
gas constant, \( R \), and volume of container, \( V \), are constants, the gas equation
becomes:

\[
P = \frac{nR}{T} = kn \text{ where } k = \frac{R}{V}
\]

\[
\therefore \frac{4.5}{473} = k (n_1 + n_2) = 9.513 \times 10^{-3}
\]

and \[
\frac{1.5}{233} = kn_1 = 6.437 \times 10^{-3}
\]

\[
\therefore kn_2 = 9.513 \times 10^{-3} - 6.437 \times 10^{-3} = 3.076 \times 10^{-3}
\]

mole fraction of propane \( = \frac{3.076 \times 10^{-3}}{9.513 \times 10^{-3}} = 0.323 \)

(b) The graph below shows the variation in electromotive force (e.m.f.) of the
following electrochemical cell with \( \text{lg} [\text{Ag}^+ (aq)] \) at 298 K.

\[
\text{Cu(s)} | \text{Cu}^{2+} (aq) \parallel \text{Ag}^+ (aq) | \text{Ag(s)}
\]

(i) Using the information from the graph, calculate the standard electrode
potential of the half-cell, \( \text{Ag}^+ (aq) | \text{Ag(s)} \), at 298 K.
Let the standard electrode potential of Ag\(^+\)(aq) | Ag(s) half-cell be \(x\).
When \([\text{Ag}^+(aq)] = 1.00 \text{ mol dm}^{-3}\), \(\lg [\text{Ag}^+(aq)] = 0\)
\(E^e_{\text{cell}} = +0.46 = x - (+0.34)\)
\(x = +0.46 + (+0.34) = +0.80\) V

(ii) If the \(\text{Ag}^+(aq)\) solution of the electrochemical cell is replaced by a saturated solution of silver bromate(V), AgBrO\(_3\), in 0.1 mol dm\(^{-3}\) potassium bromate(V) and the e.m.f. of the cell measured at 298 K is +0.27 V, determine

(I) the concentration of \(\text{Ag}^+(aq)\) ions in the saturated solution, and

From the graph, when e.m.f. of cell is +0.27 V, \(\lg [\text{Ag}^+(aq)] = -3.2\).
\([\text{Ag}^+(aq)] = 6.309 \times 10^{-4} \text{ mol dm}^{-3}\)

(II) the solubility product of silver bromate(V) at 298 K.
\(K_{sp} = 6.309 \times 10^{-4} \times 0.1 = 6.309 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}\)

(c) Solid silver nitrate was slowly dissolved in a solution \(Q\) containing ethanedioate, \(\text{C}_2\text{O}_4^{2-}\), and chromate(VI), \(\text{CrO}_4^{2-}\), ions of concentrations 2.50 \times 10\(^{-2}\) mol dm\(^{-3}\) and 1.44 \times 10\(^{-5}\) mol dm\(^{-3}\) respectively.

(i) When a permanent precipitate of silver ethanedioate first appeared, the concentration of silver ions in the solution was 2.10 \times 10\(^{-5}\) mol dm\(^{-3}\). Calculate the solubility product of silver ethanedioate.

\[K_{sp}(\text{Ag}_2\text{C}_2\text{O}_4) = (2.10 \times 10^{-5})^2 \times 2.50 \times 10^{-2} = 1.10 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}\]

(ii) The dissolving of solid silver nitrate in \(Q\) was continued until a permanent red precipitate of silver chromate(VI) first appeared. Calculate the concentrations of silver ions and ethanedioate ions at that instant. \((K_{sp} \text{ of silver chromate(VI) is } 1.2 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}).\)

Given: \(K_{sp}(\text{Ag}_2\text{CrO}_4) \text{ is } 1.2 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}\).
\(1.2 \times 10^{-12} = [\text{Ag}^+]^2 \times 1.44 \times 10^{-5}\)
\([\text{Ag}^+]^2 = 8.333 \times 10^{-8}\)
\([\text{Ag}^+] = 2.89 \times 10^{-4} \text{ mol dm}^{-3}\)
\(1.102 \times 10^{-11} = (2.886 \times 10^{-8})^2 \times [\text{C}_2\text{O}_4^{2-}]\)
\([\text{C}_2\text{O}_4^{2-}] = 1.32 \times 10^{-4} \text{ mol dm}^{-3}\)

(iii) What is the amount of silver ethanedioate precipitated from 1.00 dm\(^3\) of the solution?
\[ n(\text{C}_2\text{O}_4^{2-}) \text{ removed from solution} = 2.50 \times 10^{-2} - 1.322 \times 10^{-4} \]
\[ = 0.02486 \text{ mol} \]
\[ \therefore \text{ amount of silver ethanedioate ppted} = 0.0249 \text{ mol}. \]

(d) An electrochemical cell containing an oxygen cathode and a hydrogen anode is shown below. The pistons above the gas chambers are frictionless.

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad \text{(anode)} \]
\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad \text{(cathode)} \]

(i) Write balanced equations for the half reactions and for the overall reaction in the cell.

(ii) How does the concentration of sulfuric acid affect the equilibria of the half reactions?

\[ 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2 \quad 0.00\text{V} \quad \text{(anode)} \]
\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad +1.23\text{V} \quad \text{(cathode)} \]

Increase in concentration of sulfuric acid will increase [H\(^+\)] and by Le Chatelier’s Principle, cause the position of equilibrium of anode and cathode reactions to shift right.
(iii) If weights are added to the pistons of both chambers, how would the reading of the voltmeter change? Explain your answer.

If weights are added, the pressure will increase, resulting in position of equilibrium of anode reaction shifting left to remove excess pressure on hydrogen gas. The electrode potential will decrease to less than zero volt. The position of equilibrium of the cathode reaction will shift right, resulting in a more positive electrode potential for the cathode. As a result, the reading on the voltmeter will be greater than 1.23 V.

[5]

[Total: 20]
3  (a)  (i)  Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H$_2$SO$_4$ and K$_2$Cr$_2$O$_7$.

Suggest a reason why these reagents do not attack an alkane such as CH$_4$.

Alkanes are non-polar or have no dipole or C–H bonds are strong or C and H have similar electronegativities.

(ii)  It is found by experiment that, during free-radical substitution of alkane, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

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<td>R$_3$CH → R$_3$CCl</td>
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Using this information, and considering the number and type of hydrogen atoms within the molecule, predict the relative ratio of the two possible products J and K from the monochlorination of 2-methylpropane. Explain your answer.

J:K = 2.3 : 1 or 7:3 or 21:9
reason: straightforward relative rate suggests 21:1, but there are 9 primary to 1 tertiary, so divide this ratio by 9. 21/9 = 2.33

[3]

(b)  Compounds A and B are amines with the same molecular formula. Both have a molecular mass of 73.0 and the following composition by mass: C, 65.8 % and H, 15.1 %.

Compound A has a $pK_b$ of 3.23 and contains a tri-substituted N atom.

The pH of an aqueous solution of 0.0100 mol dm$^{-3}$ of compound B is 11.5. When B undergoes free-radical substitution reaction, it only gives one mono-substituted organic product.

(i)  Calculate the molecular formulae of compounds A and B.

C:H:N ratio: 65.8/12 : 15.1/1 : 19.1/14 = 4 : 11 : 1

Empirical Formula: C$_4$H$_{11}$N

Let the molecular formula be C$_{4n}$H$_{11n}$N$_n$

$4n$(12.0) + $11n$(1.0) + $n$(14.0) = 73.0

$n$ = 1

Hence molecular formula is C$_4$H$_{11}$N
(ii) Calculate the $pK_b$ of compound B.

\[
10^{-(14-11.5)} = (0.0100 \times K_b)^{1/2}
\]

\[
K_b = 1 \times 10^{-3} \text{ mol} \text{ dm}^{-3}
\]

\[
pK_b = -\log(1 \times 10^{-3}) = 3
\]

(iii) Suggest the structural formulae of compounds A and B.

A: \[\text{H}_3\text{C}\overset{\text{N}}{\text{C}}\text{H}_3\text{CH}_2\text{C}_3\text{CH}_3\]  
B: \[\text{H}_3\text{C}\overset{\text{C}}{\text{C}}\overset{\text{NH}_2}{\text{C}}\text{CH}_3\]

(iv) State and explain the relative basicity of compounds A and B.

\[
pK_b (\text{A}) = 3.23 \quad pK_b (\text{B}) = 3
\]

B (1° amine) is more basic than A (3° amine).

Although A has 3 electron-donating alkyl groups bonded to the N atom while B has only one electron-donating group, the presence of 3 bulky substituents in A hinder the approach of $\text{H}^+$ to form dative bond with the lone pair of electrons on N.

(c) (i) The hydrolysis of 2-bromo-2-methylpropane takes place as follows.

\[
(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+ + \text{Br}^-
\]

An experiment was conducted to determine the order of reaction with respect to 2-bromo-2-methylpropane. The following results were obtained.

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It was found that the order of reaction with respect to 2-bromo-2-methylpropane is one and the half-life of the reaction is 34.5 s.

Using a non-graphical method, show that the concentration of 2-bromo-2-methylpropane at the start of the experiment is 0.0096 mol dm$^{-3}$.

The first $t_{1/2}$ corresponds to the time taken for half the final [(CH$_3$)$_3$COH] to be formed while the sum of two $t_{1/2}$ corresponds to the time taken for $\frac{3}{4}$ of the final [(CH$_3$)$_3$COH] to be formed.

The [(CH$_3$)$_3$COH] at time = 34.5 s is not given in the table but the [(CH$_3$)$_3$COH] at time = 2 x 34.5 = 69 s is given.

Hence, $\frac{3}{4}$ x final [(CH$_3$)$_3$COH] = 0.0072 mol dm$^{-3}$,

\[
\therefore \text{final } [(\text{CH}_3)_3\text{COH}] = \frac{4}{3} \times 0.0072 = 0.0096 \text{ mol} \text{ dm}^{-3}
\]
Since the mole ratio of $(\text{CH}_3)_3\text{CBr} : (\text{CH}_3)_3\text{COH} = 1:1$ and assuming that the total volume of the reaction mixture remains constant, $[(\text{CH}_3)_3\text{CBr}]$ at the start of the experiment = final $[(\text{CH}_3)_3\text{COH}]$ = 0.0096 mol dm$^{-3}$

(ii) Hence, deduce how long the reaction has proceeded when concentration of $(\text{CH}_3)_3\text{COH}$ obtained is 0.0084 mol dm$^{-3}$.

$0.0084 = \frac{7}{8} \times 0.0096$

Hence, three half-lives have passed by.

Reaction has proceed for $3 \times 34.5 = 103.5$ s.

(iii) The following two mechanisms are both consistent with the reaction being overall first order.

mechanism X $(\text{CH}_3)_3\text{CBr} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+ + \text{Br}^-$

mechanism Y $(\text{CH}_3)_3\text{CBr} \rightleftharpoons (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$ \hspace{1cm} \text{slow}
$(\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+$ \hspace{1cm} \text{fast}

Explain why both mechanisms X and Y show overall first order kinetics.

$\text{H}_2\text{O}$ is usually present in excess, hence its concentration is kept relatively constant. Since the given equation in mechanism 1 shows 1 molecule of $(\text{CH}_3)_3\text{CBr}$ participating in the reaction, the reaction is overall first order kinetics.

In mechanism 2, the slow step involves 1 molecule of $(\text{CH}_3)_3\text{CBr}$. Hence the rate equation is rate $= k[(\text{CH}_3)_3\text{Br}]$ which shows that the reaction is overall first order kinetics.
(iv) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane increases when the temperature is increased. Explain this observation with the aid of a suitable diagram.

(v) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane is R at T °C. What is the new rate if temperature is increased to (T+50) °C? Explain your answer.

Rate doubled when temperature increased by 10°C. Since temperature increased by 20°C, rate increased by $2^5$ times. Hence the new rate is 32R.

[10]

[Total: 20]
4 This question is about thermal decomposition reactions of Group II compounds.

(a) A student investigates the thermal decomposition of some Group II nitrates. He separately heats equal amounts of the nitrates of magnesium, calcium and barium for one minute, passes the gases produced through aqueous sodium hydroxide and measures the volume of the remaining gas. The following table shows the results:

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<td>Volume of remaining gas / cm$^3$</td>
<td>90</td>
<td>19</td>
<td>9</td>
</tr>
</tbody>
</table>

(i) Explain the purpose of sodium hydroxide and identify the remaining gas.

NaOH: absorb NO$_2$. O$_2$ is remaining gas.

(ii) Draw an appropriate experimental set-up that allows the student to perform the experiment and measure the volume of the remaining gas.

Sealed boiling tube and Bunsen burner, connected to U-tube containing NaOH, connected to gas syringe.

(iii) Using suitable data from the Data Booklet, explain the results obtained by the student.

- Ionic radii: Mg$^{2+}$(0.065 nm), Ca$^{2+}$(0.099 nm), Ba$^{2+}$(0.135 nm)
- Down the group, as ionic radii increases, charge density of the cation decreases, hence polarizes the nitrate anion to a lesser extent.
- Nitrate becomes more thermally stable and produces lesser gas after 1 min.

(iv) Hence, estimate the volume of remaining gas produced after 1 min if the student were to heat zinc nitrate.

- Ionic radii of Zn$^{2+}$ is 0.074 nm, in between that of Mg$^{2+}$ and Ca$^{2+}$.
- Hence, volume of gas produced is approximately 60 cm$^3$.

(v) The student heats a 10.0 g mixture of magnesium nitrate and calcium nitrate till no further changes. The volume of remaining gas produced was 780 cm$^3$ at room temperature. Calculate the mass of magnesium nitrate present.

Let mass of magnesium nitrate be $x$.

\[
\text{Mg(NO}_3\text{)}_2 \rightarrow \text{MgO + 2NO}_2 + \frac{1}{2} \text{O}_2
\]

\[
\text{Ca(NO}_3\text{)}_2 \rightarrow \text{CaO + 2NO}_2 + \frac{1}{2} \text{O}_2
\]

\[
n(\text{Mg(NO}_3\text{)}_2) = \frac{x}{148.3}
\]

\[
n(\text{O}_2) \text{ produced by Mg(NO}_3\text{)}_2 = \frac{x}{296.6}
\]

\[
V(\text{O}_2) = 24000x / 296.6
\]

\[
n(\text{Ca(NO}_3\text{)}_2) = \frac{(10.0 - x)}{164.1}
\]

\[
n(\text{O}_2) \text{ produced by Ca(NO}_3\text{)}_2 = \frac{(10.0 - x)}{328.2}
\]

\[
m(\text{Mg(NO}_3\text{)}_2) = 24000(10.0 - x) / 328.2
\]

Total volume = \[24000x / 296.6\] + \[24000(10.0 - x) / 328.2\] = 780

\[
328.2x + 296.6(10.0 - x) = 0.0325(296.6)(328.2)
\]

\[
x = 6.26 \text{ g}
\]
(b) The decomposition of calcium carbonate is as follows.

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \]

In order to determine the enthalpy change of decomposition, two pieces of calcium carbonate were selected, each with a mass of 1.25 g. The first piece was placed in 20 cm³ of excess dilute hydrochloric acid and the temperature rose by 2 °C. The second piece was heated strongly for ten minutes to decompose it thoroughly. It was then allowed to cool to room temperature before it was added to 20 cm³ of dilute hydrochloric acid. The temperature rose by 26 °C. The two experiments were estimated to be 90% efficient.

(i) By using the information above and drawing a suitable energy cycle, calculate the enthalpy change of decomposition of calcium carbonate, in kJ mol⁻¹, to 3 significant figures.

\[
\begin{align*}
\text{CaCO}_3 + 2\text{HCl} & \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H_1 \\
\Delta H_1 &= -\left[\frac{(20 \times 4.18 \times 2)}{0.9}\right] / (1.25 / 100.1) = -14.9 \text{ kJ mol}^{-1} \\
\text{CaO} + 2\text{HCl} & \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \quad \Delta H_2 \\
\Delta H_2 &= -\left[\frac{(20 \times 4.18 \times 26)}{0.9}\right] / (1.25 / 100.1) = -193.4 \text{ kJ mol}^{-1} \\
\Delta H &= \Delta H_2 - \Delta H_1 = 193.4 - 14.9 = 179 \text{ kJ mol}^{-1}
\end{align*}
\]

When calcium carbonate is heated in a sealed tube at its thermal decomposition temperature, the reaction eventually reaches an equilibrium.

(ii) Given that \( \Delta S = +161 \text{ J mol}^{-1} \text{ K}^{-1} \) and your answer in part (i), calculate the thermal decomposition temperature, in K.

\[
\Delta G = 0 = 179 - T(161/1000) \\
T = 1112 \text{ K}
\]

(iii) Hence sketch the graph of \( \Delta G \) against \( T \), labelling clearly the thermal decomposition temperature.
Iron is the sixth most abundant element in the Universe and the most common refractory element.

(a) Iron(III) oxide has a high melting point and is a good conductor of electricity when molten. Explain, in terms of its bonding and structure, why iron(III) oxide has these properties.

Fe₂O₃ has giant ionic structure with strong ionic bonds between oppositely charged ions.
Large amount of energy required to overcome the strong ionic bonds hence it has a high melting point.
In molten state, there are free mobile ions to carry charges hence it can conduct electricity.

(b) Samples of iron(III) oxide and iron(III) chloride are added, with stirring, to separate beakers of pure water. Suggest the pH value of the resulting solution in each beaker after stirring, giving a reason for your choice. Write equations for any reactions occurring.

pH 7 (Fe₂O₃). pH 3 (FeCl₃)
Fe₂O₃ is insoluble in water due to the very exothermic lattice energy.
FeCl₃ undergoes hydrolysis due to the high charge density of Fe³⁺.
FeCl₃ + 6H₂O → Fe(H₂O)₆³⁺ + 3Cl⁻
Fe(H₂O)₆³⁺ + H₂O ⇌ Fe(H₂O)₅(OH)²⁺ + H₃O⁺

(c) Give the ion-electron equations for the electrode reactions in the electrolysis of aqueous iron(III) chloride using inert electrodes.

Cathode: Fe³⁺ + e⁻ → Fe²⁺
Anode: 2H₂O → O₂ + 4H⁺ + 4e

(d) When water reacts with iron(III) ions, it acts as a ligand in the formation of the complex ion, [Fe(H₂O)₆]³⁺ to give a coloured solution.

(i) Explain what is meant by the term ligand.

Ligand is a molecule or anion with at least one lone pair of electrons that it can use to form a coordinate bond to the central metal atom/ion in a complex ion.

(ii) Explain why solutions containing iron(III) ions are coloured but those containing zinc ions are colourless.

- In an octahedral iron(III) complex ion, the ligands cause a split in the energies of the 3d orbitals.
- The energy difference, Δₒ = ħν, corresponds to wavelengths in the visible spectrum.
- An electron is promoted from a d orbital of lower energy to one of higher energy by absorbing a photon with energy Δₒ.
- Unabsorbed wavelengths are transmitted.
• The colour of the complex is complementary to the colour absorbed.
• \( \text{Zn}^{2+} \) has completely filled \( d \) orbitals and no \( d-d \) transition can take place

(e) A solution contains a mixture of iron(III) and zinc ions. You are provided with NaOH(aq) and HNO\(_3\)(aq). You are to propose a series of test-tube experiments to separate the two cations so that each cation is present as its **aqueous** ions.

(i) Give a description of your proposed sequence of steps to separate the two cations, numbering each step.

1. To 2 cm depth of solution in a test tube, add NaOH(aq) dropwise till in excess.
2. Filter the mixture
3. Add excess HNO\(_3\) to the filtrate. \( (\text{Zn}^{2+}) \)
4. Add excess HNO\(_3\) to the residue. \( (\text{Fe}^{3+}) \)

(ii) With the aid of appropriate equations, explain the reactions involved.

Precipitation reaction:
\[
\text{Fe}^{3+}(aq) + 3\text{OH}^-(aq) \rightleftharpoons \text{Fe(OH)}_2(s) \quad (I)
\]
\[
\text{Zn}^{2+}(aq) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn(OH)}_2(s) \quad (I)
\]
Formation of soluble complex:
\[
\text{Excess NaOH(aq)}: \text{Zn(OH)}_2(s) + 2\text{OH}^-(aq) \rightleftharpoons \text{Zn(OH)}_4^{2-}(aq) \quad (II)
\]

\( H^+ \) added will react with \( \text{OH}^- \) present and cause \([\text{OH}^-]\) to decrease in equilibrium (I) POE will shift left to replace the removed \( \text{OH}^- \) hence \( \text{Fe}^{3+}(aq) \) and \( \text{Zn}^{2+}(aq) \) are formed.

[6]

[Total: 20]
READ THESE INSTRUCTIONS FIRST

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

There are forty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D.
Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
For each question, there are four possible answers labelled A, B, C and D. Choose the one you consider to be correct.

1. Acidified, aqueous potassium manganate(VII) oxidises ethanedioate ions, C$_2$O$_4^{2-}$, to CO$_2$.

\[ 2\text{MnO}_4^-(\text{aq}) + 5\text{C}_2\text{O}_4^{2-}(\text{aq}) + 16\text{H}^+(\text{aq}) \rightarrow 2\text{Mn}^{2+}(\text{aq}) + 10\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l}) \]

What is the concentration of potassium manganate(VII), in mol dm$^3$, if 20 cm$^3$ is required to completely oxidise $2.0 \times 10^{-3}$ mol of the salt KHC$_2$O$_4$.H$_2$C$_2$O$_4$?

A. \[
\frac{5}{2} \times \frac{1000}{20} \times 2.0 \times 10^{-3}
\]

B. \[
\frac{5}{2} \times \frac{1000}{20} \times 4.0 \times 10^{-3}
\]

C. \[
\frac{2}{5} \times \frac{1000}{20} \times 2.0 \times 10^{-3}
\]

D. \[
\frac{2}{5} \times \frac{1000}{20} \times 4.0 \times 10^{-3}
\]

2. The radioactive decay of polonium, $^{210}_{84}$Po, can be simply represented by the following equation.

$^{210}_{84}$Po $\rightarrow$ $^{206}_{82}$Pb + $\alpha$ + 2e$^-$

What would be the path taken by the alpha particle, $\alpha$, when it is passed through an electric field?
3 What are the values of angle $x$, $y$ and $z$ in a molecule of Disperse Yellow?

![Disperse Yellow](image)

<table>
<thead>
<tr>
<th></th>
<th>angle $x$</th>
<th>angle $y$</th>
<th>angle $z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>90</td>
<td>115</td>
<td>105</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>180</td>
<td>180</td>
</tr>
<tr>
<td>C</td>
<td>120</td>
<td>115</td>
<td>105</td>
</tr>
<tr>
<td>D</td>
<td>120</td>
<td>180</td>
<td>115</td>
</tr>
</tbody>
</table>

4 Which of the following pairs of graphs share the same general shape according to ideal gas law for a fixed mass of gas?

A $p$ against $V$ (at constant $T$) and $V/T$ against $T$ (at constant $p$)
B $pV$ against $V$ (at constant $T$) and $V/T$ against $T$ (at constant $p$)
C $p$ against $T$ (at constant $V$) and $pV$ against $p$ (at constant $T$)
D $V$ against $T$ (at constant $p$) and $pV$ against $p$ (at constant $T$)

5 Travellers to countries with cold climate may sometimes use heat packs to keep warm. One example is the sodium ethanoate heat pack. This consists of a supersaturated solution of sodium ethanoate and a small metal disc containing very small crystals of sodium ethanoate.

When the disc is broken, the small crystals of sodium ethanoate are released into the solution and act as nucleation sites to catalyse the crystallisation reaction of sodium ethanoate.

Which line gives the signs of $\Delta H$, $\Delta S$ and $\Delta G$ for the overall process?

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>C</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>
Barium reacts with water to form barium hydroxide and hydrogen.

\[
\text{Ba}(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ba(OH)}_2(aq) + \text{H}_2(g)
\]

The standard enthalpy change for this reaction can be measured in the laboratory.

What further information is needed to calculate the standard enthalpy change of formation of solid barium hydroxide?

I Standard enthalpy change of formation of water
II Standard enthalpy change of solution of barium hydroxide
III Standard enthalpy change of hydration of barium ion
IV Standard enthalpy change of hydration of hydroxide ion

A I only
B I and II
C III and IV
D I, II, III and IV

The distribution of the number of molecules with energy \( E \) is given in the sketch for two temperatures, \( T_1 \) and a higher temperature \( T_2 \). The letters \( P, Q, R \) refer to the separate and differently shaded areas. The activation energy is marked on the energy axis.

Which expression gives the fraction of the molecules present which have at least the activation energy at the higher temperature \( T_2 \)?

A \( \frac{Q}{P} \)
B \( \frac{Q + R}{P} \)
C \( \frac{Q + R}{P + Q} \)
D \( \frac{Q + R}{P + Q + R} \)
Aspirin is an analgesic often used to relieve minor aches and pains. The chemical stability of aspirin is of great importance since it becomes less effective when exposed to high temperature and moisture.

A kinetic study on the reaction of aspirin and water was conducted.

\[
\text{aspirin} + \text{H}_2\text{O} \rightarrow \text{salicylic acid} + \text{acetic acid}
\]

The graph below shows the concentration of aspirin against time for this reaction.

What does the shape of the graph suggest about this reaction?

A. It is exothermic.
B. It is endothermic.
C. It shows first order kinetics.
D. It produces its own catalyst.
Use of the Data Booklet is relevant to this question.

A cell is set up by connecting a Cu\textsuperscript{2+}/Cu half-cell and an acidified Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2−}/Cr\textsuperscript{3+} half-cell under standard conditions.

Which of the following correctly describes the effect on the e.m.f of the cell when the corresponding change is made?

<table>
<thead>
<tr>
<th>Change</th>
<th>Effect on e.m.f of cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>replace copper with an alloy of copper and silver</td>
</tr>
<tr>
<td>B</td>
<td>addition of concentrated H\textsubscript{2}SO\textsubscript{4} into reduction half-cell</td>
</tr>
<tr>
<td>C</td>
<td>addition of dilute NaOH into oxidation half-cell</td>
</tr>
<tr>
<td>D</td>
<td>addition of water into oxidation half-cell</td>
</tr>
</tbody>
</table>

When a dilute sulfate solution of a metal J is electrolysed, the metal J and a diatomic gas K are produced at the cathode and the anode respectively in the molar ratio 2:1. In another experiment, the same quantity of electricity is used to electrolyse a saturated sodium chloride solution and a gas L is evolved at the anode.

What is the molar ratio of J:K:L?

<table>
<thead>
<tr>
<th>A</th>
<th>2:1:1</th>
<th>B</th>
<th>2:1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4:2:1</td>
<td>D</td>
<td>4:2:3</td>
</tr>
</tbody>
</table>
The following equation represents the conversion of $Y_2$ to $Y$.

$$Y_2(g) \rightleftharpoons 2Y(g)$$

The conversion was studied using a fixed amount of $Y_2$ in a reaction vessel. At different times during the experiment, changes were made to the conditions in the reaction vessel. The change in the concentrations in the equilibrium mixture with time is given by the graph below:

Which one of the following statements is correct?

A A catalyst was added at $T_1$.

B There was a decrease in volume of the reaction vessel at $T_2$.

C There was an increase in temperature at $T_2$.

D More $Y_2$ was introduced at $T_2$.

A pure sample of dinitrogen tetraoxide at an initial pressure of 1 atm is allowed to reach equilibrium in a vessel of constant volume and constant temperature.

$$N_2O_4 \rightleftharpoons 2NO_2$$

What is the equilibrium constant, $K_p$, for this reaction, given that the equilibrium pressure is 1.5 times greater than the initial pressure?

A 1 atm  
B 2 atm  
C 3 atm  
D 4 atm
13 The table below shows the values of the ionic product of water, $K_w$, at two different temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$K_w$ / mol$^2$ dm$^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$1.00 \times 10^{-14}$</td>
</tr>
<tr>
<td>62</td>
<td>$1.00 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Which of the following statements is correct for pure water?

A  The ionic dissociation of water is an exothermic process.
B  At 62 °C, pH = 14 − pOH.
C  At 62 °C, pH < pOH.
D  At 62 °C, it is neutral and pH < 7.

14 A sample of waste solution at pH 1 is found to contain 0.100 mol dm$^{-3}$ zinc sulfate and 0.100 mol dm$^{-3}$ lead(II) sulfate. Solid sodium hydroxide is slowly added until the pH is 5.

The solubility product of zinc hydroxide is $3.00 \times 10^{-17}$ mol$^3$ dm$^{-9}$ and that of lead(II) hydroxide is $1.42 \times 10^{-20}$ mol$^3$ dm$^{-9}$.

Which statement describes what happens in the solution?

A  No precipitate is formed.
B  Only lead(II) hydroxide is precipitated.
C  Only zinc hydroxide is precipitated.
D  Both zinc hydroxide and lead(II) hydroxide are precipitated.

15 $P$, $Q$ and $R$ are elements of the third period of the Periodic Table. The oxide of $P$ is amphoteric, the oxide of $Q$ is basic and oxide of $R$ is acidic.

What is the order of decreasing ionic radius?

A  $RQP$
B  $RPQ$
C  $QPR$
D  $PQR$
16. Which property of the Group II elements (magnesium to barium) and their compounds increases with increasing proton number?

A. The ease of thermal decomposition of the carbonate
B. The pH of the aqueous chloride
C. The solubility of hydroxide in water
D. The magnitude of the enthalpy change of hydration of the metal ion

17. The ash from burnt seaweed contains chlorides and iodides of some Group I and Group II elements. Some seaweed ash was treated with concentrated sulfuric acid and the resulting fumes passed first through a cold tube and then bubbled through aqueous silver nitrate.

What would be observed during the experiment?

<table>
<thead>
<tr>
<th>inside the cold tube</th>
<th>with aqueous silver nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>no deposit</td>
</tr>
<tr>
<td>B</td>
<td>no deposit</td>
</tr>
<tr>
<td>C</td>
<td>black deposit</td>
</tr>
<tr>
<td>D</td>
<td>black deposit</td>
</tr>
</tbody>
</table>

A. no deposit          white precipitate
B. no deposit          yellow precipitate
C. black deposit       white precipitate
D. black deposit       yellow precipitate
Nickel(II) ion forms a red complex with ligand L (shown below) at room temperature.

The graph below was obtained when the colour intensities of mixtures of a 4 x 10^{-3} mol dm^{-3} solution of L and a 3 x 10^{-3} mol dm^{-3} solution of nickel(II) chloride were measured using a colorimeter at room temperature.

Which one of the following statements regarding the ligand L or the nickel(II) complex is correct?

A L is a monodentate ligand.
B The nickel(II) complex is negatively charged.
C The nickel(II) complex absorbs red light strongly.
D The co-ordination number of nickel in the complex is 4.
19 What is the total number of possible isomers that can be formed when the following compound reacts with hot excess concentrated H$_2$SO$_4$?

![Chemical Structure](image)

A 2  B 4  C 6  D 8

20 How many esters with molecular formula C$_4$H$_8$O$_2$ react with hot, acidified potassium manganate(VII) to give carbon dioxide?

A 2  B 3  C 4  D 5

21 When excess BrCl is added to the methylbenzene in the presence of $uv$ light, which organic compound will be produced in the smallest proportion?

A  ![Chemical Structure](image)  B  ![Chemical Structure](image)  C  ![Chemical Structure](image)  D  ![Chemical Structure](image)
22 Which of the following statements regarding compound Z is **incorrect**?

![Compound Z](image)

A. There is only one sp hybridised carbon atom in a molecule of Z.
B. A molecule of Z contains four π bonds.
C. After Z reacts with LiA/H₂, all the carbon atoms in the product formed are sp³ hybridised.
D. After Z reacts with HCl(g), all but one carbon atom in the product formed are sp³ hybridised.

23 Compound V may be synthesised from benzene.

![Compound V](image)

Which of the following synthetic routes will yield compound V?

A. alkylation → nitration → oxidation → bromination → reduction
B. bromination → nitration → reduction → alkylation → oxidation
C. nitration → alkylation → reduction → bromination → oxidation
D. nitration → reduction → bromination → alkylation → oxidation
24 Putrescine is used in the production of Nylon-4,6. It can be synthesised from ethene by the following reactions.

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \xrightarrow{\text{I}} \text{Y} \xrightarrow{\text{II}} \text{NCCH}_2\text{CH}_2\text{CN} \xrightarrow{\text{III}} \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \\
& \text{Putrescine}
\end{align*}
\]

Which of the following gives the correct reagents and conditions for steps I to III?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Br\textsubscript{2}</td>
<td>KCN in ethanol, heat</td>
<td>H\textsubscript{2}, Ni, 200 °C</td>
</tr>
<tr>
<td>B</td>
<td>Br\textsubscript{2}</td>
<td>HCN, trace NaCN, 15 °C</td>
<td>LiA/H\textsubscript{4}, dry ether</td>
</tr>
<tr>
<td>C</td>
<td>cold, alkaline KMnO\textsubscript{4}</td>
<td>KCN in ethanol, heat</td>
<td>LiA/H\textsubscript{4}, dry ether</td>
</tr>
<tr>
<td>D</td>
<td>cold, alkaline KMnO\textsubscript{4}</td>
<td>HCN, trace NaCN, 15 °C</td>
<td>H\textsubscript{2}, Ni, 200 °C</td>
</tr>
</tbody>
</table>

25 Which of the following compounds would not give sodium ethanoate when treated with hot, aqueous sodium hydroxide?

A CH\textsubscript{3}CONHCH\textsubscript{3}  
B C\textsubscript{6}H\textsubscript{5}OCOCH\textsubscript{3}  
C CH\textsubscript{3}CH\textsubscript{2}CN  
D CH\textsubscript{3}COCl

26 When treated with concentrated potassium hydroxide, benzaldehyde undergoes disproportionation.

What compounds are produced in this reaction?

A C\textsubscript{6}H\textsubscript{5}O\textsuperscript{−}K\textsuperscript{+} and C\textsubscript{6}H\textsubscript{5}CO\textsubscript{2}K\textsuperscript{+}  
B C\textsubscript{6}H\textsubscript{5}O\textsuperscript{−}K\textsuperscript{+} and C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OH  
C C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}O\textsuperscript{−}K\textsuperscript{+} and C\textsubscript{6}H\textsubscript{5}CO\textsubscript{2}K\textsuperscript{+}  
D C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OH and C\textsubscript{6}H\textsubscript{5}CO\textsubscript{2}K\textsuperscript{+}
27 Which of the following compounds

(i) does not decolourise hot, acidified KMnO₄(aq) and
(ii) gives a salt when reacted with NaOH(aq)?

A  CH₃CO₂CH₂CO₂H
B  CH₂(OH)COCH₂CO₂H
C  (CH₃)₂C(OH)CH₂COOH
D  \[\text{苯酚} \]

28 Compounds X, Y and Z all react with PCl₅ to release hydrogen chloride, but only one reacts with Fehling’s solution.

Which one of the following combinations could be X, Y and Z?

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₂OH</td>
<td>CH₂OH</td>
<td>CHO</td>
</tr>
<tr>
<td></td>
<td>CH₂CH₂OH</td>
<td>CH₂CHO</td>
<td>CH₂CHO</td>
</tr>
<tr>
<td></td>
<td>CH₂OH</td>
<td>CH₂OH</td>
<td>CH₂OH</td>
</tr>
<tr>
<td>B</td>
<td>CO₂H</td>
<td>CO₂H</td>
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<td>D</td>
<td>CO₂H</td>
<td>CHO</td>
<td>CH₂CH₂OH</td>
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</tbody>
</table>
Morphine is an effective pain killer.

Which of the following statements about morphine is correct?

A  It contains 4 chiral centres.
B  It reacts with \( \text{Br}_2(\text{aq}) \) to incorporate up to 3 atoms of bromine atoms in each molecule.
C  It decolourises Baeyer’s reagent (alkaline \( \text{KMnO}_4 \)) at room temperature.
D  With excess \( \text{PCl}_5 \), 1 mole of morphine reacts with excess \( \text{PCl}_5 \) to give 2 moles of \( \text{HCl} \).

A mixture of amino acids can be separated using electrophoresis. The solution of amino acids is buffered at a specific pH and placed in a well in a gel conducting current between two electrodes.

At a buffer \( \text{pH} \) of 8, which of the following amino acids will appear closest to the anode at the end of electrophoresis?

A  \[
\begin{align*}
\text{NH}_2 \\
\text{HO}_2\text{C} &\text{CH} &\text{CH}_2\text{CH}_2\text{OH}
\end{align*}
\]
B  \[
\begin{align*}
\text{NH}_2 \\
\text{HO}_2\text{C} &\text{CH} &\text{CH}_2\text{CO}_2\text{H}
\end{align*}
\]
C  \[
\begin{align*}
\text{NH}_2 \\
\text{HO}_2\text{C} &\text{CH} &\text{CH}_2\text{CONH}_2
\end{align*}
\]
D  \[
\begin{align*}
\text{NH}_2 \\
\text{HO}_2\text{C} &\text{CH} &\text{CH}_2\text{C}_6\text{H}_4\text{OH}
\end{align*}
\]
Section B

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

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

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

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<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 Gases A and B are both gaseous hydrocarbons. When a 30 cm$^3$ mixture of A and B in the ratio of 1:2 is sparked continuously with excess oxygen gas, 70 cm$^3$ of the residual gas is absorbed by aqueous sodium hydroxide.

Which of the following pairs of hydrocarbons could be A and B?

- A methane
- B propane
- A propane
- B ethane
- A pentane
- B methane

32 Which of the following pairs of elements have the same number of unpaired electrons in their ground state?

- 1 carbon and titanium
- 2 nitrogen and cobalt
- 3 fluorine and copper

33 Which of the following could act as acidic buffers?

- 1 A 1:2 mixture of NaOH and C$_6$H$_5$COOH
- 2 A 1:2 mixture of HC$_2$ and NaHCO$_3$
- 3 A 1:2 mixture of HC$_2$ and CH$_3$CO$_2$Na
The responses A to D should be selected on the basis of

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<td>1 only is correct</td>
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</table>

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

34 A chloride and an oxide of two elements were dissolved in water.

Only one of the solutions can dissolve Al₂O₃ but both solutions cannot dissolve SiO₂.

Which of the following could be the chloride and the oxide?

1 NaCl and SO₃
2 SiCl₄ and P₄O₁₀
3 PCl₅ and Na₂O

35 The hexa-aquairon(III) ion hydrolyses as shown.

\[ [\text{Fe(H₂O)}₆]^{3+}(aq) + \text{H₂O}(l) \rightleftharpoons [\text{Fe(H₂O)}₅\text{OH}]^{2+}(aq) + \text{H}_3\text{O}^+(aq) \]

Which of the following statements are correct?

1 The corresponding iron(II) ion [Fe(H₂O)₆]²⁺ is less likely to undergo hydrolysis.
2 The iron undergoes a change in oxidation state.
3 This hydrolysis is favoured by low pH values.

36 Which of the following statements about the chemical reactions of cyclohexane, cyclohexene and methylbenzene are correct?

1 Upon reduction under suitable conditions, one mole each of cyclohexene and methylbenzene will react with one mole and three moles of hydrogen gas respectively.
2 All the three compounds decolourise bromine under \( \text{uv} \) light.
3 Only cyclohexene and methylbenzene will react with hot, acidified potassium dichromate(VI).
The responses A to D should be selected on the basis of

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</table>

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

37 For the reaction,

\[(\text{CH}_3)_3\text{CX} + \text{CH}_3\text{CH}_2\text{O}^- \rightarrow (\text{CH}_3)_3\text{COCH}_2\text{CH}_3 + X^- \text{ (where } X = \text{Cl, Br or I)}\]

which of the following statements are likely to be correct?

1 The reaction involves a nucleophilic attack by \(\text{CH}_3\text{CH}_2\text{O}^-\).
2 The rate determining step involves the formation of a carbocation.
3 The reaction will take place more rapidly when \(X\) is \(\text{I}\) than when \(X\) is \(\text{Cl}\).

38 In some organic reactions, the reactive carbon atom is not tetrahedral in the reactant molecule but becomes tetrahedral in the organic intermediate.

To which of the following reactions does this statement apply?

1 \[
\text{C}_6\text{H}_5\text{OH} + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}
\]
2 \[
\text{CH}_3\text{CHO} + \text{HCN} \xrightarrow{\text{NaCN}} \text{CH}_3\text{CH(OH)CN}
\]
3 \[
\text{C}_6\text{H}_5\text{Br} + \text{Br}_2 \xrightarrow{\text{uv light}} \text{C}_6\text{H}_5\text{Br} + \text{HBr}
\]
The responses A to D should be selected on the basis of

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<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
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</tbody>
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No other combination of statements is used as a correct response.

39 Which of the following pairs of compounds can be distinguished using the stated reagents and conditions?

1. \( \text{CH}_3\text{NH}_2 \) and \( \text{CH}_3\text{N} \)
   - NaOH(aq) and heat

2. \( \text{CH}_3\text{CH}_3 \) and \( \text{CH}_3\text{NH}_2 \)
   - HCl(aq)

3. \( \text{CH}_3\text{O} \) and \( \text{OCH}_3\text{CH}_3 \)
   - NaOH(aq), I\(_2\)(aq), warm

40 \( \alpha\)-aminobutyric acid and \( \gamma\)-aminobutyric acid are isomers.

\( \begin{align*}
\text{CH}_3\text{NH}_2\text{OH} & \quad \text{NH}_2\text{CH}_2\text{CH}_2\text{COOH} \\
\alpha\text{-aminobutyric acid} & \quad \gamma\text{-aminobutyric acid}
\end{align*} \)

Which of the following statements are correct?

1. Both are soluble in water.
2. Both can form zwitterions.
3. Both can be obtained from the hydrolysis of protein.

END OF PAPER
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PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CANDIDATE NAME

CT GROUP 1 1

INDEX NUMBER

CHEMISTRY 9647/02
Paper 2 Structured
10 September 2012
2 hours

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Answer all questions.

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

FOR EXAMINER’S USE

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This document consists of 19 printed pages.
1 Planning (P)

You are provided with solutions FA 1, FA 2 and FA 3.

FA 1 and FA 2 are either
1.0 mol dm\(^{-3}\) nitric acid or
1.0 mol dm\(^{-3}\) ethanoic acid

whereas FA 3 is 2.0 mol dm\(^{-3}\) sodium hydroxide.

You are to plan an experiment that will enable you to identify FA 1 and FA 2, and hence, calculate the enthalpy change of neutralisation for the reaction between ethanoic acid and sodium hydroxide.

You are provided with the following apparatus:

a thermometer,
a polystyrene cup,
other common apparatus in the laboratory

(a) State the independent and dependent variables when determining the identity of each solution, FA 1 and FA 2. \[1\]

Independent variable ……………………………………………………………………………………………

Dependent variable ……………………………………………………………………………………………

(b) Plan an experiment to identify which of the two solutions, FA 1 and FA 2, is 1.0 mol dm\(^{-3}\) nitric acid and which is 1.0 mol dm\(^{-3}\) ethanoic acid.

Your plan must identify the acids solely based on the change in temperature. Mathematical processing of the temperature change is thus not required.

Your plan should give a step by step description of the method including:
- the apparatus used for measurement
- appropriate volumes of reagents
- how you would measure the various variables

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(c) Either a burette with 0.1 cm$^3$ interval or a measuring cylinder with 1 cm$^3$ interval can be used to measure the volume of FA 3 required.

It is known that the error (or uncertainty) that is associated with each reading when using a measuring cylinder with 1 cm$^3$ interval is ±0.5 cm$^3$, while that using a burette with 0.1 cm$^3$ interval is ±0.05 cm$^3$.

Assuming that the volume of FA 3 measured is $V$ cm$^3$, calculate the maximum total percentage error (or uncertainty) in the measurement of the volume of FA 3, in terms of $V$, when using:

(i) a measuring cylinder with 1 cm$^3$ interval,

(ii) a burette with 0.1 cm$^3$ interval.
(d) Explain clearly how you could determine the identity of the acids using the difference in temperature rise in the experiment proposed in (b). [2]

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(e) (i) Define the term *standard enthalpy change of neutralisation*.

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(ii) Show the mathematical expression for the enthalpy change of neutralisation between ethanoic acid and sodium hydroxide, using the volumes proposed in (b).

The temperature change measured in (b) should be represented by $\Delta T$.

[You may assume that 4.2 J of heat energy raised the temperature of 1 cm$^3$ of any solution by 1° C.]
(f) A student suggests titrating FA 3 against FA 1 and FA 2 separately, using phenolphthalein as indicator, to identify two acids. Explain why this proposed method cannot work.

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[Total: 12]

2 Nitrogen dioxide, NO₂ undergoes dimerisation to form dinitrogen tetraoxide, N₂O₄.

\[ 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]

(a) (i) Draw the dot-and-cross diagram of NO₂.

(ii) State the shape and bond angle of the O–N–O bond in NO₂.

Shape .................................................................

Bond angle ..........................................................
(iii) Draw the dot-and-cross diagram of NO$_2^-$ ion. With reference to your answer in (a)(i) and (ii), suggest a bond angle of the O–N–O in NO$_2^-$ ion, as compared to NO$_2$. Explain your answer.

The general rate equation for the dimerisation of nitrogen dioxide can be represented as:

\[
\text{Rate} = k(p_{\text{NO}_2})^n,
\]

where $n$ represents the order of reaction with respect to nitrogen dioxide.

To determine the value of $n$, an experiment was carried out to collect experiment data on the partial pressure of nitrogen dioxide ($p_{\text{NO}_2}$) measured at a constant temperature of 500 K. The results were given below.

<table>
<thead>
<tr>
<th>Time/ s</th>
<th>$p_{\text{NO}_2}$/ atm</th>
<th>Rate / atm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.917</td>
<td>9.48 x 10$^{-5}$</td>
</tr>
<tr>
<td>1000</td>
<td>0.827</td>
<td>7.75 x 10$^{-5}$</td>
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<tr>
<td>2000</td>
<td>0.753</td>
<td>6.45 x 10$^{-5}$</td>
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<td>5.45 x 10$^{-5}$</td>
</tr>
<tr>
<td>4000</td>
<td>0.638</td>
<td>4.67 x 10$^{-5}$</td>
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</tbody>
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Table 1

(b) (i) Given that $n$ is 2, process the results in the Table 1 to produce data that would enable you to plot a straight line graph.
(ii) Hence, use the processed data above to plot the graph on the grid below.

(iii) A student repeated the experiment at the temperature of 250 K. Sketch, on the same axes in (ii), the graph obtained by this student. Label this graph as 250 K.

[Total: 9]
The following reaction scheme shows the chemistry of some chromium-containing species in aqueous solution.

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} & \xrightarrow{\text{SO}_2} \text{I} \quad \text{green solution} \\
& \xrightarrow{\text{Zn}} \text{II} \quad \text{blue solution} \\
& \quad \text{III} \xrightarrow{\text{Na}_2\text{CO}_3(aq)} \text{B} + \text{CO}_2 \\
\quad \text{IV} \xrightarrow{\text{NaOH(aq)}} \text{V} \\
\quad \text{V} \xrightarrow{\text{NH}_3(aq)} \text{VIII} \quad \text{violet solution} \\
\text{V} & \quad \text{VI} \xrightarrow{\text{H}_2\text{O}_2} \text{C} \quad \text{yellow solution}
\end{align*}
\]

(a) (i) Write the formulae of the following chromium-containing species.

A: ...............................................................................

B: ...............................................................................

C: ...............................................................................

D: ...............................................................................


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(ii) State the type of reaction that has occurred in VIII. Construct a balanced equation to represent the reaction.

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(iii) Hence, using your knowledge of Gibbs free energy, explain why the reaction in (a)(ii) occurs spontaneously.

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(b) Explain why carbon dioxide is evolved when Na₂CO₃(aq) is added to A in III. Include any relevant equations in your answer.

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(c) Explain why aqueous solutions of chromium ions are coloured. [3]

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(d) In a separate experiment, a chemist prepared two compounds with the general formula \( \text{CrCl}_x\text{H}_2\text{O} \). Upon adding \( \text{AgNO}_3(\text{aq}) \) to aqueous solutions of compounds \( \text{E} \) and \( \text{F} \) separately, he noted the following:

<table>
<thead>
<tr>
<th>Solution containing</th>
<th>Amount of AgCl precipitated per mole of compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound E</td>
<td>1</td>
</tr>
<tr>
<td>compound F</td>
<td>2</td>
</tr>
</tbody>
</table>

Based on these observations, deduce the formula of compounds \( \text{E} \) and \( \text{F} \) in the solutions. Explain your answer. [3]

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[Total: 15]
In the vapour phase, ethanoic acid associates to form dimers and an equilibrium is established as shown.

\[ 2\text{CH}_3\text{COOH}(g) \rightleftharpoons (\text{CH}_3\text{COOH})_2(g) \]

At 177 °C and 1 atm, 0.084 g of the equilibrium mixture occupies 37.8 cm³.

(a) (i) Calculate the average relative molecular mass of the gaseous mixture, giving your answer to 1 decimal place.

(ii) Calculate the proportion of ethanoic acid and its dimer in the equilibrium mixture.

(iii) Hence, calculate the value of \( K_p \) for the dimerisation of ethanoic acid at 177 °C, giving its units.
(c) State and explain the effect of an increase in temperature on the average \( M_r \) of the equilibrium mixture. [3]

5 Cinnamaldehyde is an essential oil with the distinctive odour of cinnamon.

\[
\text{CH} = \text{CH} - \text{CHO}
\]

\[\text{cinnamaldehyde}\]

(a) Sketch the shapes of the hybrid orbitals around one carbon atom in the cinnamaldehyde molecule, indicate clearly the hybridisation of the carbon atom. [1]

(b) A yellow oil is suspected to be cinnamaldehyde.

(i) Assuming the oil is cinnamaldehyde, complete the table below, giving the reagent and conditions to confirm the presence of the two functional groups. Give the expected observation for each test.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Reagent and conditions</th>
<th>Expected observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldehyde</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(ii) Write an equation for the reaction between cinnamaldehyde with the reagent you have chosen to test for presence of the aldehyde.

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

[3]

(c) Cinnamaldehyde undergoes electrophilic addition with hydrogen bromide according to the equation as shown.

\[
\text{CH} = \text{CH} - \text{CHO} + \text{HBr} \rightarrow \text{CHBr} - \text{CH}_2 - \text{CHO}
\]

Draw the mechanism of the reaction and explain why the product obtained does not rotate the plane of polarised light.

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

[4]

[Total: 8]
Tyrosine, one of the 20 α-amino acids commonly found in proteins, was discovered 1846 by German chemist Justus von Liebig in the protein casein from cheese. It has the following structure.

\[
\text{tyrosine}
\]

The Hell-Volhard-Zelinskii reaction is the one of oldest methods of α-amino acids synthesis. It involves α bromination of a carboxylic acid by treatment with \( \text{Br}_2 \) and \( \text{PBr}_3 \), followed by the conversion of the α-bromo acid to the α-amino acid.

\[
\begin{align*}
\text{R-CH}_2\text{CO}_2\text{H} & \xrightarrow{1. \text{Br}_2, \text{PBr}_3} \text{R-CHBrCO}_2\text{H} & \xrightarrow{2. \text{H}_2\text{O}} & \text{R-CH(NH}_2\text{)CO}_2\text{H} \\
\text{I} & & \text{II}
\end{align*}
\]

(i) Give the structure of the carboxylic acid that could be converted to tyrosine by the above reaction scheme.

(ii) Suggest reagent and condition for step II.

The yield of the amino acid obtained in step II of the above reaction scheme tends to be low. A better method is to carry out the Gabriel amine synthesis, which involves the use of phthalimide as shown.

\[
\begin{align*}
\text{A} & \xrightarrow{\text{KOH, ethanol}} \text{B} & \xrightarrow{\text{NaOH(aq)}} \text{C} \\
\text{phthalimide} & \xrightarrow{\text{RCHBrCO}_2\text{H}} \text{RCH(NH}_2\text{)CO}_2\text{H}
\end{align*}
\]
(iii) State the role of KOH in step A.

……………………………………………………………………………………..

(iv) What is the type of reaction in step B?

……………………………………………………………………………………..

(v) Suggest a reason for the low yield of the amino acid obtained in step II of Hell-Volhard-Zelinskii the reaction. Hence, explain how the use of phthalimide in Gabriel amine synthesis would give a higher yield.

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……………………………………………………………………………………..

……………………………………………………………………………………..

(vi) The protons of amide (\(-\text{CONH}_2\)) are not known to be acidic ($pK_a > 500$). Explain why the proton of phthalimide is acidic ($pK_a = 8.3$).

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

……………………………………………………………………………………..

(vii) Give the structure of the other organic product obtained when alkaline hydrolysis is carried out in step C of the Gabriel amine synthesis.

……………………………………………………………………………………..
(b) The three $pK_a$ values associated with tyrosine are 2.20, 9.11 and 10.13.

Make use of these $pK_a$ values to suggest the major species present in solutions of tyrosine with the following pH values.

pH 1

pH 6

pH 11

[3]
[Total: 12]
7 Benzoic acid can be prepared by the oxidation of benzaldehyde using alkaline potassium manganate(VII) as described below.

Data about the benzaldehyde and benzoic acid are given below.

<table>
<thead>
<tr>
<th>compound</th>
<th>density / g cm$^{-3}$</th>
<th>melting point / °C</th>
<th>boiling point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>1.05</td>
<td>-26</td>
<td>179</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>1.27</td>
<td>122</td>
<td>229</td>
</tr>
</tbody>
</table>

Preparation of impure benzoic acid

1 Place 2.00 g of solid potassium manganate(VII), 30 cm$^3$ of 1 mol dm$^{-3}$ sodium hydroxide and 1.5 cm$^3$ of benzaldehyde in a round-bottomed flask. Swirl the flask carefully to mix the contents thoroughly.

2 Fit a reflux condenser onto the round-bottomed flask and boil the mixture gently for 10 minutes.

3 Filter off the brown precipitate of manganese(IV) oxide formed, collect the filtrate in a 100 cm$^3$ beaker and allow the filtrate to cool.

4 Carefully add concentrated hydrochloric acid, with constant swirling, to the filtrate till the mixture is acidic enough to precipitate the benzoic acid.

(a) By means of two ion-electron half-equations, write an equation for the oxidation of benzaldehyde by alkaline potassium manganate(VII). [2]

(b) Show by calculation, which reagent, benzaldehyde or potassium manganate(VII), is in excess. [2]
(c) Draw a diagram of the assembled apparatus for heating under reflux. Indicate clearly how water enters and leaves the condenser. [2]

Purification of impure benzoic acid

5 Filter the benzoic acid that has been precipitated and wash it once with cold water.

6 The crude benzoic acid product is purified by recrystallisation from water.

7 Filter the recrystallised solid, wash with water and dry the solid by pressing it under several layers of filter paper.

8 Weigh the solid obtained.

(d) Give a description of the procedure you would use to purify the crude benzoic acid. [1]
(e) Explain how you would check for purity of the benzoic acid. [1]

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(f) Given that 1.40 g of benzoic acid is obtained from the preparation, calculate the percentage yield of the reaction. [1]

[Total: 9]

END OF PAPER
READ THESE INSTRUCTIONS FIRST

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

Answer all questions.

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

You are provided with solutions **FA 1**, **FA 2** and **FA 3**.

**FA 1** and **FA 2** are either
1.0 mol dm$^{-3}$ nitric acid or 1.0 mol dm$^{-3}$ ethanoic acid

whereas **FA 3** is 2.0 mol dm$^{-3}$ sodium hydroxide.

You are to plan an experiment that will enable you to identify **FA 1** and **FA 2**, and hence, calculate the enthalpy change of neutralisation for the reaction between ethanoic acid and sodium hydroxide.

You are provided with the following apparatus:
- a thermometer,
- a polystyrene cup,
- other common apparatus in the laboratory

**(a)** State the independent and dependent variables when determining the identity of each solution, **FA 1** and **FA 2**. [1]

**Independent variable – Strength of acid**

**Dependent variable – Rise in temperature**

**(b)** Plan an experiment to identify which of the two solutions, **FA 1** and **FA 2**, is 1.0 mol dm$^{-3}$ nitric acid and which is 1.0 mol dm$^{-3}$ ethanoic acid.

Your plan must identify the acids solely based on the change in temperature. Mathematical processing of the temperature change is thus not required.

Your plan should give a step by step description of the method including:
- the apparatus used for measurement
- appropriate volumes of reagents
- how you would measure the various variables

[3]

**Step 1:** Using a 100 cm$^3$ measuring cylinder, measure out 25 cm$^3$ of **FA 3** into the polystyrene cup and record its initial temperature using a thermometer. Rinse the thermometer.

**Step 2:** Using ANOTHER 100 cm$^3$ measuring cylinder, measure 50 cm$^3$ of **FA 1**. Record its initial temperature.

**Step 3:** The initial temperature is given by the average of the initial temperature of **FA 1** and **FA 3**.
Step 4: Carefully transfer the 50 cm³ of FA 1 into the polystyrene cup containing FA 3, stir with the thermometer and record the highest temperature reached. Rinse the cup.

Step 5: Repeat steps 1 to 4, this time replacing FA1 with FA2.

(c) Either a burette with 0.1 cm³ interval or a measuring cylinder with 1 cm³ interval can be used to measure the volume of FA 3 required.

It is known that the error (or uncertainty) that is associated with each reading when using a measuring cylinder with 1 cm³ interval is ±0.5 cm³, while that using a burette with 0.1 cm³ interval is ±0.05 cm³.

Assuming that the volume of FA 3 measured is \( V \) cm³, calculate the maximum total percentage error (or uncertainty) in the measurement of the volume of FA 3, in terms of \( V \), when using:

(i) a measuring cylinder with 1 cm³ interval,
\[
\text{Percentage error in measuring } V \text{ cm}^3 = \pm \left( \frac{0.5}{V} \right) \times 100\% = \pm \frac{50}{V}\%
\]

(ii) a burette with 0.1 cm³ interval.
\[
\text{Percentage error in measuring } V \text{ cm}^3 = \pm \left[ \left( \frac{0.05}{V} \right) \times 100\% \right] \times 2 = \pm \frac{10}{V}\%
\]

(d) Explain clearly how you could determine the identity of the acids using the difference in temperature rise in the experiment proposed in (b).

Ethanoic acid is a weak acid and nitric acid is a strong acid. The temperature rise will be lower when 1.0 mol dm⁻³ ethanoic acid is used compared to 1.0 mol dm⁻³ nitric acid for the same number of moles of water formed.

This is because some of the energy evolved from the neutralisation process is used to further dissociate the ethanoic acid completely.

(e) (i) Define the term \textit{standard enthalpy change of neutralisation}.

The heat evolved when one mole of water is formed when an acid neutralises a base under standard conditions of 298K and 1 atm.

(ii) Show the mathematical expression for the enthalpy change of neutralisation for the reaction between ethanoic acid and sodium hydroxide, using the volumes proposed in (b).

The temperature change measured in (b) should be represented by \( \Delta T \).

[You may assume that 4.2 J of heat energy raised the temperature of 1 cm³ of any solution by 1°C.]
Heat evolved by neutralisation reaction
\[ \Delta H_{\text{neutralisation}} = mc\Delta T \]
\[ = (\text{vol. of FA1 or FA2} + \text{vol of FA3}) \times c \times \Delta T \]
\[ = (50 + 25) \times 4.2 \times \Delta T \]
\[ = 315 \Delta T \ \text{J} \]
\[ \Delta H_{\text{neutralisation}} = -315 \Delta T / \text{amount of water formed} \]
\[ = -315 \Delta T / 0.050 \]
\[ = -6300 \Delta T \ \text{J mol}^{-1} \]

\[ [3] \]

(f) A student suggests titrating FA 3 against FA 1 and FA 2 separately, using phenolphthalein as indicator, to identify the acids. Explain why this proposed method cannot work.

Both FA 1 and FA 2 are of the same concentration and basicity (monobasic).
Both acids would hence require the same amount of NaOH for a complete reaction, and hence same volume. The volume of FA 3 (NaOH) required at end point would hence be the same.

[Total: 12]

2 Nitrogen dioxide, NO\(_2\) undergoes dimerisation to form dinitrogen tetraoxide, N\(_2\)O\(_4\).

\[ 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]

(a) (i) Draw the dot-and-cross diagram of NO\(_2\).

\[ \text{NO}_2 \text{ molecule} \]

(ii) State the shape and bond angle of the O–N–O bond in NO\(_2\).
Shape of NO\(_2\): Bent
Bond angle: accept any value where \(110^\circ < \text{angle} < 120^\circ\)

(iii) Draw the dot-and-cross diagram of NO\(_2^–\) ion. With reference to your answer in (a)(i) and (ii), suggest a bond angle of the O–N–O in NO\(_2^–\) ion, as compared to NO\(_2\). Explain your answer.
Bond angle of \( \text{NO}_2^- \) ion: bond angle must be smaller than \( \text{NO}_2 \), but still within range of \( 110^\circ < \text{angle} < 120^\circ \).

Lone pair of electrons present in \( \text{NO}_2^- \) ion occupies a larger volume of space than the single lone electron present in \( \text{NO}_2 \) molecule. Hence, lone pair-bond pair repulsion in \( \text{NO}_2^- \) ion is greater than lone electron-bond pair repulsion in \( \text{NO}_2 \), causing \( \text{NO}_2^- \) ion to have a smaller bond angle than \( \text{NO}_2 \).

The general rate equation for the dimerisation of nitrogen dioxide can be represented as:

\[
\text{Rate} = k(p_{\text{NO}_2})^n,
\]

where \( n \) represents the order of reaction with respect to nitrogen dioxide.

To determine the value of \( n \), an experiment was carried out to collect experiment data on the partial pressure of nitrogen dioxide \( (p_{\text{NO}_2}) \) measured at a constant temperature of 500 K. The results were given below.

<table>
<thead>
<tr>
<th>Time/ s</th>
<th>( p_{\text{NO}_2} )/ atm</th>
<th>Rate /atm s(^{-1} )</th>
<th>( (p_{\text{NO}_2})^2 )/ atm(^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.917</td>
<td>9.48 x 10(^{-5} )</td>
<td>0.841</td>
</tr>
<tr>
<td>1000</td>
<td>0.827</td>
<td>7.75 x 10(^{-5} )</td>
<td>0.683</td>
</tr>
<tr>
<td>2000</td>
<td>0.753</td>
<td>6.45 x 10(^{-5} )</td>
<td>0.567</td>
</tr>
<tr>
<td>3000</td>
<td>0.691</td>
<td>5.45 x 10(^{-5} )</td>
<td>0.477</td>
</tr>
<tr>
<td>4000</td>
<td>0.638</td>
<td>4.67 x 10(^{-5} )</td>
<td>0.407</td>
</tr>
</tbody>
</table>

Table 1

(b) (i) Given that \( n \) is 2, process the results in the Table 1 to produce data that would enable you to plot a straight line graph.
(ii) Hence, use the processed data to plot the graph on the grid below.

\[\text{Rate / atm s}^{-1}\]

\[\text{(p}_{\text{NO}_2}\text{)}^2 /\text{atm}^2\]

500 K

250 K

0

(ii) A student repeated the experiment at the temperature of 250 K. Sketch, on the same axes in (ii), the graph obtained by this student. Label this graph as 250 K.

Straight line graph still obtained, with y-intercept = 0. Gradient (k) decreases.

[4]

[Total: 9]
The following reaction scheme shows the chemistry of some chromium-containing species in aqueous solution.

(a) (i) Write the formulae of the following chromium-containing species.

\[ \text{A: } [\text{Cr(H}_2\text{O)}_6]^3+ \text{ or } \text{Cr}^3+ \text{ or } \text{Cr}_2(\text{SO}_4)_3 \]
\[ \text{B: } \text{Cr(OH)}_3 \]
\[ \text{C: } \text{CrO}_4^{2-} \text{ or } \text{Na}_2\text{CrO}_4 \]

(ii) State the type of reaction that has occurred in VIII. Construct a balanced equation to represent the reaction.

Ligand exchange has taken place.

\[ [\text{Cr(NH}_3)_6]^3+ + 3 \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \Rightarrow [\text{Cr(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^3+ + 6 \text{NH}_3 \]

(iii) Hence, using your knowledge of Gibbs free energy, explain why the reaction in (a)(ii) occurs spontaneously.
\[ [\text{Cr(NH}_3\text{)}_6]^{3+} + 3 \text{en} \rightleftharpoons [\text{Cr(en)}_3]^{3+} + 6 \text{NH}_3 \]

This ligand exchange proceeds with the breaking and formation of similar chemical bonds (N:"Cr dative bonds). \( \Delta H \) of reaction is hence approximately zero.

However, displacement of monodentate \( \text{NH}_3 \) ligands by bidentate \( \text{en} \) ligands causes an increase in number of molecules in the system, resulting in an increase in disorderliness and hence \( \Delta S \) is positive.

Since \( \Delta G = \Delta H - T\Delta S \), \( \Delta G \) is always negative, accounting for spontaneity of ligand exchange.

(b) Explain why carbon dioxide is evolved when Na\(_2\)CO\(_3\)(aq) is added to A in III. Include any relevant equations in your answer.

Cr\(^{3+}\) ion has a high charge density and high polarising power. Hence [Cr(H\(_2\)O\(_6\)]\(^{3+}\) can undergo hydrolysis in water, polarising and weakening the O-H bonds of surrounding H\(_2\)O molecules, to release H\(^+\) ions. H\(^+\) ions react with carbonate ions via acid-base reaction to form CO\(_2\).

\[ [\text{Cr(H}_2\text{O)}_6]^{3+}(aq) \rightleftharpoons [\text{Cr(OH)(H}_2\text{O)}_5]^{2+}(aq) + \text{H}^+(aq) \]

\[ 2\text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} \]

(c) Explain why aqueous solutions of chromium ions are coloured.

In the presence of ligands, the partially filled, originally degenerate 3d orbitals of Cr split into two different sets of energy, separated by a small energy gap \( \Delta E \). An electron from the lower energy d-orbital absorbs a specific wavelength of light from the visible light spectrum corresponding to \( \Delta E \) and is promoted to a higher energy d-orbital, undergoing d to d electron transition. The colour absorbed is complementary to colour observed.

(d) In a separate experiment, a chemist prepared two compounds with the general formula CrCl\(_3\).6H\(_2\)O. Upon adding AgNO\(_3\)(aq) to aqueous solutions of compounds E and F separately, he noted the following:

<table>
<thead>
<tr>
<th>Solution containing</th>
<th>Amount of AgCl precipitated per mole of compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound E</td>
<td>1</td>
</tr>
<tr>
<td>Compound F</td>
<td>2</td>
</tr>
</tbody>
</table>

Based on these observations, deduce the formula of compounds E and F in the solutions. Explain your answer.
Formula of E: $[\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\text{Cl}.2\text{H}_2\text{O}$

Formula of F: $[\text{Cr(H}_2\text{O)}_5\text{Cl}]\text{Cl}_2.\text{H}_2\text{O}$

Only free chloride ions can be precipitated as AgCl. Chloride ions coordinated to Cr$^{3+}$ as ligands cannot be precipitated.

**OR:**

E contains 1 free Cl$^-$ ion, which can be precipitated as AgCl by Ag$^+$.  
F contains 2 free Cl$^-$ ions, which can be precipitated as AgCl by Ag$^+$.

4 In the vapour phase, ethanoic acid associates to form dimers and an equilibrium is established as shown.

$$2\text{CH}_3\text{COOH(g)} \rightleftharpoons (\text{CH}_3\text{COOH})_2\text{(g)}$$

At 177 °C and 1 atm, 0.084 g of the equilibrium mixture occupies 37.8 cm$^3$.

(a) (i) Calculate the average relative molecular mass of the gaseous mixture, giving your answer to 1 decimal place.

$$\frac{(101000)(37.8 \times 10^{-6})}{\text{average } M_r} = \frac{0.084}{(8.31)(177 + 273)}$$

Average $M_r = 82.3$

(ii) Calculate the proportion of ethanoic acid and its dimer in the equilibrium mixture.

Let fraction of CH$_3$COOH in mixture be $x$ and that of (CH$_3$COOH)$_2$ be $(1 - x)$.

$$60x + 120(1 - x) = 82.3$$

$$x = 0.628$$

Fraction of CH$_3$COOH in mixture = 0.628  
Fraction of (CH$_3$COOH)$_2$ in mixture = 0.372

(iii) Hence, calculate the value of $K_p$ for the dimerisation of ethanoic acid at 177 °C, giving its units.

$$K_p = \frac{P_{(\text{CH}_3\text{COOH})_2}}{(P_{\text{CH}_3\text{COOH}})^2}$$

$$= \frac{0.372 \times 1}{(0.628 \times 1)^2}$$

$$= 0.943 \text{ atm}^{-1}$$
(c) State and explain the effect of an increase in temperature on the average $M_r$ of the equilibrium mixture.

The dimerisation of CH$_3$COOH is an exothermic process as it involves the formation of two hydrogen bonds.

According to Le Chatelier’s Principle, increasing the temperature favours an endothermic reaction. Thus, position of equilibrium shifts to the left. There will be a greater proportion of CH$_3$COOH in the reaction mixture, causing the average $M_r$ of the reaction mixture to decrease.

[Total: 7]

5 Cinnamaldehyde is an essential oil with the distinctive odour of cinnamon.

\[
\text{CH} = \text{CH} - \text{CHO}
\]

Cinnamaldehyde

(a) Sketch the shapes of the hybrid orbitals around one carbon atom in the cinnamaldehyde molecule, indicate clearly the hybridisation of the carbon atom.\[1\]

\[
\text{sp}^2 \text{ hybridised}
\]

(b) A yellow oil is suspected to be cinnamaldehyde.

(i) Assuming the oil is cinnamaldehyde, complete the table below, giving the reagent and conditions to confirm the presence of the two functional groups. Give the expected observation for each test.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Reagent and conditions</th>
<th>Expected observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkene</td>
<td>Br$_2$(aq)</td>
<td>Orange/ reddish-brown Br$_2$(aq) decolourises.</td>
</tr>
<tr>
<td>aldehyde</td>
<td>Tollens’ reagent and warm Or Fehling’s solution and warm</td>
<td>Silver mirror observed. Or Brick red precipitate observed.</td>
</tr>
</tbody>
</table>
(ii) Write an equation for the reaction between cinnamaldehyde with the reagent you have chosen to test for presence of the aldehyde.

\[
\text{C}_6\text{H}_5\text{CH}=\text{CHCHO} + 2\text{Ag}^+ + 3\text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCOO}^- + 2\text{Ag} + 2\text{H}_2\text{O}
\]

Or

\[
\text{C}_6\text{H}_5\text{CH}=\text{CHCHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{CH}==\text{CHCOO}^- + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}
\]

(c) Cinnamaldehyde undergoes electrophilic addition with hydrogen bromide according to the equation as shown.

\[
\text{CH}=\text{CH}-\text{CHO} + \text{HBr} \rightarrow \text{CHBr}-\text{CH}_2-\text{CHO}
\]

Draw the mechanism of the reaction and explain why the product obtained does not rotate the plane of polarised light.

The reaction takes place with the formation of a carbocation. The C atom bearing the positive charge has a trigonal planar arrangement. There is equal likelihood of the Br\(^-\) attacking from above and below the plane. Thus, resulting in the formation of a racemic mixture (equimolar quantities of the two enantiomers) in which the optical activity cancels out.

[Total: 8]
6 (a) Tyrosine, one of the 20 \( \alpha \)-amino acids commonly found in proteins, was discovered in 1846 by German chemist Justus von Liebig in the protein casein from cheese. It has the following structure.

![Tyrosine structure](image)

The Hell-Volhard-Zelinskii reaction is the one of oldest methods of \( \alpha \)-amino acids synthesis. It involves \( \alpha \) bromination of a carboxylic acid by treatment with \( \text{Br}_2 \) and \( \text{PBr}_3 \), followed by the conversion of the \( \alpha \)-bromo acid to the \( \alpha \)-amino acid.

\[
\begin{align*}
R-\text{CH}_2\text{CO}_2\text{H} & \quad \text{1. Br}_2, \text{PBr}_3 \\
& \quad \text{2. H}_2\text{O} \\
\end{align*}
\]

(i) Give the structure of the carboxylic acid that could be converted to tyrosine by the above reaction scheme.

![Carboxylic acid structure](image)

(ii) Suggest reagent and condition for step II.

*Excess NH\(_3\) in ethanol, heat in sealed tube*

The yield of the amino acid obtained in step II of the above reaction scheme tends to be low. A better method is to carry out the Gabriel amine synthesis, which involves the use of phthalimide as shown.

![Gabriel amine synthesis](image)

(iii) State the role of KOH in step A.

*KOH acts as a base to deprotonate the phthalimide.*
What is the type of reaction in step B?

**Nucleophilic substitution**

Suggest a reason for the low yield of the amino acid obtained in step II of Hell-Volhard-Zelinskii the reaction. Hence, explain how the use of phthalimide in Gabriel amine synthesis would give a higher yield.

*Multiple substitution (alkylation) may occur, giving a mixture of 2° amine, 3° amine and possibly a quaternary ammonium salt, instead of the desired 1° amine. By having N bonded to two CO groups, multiple alkylation cannot take place, hence a higher yield is obtained.*

The protons of amide (CONH₂) are not known to be acidic (pKₐ > 500). Explain why the proton of phthalimide is acidic (pKₐ = 8.3).

*The presence of the two electron withdrawing CO group helps to disperse the negative charge on the anion / the negative charge of the anion formed from deprotonation can be delocalised with the pi electron system of the two CO groups. This stabilises the anion, making it acidic.*

Give the structure of the other organic product obtained when alkaline hydrolysis is carried out in step C of the Gabriel amine synthesis.

(b) The three pKₐ values associated with tyrosine are 2.20, 9.11 and 10.13.

Make use of these pKₐ values to suggest the major species present in solutions of tyrosine with the following pH values.

pH 1
Benzoic acid can be prepared by the oxidation of benzaldehyde using alkaline potassium manganate(VII) as described below.

Data about the benzaldehyde and benzoic acid are given below.

<table>
<thead>
<tr>
<th>compound</th>
<th>density / g cm⁻³</th>
<th>melting point / °C</th>
<th>boiling point / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>1.05</td>
<td>-26</td>
<td>179</td>
</tr>
<tr>
<td>benzoic acid</td>
<td>1.27</td>
<td>122</td>
<td>229</td>
</tr>
</tbody>
</table>

Preparation of impure benzoic acid

1. Place 2.00 g of solid potassium manganate(VII), 30 cm³ of 1 mol dm⁻³ sodium hydroxide and 1.5 cm³ of benzaldehyde in a round-bottomed flask. Swirl the flask carefully to mix the contents thoroughly.

2. Fit a reflux condenser onto the round-bottomed flask and boil the mixture gently for 10 minutes.

3. Filter off the brown precipitate of manganese(IV) oxide formed, collect the filtrate in a 100 cm³ beaker and allow the filtrate to cool.

4. Carefully add concentrated hydrochloric acid, with constant swirling, to the filtrate till the mixture is acidic enough to precipitate the benzoic acid.

(a) By means of two ion-electron half-equations, write an equation for the oxidation of benzaldehyde by alkaline potassium manganate(VII).

\[ \text{C}_6\text{H}_5\text{CHO} + 3\text{OH}^- \rightarrow \text{C}_6\text{H}_5\text{CO}_2^- + 2\text{H}_2\text{O} + 2\text{e} \]

\[ \text{MnO}_4^- + 3\text{e} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{OH}^- \]

\[ 3\text{C}_6\text{H}_5\text{CHO} + \text{OH}^- + 2\text{MnO}_4^- \rightarrow 3\text{C}_6\text{H}_5\text{CO}_2^- + 2\text{MnO}_2 + 2\text{H}_2\text{O} \]
(b) Show by calculation, which reagent, benzaldehyde or potassium manganate(VII), is in excess. [2]

\[
\text{Amount of benzaldehyde used} = \frac{(1.5 \times 1.05)}{106} = 0.0149 \text{ mol}
\]

\[
\text{Amount of KMnO}_4 \text{ used} = \frac{2.00}{158} = 0.0127 \text{ mol}
\]

\[
2 \text{ mol of KMnO}_4 \equiv 3 \text{ mol } C_6H_5CHO
\]

\[
0.0127 \text{ mol of KMnO}_4 \equiv 0.01905 \text{ mol of } C_6H_5CHO
\]

Potassium manganate(VII) is in excess.

(c) Draw a diagram of the assembled apparatus for heating under reflux. Indicate clearly how water enters and leaves the condenser. [2]

Purification of impure benzoic acid

5 Filter the benzoic acid that has been precipitated and wash it once with cold water.

6 The crude benzoic acid product is purified by recrystallisation from water.

7 Filter the recrystallised solid, wash with water and dry the solid by pressing it under several layers of filter paper.

8 Weigh the solid obtained.
(d) Give a description of the procedure you would use to purify the crude benzoic acid.

*Dissolve the crude benzoic acid in a minimum volume of hot water. Cool the hot saturated solution to obtain the crystallised product.*

(e) Explain how you would check for purity of the benzoic acid.

*Purity of benzoic acid can be checked by melting point determination. Pure benzoic acid should melt very sharply at 122°C.*

(f) Given that 1.40 g of benzoic acid is obtained from the preparation, calculate the percentage yield of the reaction.

*Theoretical yield = 0.0149 x 122  
= 1.818 g* 
*Percentage yield = (1.40 / 1.818) x 100  
= 77.0%*
READ THESE INSTRUCTIONS FIRST

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

Answer any four out of five questions.
State the question number of the questions that you have attempted on the cover page provided.
The question numbers should be stated in sequence.

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

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.
Enzymes are biological molecules that catalyse chemical reactions. Almost all chemical reactions in a biological cell need enzymes in order to occur at rates sufficient for life.

(a) Acquired Immuno-Deficiency Syndrome (AIDS) is a disease of the human immune system caused by the Human Immunodeficiency Virus (HIV). HIV-1 Protease is an enzyme which speeds up the reproduction of HIV. In the development of anti-HIV drugs, scientists often study the amino acid sequence of the HIV-1 Protease to understand how this enzyme displays its biological properties in the human body.

(i) A segment of the polypeptide structure of HIV-1 Protease, containing 10 amino acids, was digested using an enzyme and the following fragments were obtained.

\[
\text{leu – asn – phe} \\
\text{ile – gly – cys – thr – leu} \\
\text{leu – thr – glu – ile – gly}
\]

Deduce the primary structure of this segment of HIV-1 Protease.

(ii) A segment of the HIV strand acts as a substrate, which binds to the active site of the HIV-1 Protease which speeds up the reproduction of the HIV virus. The rate of this enzyme-catalysed reaction is investigated and can be represented by the following graph.

Explain the difference in the rate of reaction at high and low concentrations of substrate.
(iii) The structural formulae of the three most common amino acids present in the protein chain in HIV-1 Protease are shown below.

\[
\begin{align*}
\text{glutamic acid} & : \quad \text{NH}_2-\text{C}-\text{COOH} \\
\text{leucine} & : \quad \text{NH}_2-\text{C}-\text{COOH} \\
\text{cysteine} & : \quad \text{NH}_2-\text{C}-\text{COOH}
\end{align*}
\]

In how many different ways can these three amino acids be coupled by peptide bonds to form a tripeptide? Draw the structural formula of one such peptide.

(iv) The side chains of these three amino acids are responsible for maintaining the tertiary structure of HIV-1 Protease.

State and draw the type of side-chain interaction between two cysteine (cys) residues.

State the type of reaction that is involved in the formation of the side-chain interaction.

(v) Since its discovery in 1981, scientists have studied the protein structure of HIV in order to prevent its transmission. The World Health Organisation recommends heat treatment of breast-milk prior to giving it to the child, as a way to reduce the risk of HIV transmission to the baby in sub-Saharan Africa.

Explain how this treatment of breast-milk reduces the risk of HIV infection in infants.
(b) An example of a copper-containing enzyme is superoxide dismutase (SOD) that aids in the disproportionation of the strongly oxidising superoxide ion, $O_2^-$ to oxygen and hydrogen peroxide. Thus, they are an important antioxidant defense in nearly all cells exposed to oxygen, thereby protecting the body from harm.

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$$

(i) The activity of SOD hinges on the active site Cu$^{2+}$ ion.

By referring to the following $E^\circ$ data, suggest a mechanism for the catalysis of the disproportionation of $O_2^-$ by SOD.

You may represent the oxidised and reduced forms of the enzyme as SOD–Cu$^{2+}$ and SOD–Cu$^+$ respectively.

<table>
<thead>
<tr>
<th>$E^\circ$/ V</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.33</td>
<td>$O_2 + e^- \rightleftharpoons O_2^-$</td>
</tr>
<tr>
<td>+0.89</td>
<td>$O_2^- + e^- + 2H^+ \rightleftharpoons H_2O_2$</td>
</tr>
<tr>
<td>+0.42</td>
<td>SOD–Cu$^{2+}$ + e$^-$ $\rightleftharpoons$ SOD–Cu$^+$</td>
</tr>
</tbody>
</table>

(ii) State the type of catalysis and explain how SOD–Cu$^{2+}$ can act as a catalyst.

(iii) With the aid of a sketch of the Boltzmann distribution, explain how the presence of a catalyst affects the rate of reaction.

(iv) The secondary structure of SOD is composed mainly of beta-pleated sheets, as well as some regions of alpha-helices.

Draw a diagram of the beta-pleated sheet, showing the bonding which maintains the structure of the secondary structure of the enzyme.

[11]

[Total: 20]
Ginger has been used as a natural remedy for many ailments for centuries. Researchers around the world are finding that ginger works wonders in the treatment of everything from cancer to migraines. Ginger consists of many chemicals. Vitamin C and chlorogenic acid are two of the chemicals present in ginger.

(a) The structure of vitamin C and its reaction pathway is shown below.

(i) Draw the structural formula of the compound formed when vitamin C reacts with hot acidified potassium dichromate(VI).

(ii) Compound A undergoes elimination to produce compounds B and D. State and explain which compound is the major product.

(iii) Determine the maximum number of stereoisomers of compound D. Draw the pair that has the same boiling point.
(b) The structure of chlorogenic acid and its reaction pathway is shown below.

![Diagram of chlorogenic acid and compounds F and G, with steps 1, 2, and 3]

(i) Compound F can be converted to compound G in two steps. Suggest reagents and conditions for steps 2 and 3.

(ii) Draw the structures of compounds formed when compound G reacts with

   |   |   |
   | I  | H₂, Ni(s), 200°C |
   | II | NaBH₄ in methanol |

(c) Ginger also contains nutrients like magnesium. Magnesium is a vital component of a healthy human diet. Magnesium taken in the proper amount plays a role in preventing both stroke and heart attack.

(i) Describe what is observed when a piece of magnesium ribbon is burnt in air.

(ii) The product obtained in (i) is placed in a beaker of water containing a few drops of universal indicator. State the observation(s) and write equations for the reaction(s) that occur.
(d) Sketch a graph of the pH of the solution when the chlorides of the elements from sodium to phosphorus are added separately to water. Label your graph clearly. [2]

(e) Hydrofluoric acid dissociates in water according to the following equation:

\[
\Delta H^\circ_{\text{dissociation}} \quad \text{HF}(aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)
\]

The following are some enthalpy changes related to hydrogen fluoride.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH°/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>First electron affinity of fluorine/ kJ mol⁻¹</td>
<td>-328</td>
</tr>
<tr>
<td>Standard enthalpy change of hydration of fluoride ion / kJ mol⁻¹</td>
<td>-506</td>
</tr>
<tr>
<td>Standard enthalpy change of reaction, HF(aq) → HF(g) / kJ mol⁻¹</td>
<td>+39</td>
</tr>
<tr>
<td>Standard enthalpy change of hydration of hydrogen ion / kJ mol⁻¹</td>
<td>-1090</td>
</tr>
</tbody>
</table>

(i) By using the data provided and other relevant data from the *Data Booklet*, construct an energy cycle and calculate the standard enthalpy change of dissociation of hydrofluoric acid.

(ii) Aqueous hydrofluoric acid is a weak acid under standard conditions. One explanation for the relatively weaker acid strength of hydrofluoric acid is its negative standard entropy change of dissociation, ΔS°_{dissociation}. Account for the sign of ΔS°_{dissociation}. [6]

[Total: 20]
3 (a) Hydrazine (N₂H₄) is a colourless liquid with a slight odour like ammonia. However, the solubility of hydrazine in water is very much higher than that of ammonia.

Draw a diagram to show the bonding between a molecule of hydrazine and a molecule of water. Account for the difference in solubility of hydrazine and ammonia in water. [2]

(b) The Italian catalyst manufacturer Acta proposed using hydrazine as an alternative to hydrogen in fuel cells. The chief benefit of using hydrazine is that it can produce more energy than a similar hydrogen-oxygen cell.

The following diagram shows a typical hydrazine-oxygen fuel cell system incorporated with an anion exchange membrane between the electrodes.

(i) Write the two ion-electron half equations for the reactions that take place at each electrode. Hence, write an overall equation for the cell reaction.

(ii) Given that $E^\circ(N_2/N_2H_4)$ is -1.16 V, calculate the cell e.m.f. if the process takes place under standard conditions.

(iii) The hydrazine-oxygen fuel cell that is used to power a satellite produces an average current of 5 A per day. Assuming that the fuel cell is only 70% efficient, calculate the mass of hydrazine required in a day.

(iv) Based on the physical properties of hydrazine, suggest an advantage of the hydrazine-oxygen fuel cell over the hydrogen-oxygen fuel cell. [6]

(c) Wolff-Kishner reaction was discovered independently in 1911 by Ludwig Wolff in Germany and N. M. Kishner in Russia. It is a valuable synthetic method for converting ketones or aldehydes into alkanes using hydrazine in the presence of potassium hydroxide.

$$\text{R} = \text{C} = \text{O} + \text{H} - \text{N} - \text{N} \text{H} \text{H} \xrightarrow{\text{KOH}} \text{R} = \text{C} \text{H} + \text{N}_2 + \text{H}_2\text{O}$$
Indene \((C_9H_8)\) is a colourless organic liquid obtained from coal tar and used in preparing synthetic resins. It can be synthesised from phenylethene by the following route, incorporating Wolff-Kishner reaction.

\[
\begin{align*}
\text{phenylethene} & \quad \xrightarrow{\text{Br}_2(aq)} \quad A \quad \xrightarrow{\text{Step 1}} \quad \text{B} \quad \xrightarrow{\text{Step 2}} \\
& \quad \xrightarrow{\text{H}_2\text{SO}_4(aq), \text{heat}} \quad \\
& \quad \xrightarrow{\text{Step 3}} \\
& \quad \xrightarrow{\text{Step 4}} \\
& \quad \xrightarrow{\text{Step 5}} \\
& \quad \xrightarrow{\text{anhydrous } \text{FeCl}_3} \\
& \quad \xrightarrow{\text{Step 6}} \\
& \quad \xrightarrow{\text{H}_2\text{NNH}_2, \text{KOH}} \\
& \quad \xrightarrow{\text{Step 7}} \quad \text{indene}
\end{align*}
\]

(i) Give the structures of compounds A, B and D.

(ii) State the reagents and conditions for Steps 2, 4 and 5.

(iii) State the types of reaction occurring in Steps 6 and 7.

(iv) When aqueous silver nitrate is added to compound C, a white precipitate is observed immediately. The precipitate dissolves when dilute aqueous ammonia is added to it. The addition of aqueous sodium iodide to the resulting mixture produces a yellow precipitate. Identify the precipitates formed and account for the observation.

[12]

[Total: 20]
4 (a) A solution of carbonate reacts with \( H^+ \) in two stages.

\[
\begin{align*}
\text{CO}_3^{2-} & \xrightarrow{+H^+} \text{HCO}_3^- \xrightarrow{+H^+} \text{CO}_2 + \text{H}_2\text{O} \\
\text{pK}_{b_1} & \text{pK}_{b_2}
\end{align*}
\]

The pH changes during the addition of 0.200 mol dm\(^{-3}\) nitric acid to a 20.0 cm\(^3\) solution of sodium carbonate and sodium hydrogencarbonate are shown below.

(i) A list of indicators and their pK\(a\) values is given below.

<table>
<thead>
<tr>
<th>indicator</th>
<th>thymol blue</th>
<th>methyl yellow</th>
<th>methyl red</th>
<th>cresol red</th>
<th>thymolphthalein</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK(a)</td>
<td>1.7</td>
<td>3.1</td>
<td>5.1</td>
<td>8.3</td>
<td>9.2</td>
</tr>
</tbody>
</table>

From the given list of indicators, choose two suitable indicators that can be used to determine the two end-points in the titration. Explain your choice.

(ii) Calculate the concentration, in g dm\(^{-3}\), of sodium carbonate present in the original solution, given that the end-point between B and C occurs after 8.40 cm\(^3\) of nitric acid is added.

(iii) Calculate the concentration, in g dm\(^{-3}\), of sodium hydrogencarbonate present in the original solution, given that the end-point between D and E occurs after 18.80 cm\(^3\) of nitric acid is added.

[4]
(b) Dicarboxylic acids ionise in two stages.

\[ \text{HO}_2\text{C}-(\text{CH}_2)_n\text{CO}_2\text{H} \overset{-\text{H}^+}{\longrightarrow} \text{HO}_2\text{C}-(\text{CH}_2)_n\text{CO}_2^- \quad \overset{-\text{H}^+}{\longrightarrow} \text{O}_2\text{C}-(\text{CH}_2)_n\text{CO}_2^- \]

The following table compares the pK\(_a\) values of three dicarboxylic acids.

<table>
<thead>
<tr>
<th>acid</th>
<th>formula</th>
<th>pK(_{a1})</th>
<th>pK(_{a2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic</td>
<td>HO(_2)C–CO(_2)H</td>
<td>1.25</td>
<td>4.27</td>
</tr>
<tr>
<td>malonic</td>
<td>HO(_2)C–CH(_2)–CO(_2)H</td>
<td>2.85</td>
<td>5.70</td>
</tr>
<tr>
<td>succinic</td>
<td>HO(_2)C–(CH(_2))(_2)–CO(_2)H</td>
<td>4.21</td>
<td>5.64</td>
</tr>
</tbody>
</table>

(i) Explain why succinic acid has the highest pK\(_{a1}\) value.

(ii) An amphiprotic species is one that reacts with an acid and a base. The monocarboxylate ion of a dicarboxylic acid, HO\(_2\)C–(CH\(_2\))\(_n\)–CO\(_2\)\(^-\), is an amphiprotic species.

The pH of an amphiprotic species is given by the following expression.

\[ \text{pH} = \frac{1}{2}(\text{pK}_{a1} + \text{pK}_{a2}) \]

Using malonic acid as an example, write two equations to show that its monocarboxylate ion is an amphiprotic species.

(iii) The pH-volume added curve when 55 cm\(^3\) of 0.20 mol dm\(^{-3}\) NaOH is added to 25 cm\(^3\) of 0.20 mol dm\(^{-3}\) oxalic acid is shown below.

Calculate the pH of the curve at points X, Y and Z.
(c) Thermal decomposition of the calcium salt of oxalic acid, calcium oxalate, produces calcium oxide and oxides of carbon.

The graph below is an Ellingham diagram, which shows the variation in the standard Gibbs free energy change of formation, $\Delta G_f^\circ$, with temperature, $T$, for various oxides.

(i) Which oxide, calcium oxide, zinc oxide or silver(I) oxide, could be decomposed by heat at 1000 K? Explain your choice.

(ii) What does the gradient of the graph in the Ellingham diagram represent? Hence, explain why the gradient for $2C + O_2 \rightarrow 2CO$ is as shown.

(iii) From the Ellingham diagram, find the $\Delta G^\circ$ values of the following reactions at 1500 K.

   I. $2C(s) + O_2(g) \rightarrow 2CO(g)$
   II. $2Zn(s) + O_2(g) \rightarrow 2ZnO (s)$

(iv) Use your answer in (iii) to calculate $\Delta G^\circ$ value for the reaction in which carbon reduces zinc oxide at 1500 K.

   $2ZnO + 2C \rightarrow 2Zn + 2CO$

   Hence, comment on the feasibility of the reaction at 1500 K.

[5]
(d) In **no more than 3 steps**, suggest how each of the following transformations can be achieved. You are required to state the reagents and conditions for each step and give the structures of the intermediate compounds.

(i)  
\[
\text{HO-\text{C-C-C-C-C-H}} \xrightarrow{\text{Br}} \text{HO-\text{C-C-C-C-C-C}} \xrightarrow{\text{O}} \text{HO-\text{C-C-C-C-C-O}}
\]

(ii)  
\[
\text{CH}_3 \xrightarrow{\text{C}} \text{CH}_3 \xrightarrow{\text{O}} \text{CH}_3 \xrightarrow{\text{O}} \text{CH}_3 \xrightarrow{\text{O}} \text{CH}_3 \xrightarrow{\text{O}}
\]

[5]

[Total: 20]
Magnesium carbonate occurs naturally in several forms. Due to its hygroscopic properties, anhydrous magnesium carbonate is used in organic reactions to remove moisture.

The decomposition temperature of magnesium carbonate is 540 °C. Explain how you would expect the decomposition temperature of barium carbonate to differ from magnesium carbonate. [3]

The solubility of magnesium carbonate is 0.267 g dm⁻³.

(i) Calculate the solubility product, $K_{sp}$, of magnesium carbonate.

(ii) To a 1.0 dm³ saturated solution of magnesium carbonate, 50.0 cm³ of 1.00 mol dm⁻³ aqueous magnesium chloride was added. Find the mass of precipitate formed. [4]

Compound A (C₁₁H₂₂) decolourises aqueous bromine. Compound A was heated with a mixture of aqueous sodium hydroxide and potassium manganate(VII). After the reaction was completed (assuming 100% yield), the reaction mixture was extracted several times with an organic solvent.

The aqueous and organic layers were then collected separately. Acidification of the aqueous layer yielded compound B ($M_r = 102$), which rotated the plane of polarised light. Compound B produced a colourless gas with sodium metal.

(i) Use all of the information to determine the identity of functional group present in

   I  compound A,
   II  compound B.

For each functional group you identify, explain how you came to your decision.

(ii) Deduce the molecular formula of compound B and hence, draw its displayed formula.

(iii) Explain why the salt of compound B was found in the aqueous layer after the separation of the reaction mixture.

The organic layer was then distilled to give compound C (C₆H₁₂O). Warming compound C with aqueous alkaline iodine, followed by controlled addition of concentrated hydrochloric acid produced compound B.

(iv) Propose the structure of compound C and give a balanced equation for its reaction with aqueous alkaline iodine.

(v) Hence or otherwise, deduce the structure of compound A.
Compound C was converted to compound E via the following reaction scheme.

\[
\begin{align*}
\text{Compound C} \quad &\xrightarrow{\text{1. HCN(aq), NaCN, 10-20 °C}} \quad \text{Compound D} \\
(C_6H_{12}O) \quad &\xrightarrow{\text{2. H}_2\text{SO}_4(aq)} \quad (C_7H_{14}O_3) \\
\text{Compound D} \quad &\text{concentrated H}_2\text{SO}_4, \quad \text{heat under reflux} \\
\text{Compound E} \quad &\quad (C_{14}H_{24}O_4)
\end{align*}
\]

(vi) Draw the structures of compounds D and E.

(vii) Describe a simple chemical test to distinguish between compounds C and D, clearly stating how each compound behaves in the test. You should not use any of the reagents and conditions outlined in this question.

[13]

[Total: 20]
PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

CHEMISTRY 9647/03

Paper 3 Free Response

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number and name on all work you hand in.
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At the end of the examination, fasten all your work securely together.

This document consists of 15 printed pages.
Enzymes are biological molecules that catalyse chemical reactions. Almost all chemical reactions in a biological cell need enzymes in order to occur at rates sufficient for life.

(a) Acquired Immuno-Deficiency Syndrome (AIDS) is a disease of the human immune system caused by the Human Immunodeficiency Virus (HIV). HIV-1 Protease is an enzyme which speeds up the reproduction of HIV. In the development of anti-HIV drugs, scientists often study the amino acid sequence of the HIV-1 Protease to understand how this enzyme displays its biological properties in the human body.

(i) A segment of the polypeptide structure of HIV-1 Protease, containing 10 amino acids, was digested using an enzyme and the following fragments were obtained:

- leu – asn – phe
- ile – gly – cys – thr – leu
- leu – thr – glu – ile – gly

Deduce the primary structure of this segment of HIV-1 Protease.


(ii) A segment of the HIV strand acts as a substrate, which binds to the active site of the HIV-1 Protease which speeds up the reproduction of the HIV virus. The rate of this enzyme-catalysed reaction is investigated and can be represented by the following graph.

Explain the difference in the rate of reaction at high and low concentrations of substrate.

At low substrate concentration,
- Rate of reaction increases linearly / reaction is first order wrt the substrate concentration as active sites of the enzyme are not fully occupied.

At high substrate concentration,
- Rate of reaction is constant / rate is independent of substrate concentration / reaction is zero order wrt the substrate concentration as all active sites occupied.
(iii) The structural formulae of the three most common amino acids present in the protein chain in HIV-1 Protease are shown below.

\[
\begin{align*}
\text{glutamic acid (glu)} & : \\
\text{leucine (leu)} & : \\
\text{cysteine (cys)} & :
\end{align*}
\]

In how many different ways can these three amino acids be coupled by peptide bonds to form a tripeptide? Draw the structural formula of one such peptide.

\[3! = 6 \text{ ways}\]

(iv) The side chains of these three amino acids are responsible for maintaining the tertiary structure of HIV-1 Protease.

State and draw the type of side-chain interaction between two cysteine (cys) residues.

State the type of reaction that is involved in the formation of the side-chain interaction.

**Accept other correct tripeptides**
Type of reaction: oxidation

(v) Since its discovery in 1981, scientists have studied the protein structure of HIV in order to prevent its transmission. The World Health Organisation recommends heat treatment of breast-milk prior to giving it to the child, as a way to reduce the risk of HIV transmission to the baby in sub-Saharan Africa. Explain how this treatment of breast-milk reduces the risk of HIV infection in infants.

Heating leads to denaturation of protein. When temperature increases, molecular vibrations agitate the polypeptide chains sufficiently to overcome the weak interactions that stabilise protein conformation. (Also accept loss of 3d conformation)

As the secondary and tertiary structures are broken down, it results in the loss of function of the HIV protein.

(b) An example of a copper-containing enzyme is superoxide dismutase (SOD) that aids in the disproportionation of the strongly oxidising superoxide ion, \( \text{O}_2^- \) to oxygen and hydrogen peroxide. Thus, they are an important antioxidant defense in nearly all cells exposed to oxygen, thereby protecting the body from harm.

\[
2\text{O}_2^- + 2\text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}_2
\]

(i) The activity of SOD hinges on the active site \( \text{Cu}^{2+} \) ion.

By referring to the following \( E^\circ \) data, suggest a mechanism for the catalysis of the disproportionation of \( \text{O}_2^- \) by SOD.

You may represent the oxidised and reduced forms of the enzyme as SOD–Cu\(^{2+}\) and SOD–Cu\(^+\) respectively.

| \( E^\circ / V \) | \( \text{O}_2 + e^- \) | \( \text{O}_2^- \) |
|------------------|-----------------------------|
| –0.33            | \( \text{O}_2^- + e^- + 2\text{H}^+ \) | \( \text{H}_2\text{O}_2 \) |
| +0.89            | SOD–Cu\(^{2+}\) + e^- E(\text{SOD–Cu}^{+}) | +0.42 |

\( SOD–Cu^{2+} \) + e^- Error! Objects cannot be created from editing field codes. SOD–Cu\(^+\) respectively.
Step 1: SOD–Cu$^{2+}$ + O$_2^-$ → O$_2$ + SOD–Cu$^+$
$E^\circ_{\text{cell}} = +0.42 - (-0.33) = +0.75V (> 0, hence feasible)$

Step 2: SOD–Cu$^+$ + O$_2^-$ + 2H$^+$ → H$_2$O$_2$ + SOD–Cu$^{2+}$
$E^\circ_{\text{cell}} = +0.89 - (+0.42) = +0.47V (> 0, hence feasible)$

(ii) State the type of catalysis and explain how SOD-Cu$^{2+}$ can act as a catalyst.
Homogenous catalysis
The catalytic effect is due to the ability of Cu to have variable oxidation states.

(iii) With the aid of a sketch of the Boltzmann distribution, explain how the presence of a catalyst affects the rate of reaction.

When a catalyst is used in a reaction, it:
- increases the rate of the reaction by providing an alternative reaction pathway with lower activation energy
- increases the number of reacting particles with energy $\geq E_a$
- increases the number of effective collisions per unit time
- increases the rate of reaction.

[1] diagram
(iv) The secondary structure of SOD is composed mainly of beta-pleated sheets, as well as some regions of alpha-helices.

Draw a diagram of the beta-pleated sheet, showing the bonding which maintains the structure of the secondary structure of the enzyme.
Ginger has been used as a natural remedy for many ailments for centuries. Researchers around the world are finding that ginger works wonders in the treatment of everything from cancer to migraines. Ginger consists of many chemicals. Vitamin C and chlorogenic acid are two of the chemicals present in ginger.

(a) \[
\begin{align*}
\text{vitamin C} & \quad \rightarrow \quad \text{compound A} \\
\text{compound B} & \quad + \quad \text{compound D}
\end{align*}
\]

(i) Draw the structures of compounds formed when vitamin C reacts with hot acidified potassium dichromate(VI).
Compound A undergoes elimination to produce compounds B and D.

State and explain which compound is the major product.

**Compound B should be the major product.**

Alkene B is more highly substituted than alkene D. By Satyzev’s rule, the more highly substituted alkene is the major product.

OR

Alkene B is a more stable product as it has an extended conjugate system (involving both alkenes and the ketone group).

(iii) Determine the maximum number of stereoisomers of compound D. Draw the pair that has the same boiling point.

**Maximum no. of stereoisomers = \(2^2 = 4\)**

(b) The structure of chlorogenic acid and its reaction pathway is shown below.
(i) Compound F can be converted to compound G in two steps. Suggest reagents and conditions for steps 2 and 3.

**Step 2** – dilute HNO₃ / HNO₃(aq)
**Step 3** – Sn, concentrated HCl, heat, followed by controlled addition of NaOH(aq)

(ii) Draw the structures of the compounds formed when compound G reacts with

I  H₂, Ni(s), 200°C

II  NaBH₄ in methanol
(c) Ginger also contains nutrients like magnesium. Magnesium is a vital component of a healthy human diet. Magnesium taken in the proper amount plays a role in preventing both stroke and heart attack.

(i) Describe what is observed when a piece of magnesium ribbon is burnt in air.

Mg burns to give a bright white flame. A white solid residue (of MgO) is left behind.

(ii) The product obtained in (i) is placed in a beaker of water containing a few drops of universal indicator. State the observation(s) and write equations for the reaction(s) that occur.

\[ \text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg(OH)}_2 \]

Magnesium oxide is sparingly soluble in water.

\[ \text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq) \]

Green solution turns blue.

(d) Sketch a graph of the pH of the solution when the chlorides of the elements from sodium to phosphorus are added separately to water. Label your graph clearly. [2]
Hydrofluoric acid dissociates in water according to the following equation:

\[
\Delta H^\circ_{\text{dissociation}} \quad \text{HF(aq)} \quad \text{H}^+(aq) \quad + \quad \text{F}^-(aq)
\]

The following are some enthalpy changes related to hydrogen fluoride.

<table>
<thead>
<tr>
<th>First electron affinity of fluorine/ kJ mol(^{-1})</th>
<th>-328</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard enthalpy change of hydration of fluoride ion/ kJ mol(^{-1})</td>
<td>-506</td>
</tr>
<tr>
<td>Standard enthalpy change of reaction, HF(aq) → HF(g)/ kJ mol(^{-1})</td>
<td>+39</td>
</tr>
<tr>
<td>Standard enthalpy change of hydration of hydrogen ion/ kJ mol(^{-1})</td>
<td>-1090</td>
</tr>
</tbody>
</table>

(i) By using the data provided and other relevant data from the Data Booklet, construct an energy cycle and calculate the standard enthalpy change of dissociation of hydrofluoric acid.

\[
\Delta H^\circ_{\text{dissociation}} (HF) = \Delta H^\circ_1 + \text{BE(H-F)} + 1\text{st I.E.(H)} + 1\text{st E.A.(F)} + \Delta H^\circ_{\text{hyd}(\text{H}^+)} + \Delta H^\circ_{\text{hyd}(\text{F}^-)}
\]

\[
= +39 + (+562) + (+1310) + (-328) + (-1090) + (-506)
\]

\[
= -13.0 \text{ kJ mol}^{-1}
\]

(ii) Aqueous hydrofluoric acid is a weak acid under standard conditions. One explanation for the relatively weaker acid strength of hydrofluoric acid is its negative standard entropy change of dissociation, \(\Delta S^\circ_{\text{dissociation}}\). Account for the sign of \(\Delta S^\circ_{\text{dissociation}}\).

A negative sign of \(\Delta S^\circ_{\text{dissociation}}\) indicates a decrease in disorderliness of the system.

Small anionic radius of \(\text{F}^-\) ion leads to a high charge density, resulting in a more regular arrangement of water molecules around the \(\text{F}^-\) ions.

[6]

[Total: 20]
3 (a) Hydrazine (N₂H₄) is a colourless liquid with a slight odour like ammonia. However, the solubility of hydrazine in water is very much higher than that of ammonia.

Draw a diagram to show the bonding between a molecule of hydrazine and a molecule of water. Account for the difference in solubility of hydrazine and ammonia in water.

Each hydrazine molecule has two -NH₂ groups, which allow it to form more extensive hydrogen bonds with water molecules than ammonia. Hence, hydrazine has a higher solubility than ammonia.

(b) The Italian catalyst manufacturer Acta proposed using hydrazine as an alternative to hydrogen in fuel cells. The chief benefit of using hydrazine is that it can produce more energy than a similar hydrogen-oxygen cell.

The diagram below shows a typical hydrazine-oxygen fuel cell system incorporated with an anion exchange membrane between the electrodes.

(i) Write the two ion-electron half equations for the reactions that take place at each electrode. Hence, write an overall equation for the cell reaction.

Anode: N₂H₄ (l) + 4OH⁻ (aq) → N₂(g) + 4 H₂O(l) + 4 e⁻
Cathode: \( \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 4\text{OH}^- (\text{aq}) \)
Overall: \( \text{N}_2\text{H}_4 (\text{l}) + \text{O}_2 (\text{g}) \rightarrow \text{N}_2 (\text{g}) + 2\text{H}_2\text{O}(\text{l}) \)

(ii) Given that \( E^\circ (\text{N}_2/\text{N}_2\text{H}_4) \) is -1.16 V, calculate the cell e.m.f. if the process takes place under standard conditions.

\[
E^\circ_{\text{cell}} = E^\circ (\text{Reduction}) + E^\circ (\text{Oxidation}) = + 0.40 \text{ V} + (+ 1.16) = + 1.56 \text{ V}
\]

(iii) The hydrazine-oxygen fuel cell that is used to power a satellite produces an average current of 5 A per day. Assuming that the fuel cell is only 70% efficient, calculate the mass of hydrazine required in a day.

\[
\text{Total charge generated per day} = I \times t \times \frac{100}{70} = 5 \times (24 \times 60 \times 60) \times \frac{100}{70} = 617100 \text{ C}
\]

Amount of electron transferred = \( \frac{Q}{F} = \frac{617100}{96500} = 6.40 \text{ mol} \)

1 mol \( \text{N}_2\text{H}_4 \equiv 4 \text{ mol of e}^- \)

Amount of \( \text{N}_2\text{H}_4 \) required = \( \frac{6.40}{4} = 1.60 \text{ mol} \)

Mass of \( \text{N}_2\text{H}_4 \) required = \( 1.60 \times [2(14.0)+4(1.0)] = 51.2 \text{ g} \) (3sf)

(iv) Based on the physical properties of hydrazine, suggest an advantage of the hydrazine-oxygen fuel cell over the hydrogen-oxygen fuel cell.

**Hydrazine is a liquid at room temperature and can be handled and stored more easily than hydrogen gas.**

(c) Wolff-Kishner reaction was discovered independently in 1911 by Ludwig Wolff in Germany and N. M. Kishner in Russia. It is a valuable synthetic method for converting ketones or aldehydes into alkanes using hydrazine in the presence of potassium hydroxide.

\[
\text{C} \begin{array}{c} \text{R} \text{O} \\
+ \\
\text{H} \begin{array}{c} \text{H} \text{N} \text{N} \text{H} \\
\text{R} \end{array} \text{H} \text{KOH} \end{array} \rightarrow \text{C} \begin{array}{c} \text{R} \text{H} \\
+ \\
\text{N}_2 + \text{H}_2\text{O} \end{array}
\]

Indene (C9H8) is a colourless organic liquid obtained from coal tar and used in preparing synthetic resins. It can be synthesised from phenylethene by the
following route, incorporating Wolff-Kishner reaction.

\[
\begin{align*}
\text{phenylethene} & \quad \xrightarrow{\text{Br}_2(aq)} \quad A & \quad \xrightarrow{\text{Step 2}} \quad B \\
\text{phenylethene} & \quad \xrightarrow{\text{Step 1}} \quad A & \quad \xrightarrow{\text{Step 2}} \quad B \\
& \quad \xrightarrow{\text{H}_2\text{SO}_4(aq), \text{heat}} \quad \text{Step 3} \\
& \quad \xrightarrow{\text{Step 4}} \quad \text{COOH} \\
& \quad \xrightarrow{\text{Step 5}} \quad \text{COCl} \\
& \quad \xrightarrow{\text{anhydrous FeCl}_3} \quad \text{D} \\
& \quad \xrightarrow{\text{H}_2\text{NNH}_2, \text{KOH}} \quad \text{indene}
\end{align*}
\]

(i) Give the structures of compounds A, B and D.

(ii) State the reagents and conditions for Steps 2, 4 and 5.

- **Step 2:** KCN in ethanol, heat
- **Step 4:** excess concentrated H₂SO₄, 170°C
- **Step 5:** PC₁₅
  *Also accept PC₃, warm
  OR SOC₂, warm
(iii) State the types of reaction occurring in Steps 6 and 7.

**Step 6: Electrophilic substitution**  
**Step 7: Reduction**

(iv) When aqueous silver nitrate is added to compound C, a white precipitate is observed immediately. The precipitate dissolves when dilute aqueous ammonia is added to it. The addition of aqueous sodium iodide to the resulting mixture produces a yellow precipitate. Identify the precipitates formed and account for the observation.

**White precipitate formed is AgCl is formed.**

In the presence of aqueous ammonia, aqueous Ag⁺ ions react to form the diamminesilver(I) complex, Ag(NH₃)₂⁺. The formation of the complex, decreases [Ag⁺(aq)], lowering its ionic product. Thus, ionic product falls below the K_{sp} of AgCl, causing it to dissolve.

When aqueous sodium iodide is added to the resulting solution, a yellow precipitate of AgI is formed. As the K_{sp} (AgI) is extremely small, the ionic product exceeds its K_{sp}, accounting for the formation of the precipitate.

[Total: 20]

4 (a) A solution of carbonate reacts with H⁺ in two stages.

$$\text{CO}_3^{2-} \xrightarrow{+H^+} \text{HCO}_3^- \xrightarrow{+H^+} \text{CO}_2 + \text{H}_2\text{O}$$

The pH changes during the addition of 0.200 mol dm⁻³ nitric acid to a 20.0 cm³ solution of sodium carbonate and sodium hydrogen carbonate are shown below.
(i) A list of indicators and their $pK_a$ values is given below.

<table>
<thead>
<tr>
<th>indicator</th>
<th>thymol blue</th>
<th>methyl yellow</th>
<th>methyl red</th>
<th>cresol red</th>
<th>thymolphthalein</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_a$</td>
<td>1.7</td>
<td>3.1</td>
<td>5.1</td>
<td>8.3</td>
<td>9.2</td>
</tr>
</tbody>
</table>

From the given list of indicators, choose two suitable indicators that can be used to determine the two end-points in the titration. Explain your choice.

1st indicator: cresol red  
2nd indicator: methyl yellow  
both correct

$pK_a$ of indicator matches the pH change at equivalence point  
OR  
Equivalence point pH lies within the working range of the indicator.

(ii) Calculate the concentration, in g dm$^{-3}$, of sodium carbonate present in the original solution, given that the end-point between B and C occurs after 8.40 cm$^3$ of nitric acid is added.

\[
\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^{-}
\]

amount of Na$_2$CO$_3$ = amount of HNO$_3$ = 0.00168 mol

concentration of Na$_2$CO$_3$ = \[
\frac{0.00168}{20.0} \times 106 = 8.90 \text{ g dm}^{-3}
\]

(iii) Calculate the concentration, in g dm$^{-3}$, of sodium hydrogen carbonate present in the original solution, given that the end-point between D and E occurs after 18.80 cm$^3$ of nitric acid is added.

\[
\text{HCO}_3^{-} + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]

volume of HNO$_3$ used to react with the total amount of HCO$_3^{-}$
\[ 18.80 - 8.40 = 10.40 \text{ cm}^3 \]

total amount of \( \text{HCO}_3^- \) = amount of \( \text{HNO}_3 \) used = 0.00208 mol

At first end-point, \( 1\text{CO}_3^{2-} = 1\text{HCO}_3^- \),
amount of \( \text{HCO}_3^- \) formed from \( \text{Na}_2\text{CO}_3 \) = 0.00168 mol

\[ \therefore \text{original amount of } \text{HCO}_3^- = 0.00208 - 0.00168 = 0.0004 \text{ mol} \]

concentration of \( \text{NaHCO}_3 \) = \[
\frac{0.0004 \times 84.0}{20.0 \times 1000} = 1.68 \text{ g dm}^{-3}
\]

(b) Dicarboxylic acids ionise in two stages.

\[
\text{HO}_2\text{C–(CH}_2\text{)}_n\text{–CO}_2\text{H} \xrightarrow{-\text{H}^+}{pK_{a1}} \text{HO}_2\text{C–(CH}_2\text{)}_n\text{–CO}_2^- \xrightarrow{-\text{H}^+}{pK_{a2}} ^{\text{O}2\text{C–(CH}_2\text{)}_n\text{–CO}_2^-}
\]

The following table compares the \( pK_a \) values of three dicarboxylic acids.

<table>
<thead>
<tr>
<th>acid</th>
<th>formula</th>
<th>( pK_{a1} )</th>
<th>( pK_{a2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxalic</td>
<td>( \text{HO}_2\text{C–CO}_2\text{H} )</td>
<td>1.25</td>
<td>4.27</td>
</tr>
<tr>
<td>malonic</td>
<td>( \text{HO}_2\text{C–CH}_2\text{–CO}_2\text{H} )</td>
<td>2.85</td>
<td>5.70</td>
</tr>
<tr>
<td>succinic</td>
<td>( \text{HO}_2\text{C–(CH}_2\text{)}_2\text{–CO}_2\text{H} )</td>
<td>4.21</td>
<td>5.64</td>
</tr>
</tbody>
</table>

(i) Explain why succinic acid has the highest \( pK_{a1} \) value.

In succinic acid, the two \( –\text{CO}_2\text{H} \) groups are unable to form intramolecular hydrogen bond to stabilise the negative charge of the monoanion formed after the first dissociation.

(ii) An amphiprotic species is one that reacts with an acid and a base. The monocarboxylate ion of a dicarboxylic acid, \( \text{HO}_2\text{C–(CH}_2\text{)}_n\text{–CO}_2^- \), is an amphiprotic species.

The \( \text{pH} \) of an amphiprotic species is given by the following expression.

\[
\text{pH} = \frac{1}{2}(pK_{a1} + pK_{a2})
\]

Using malonic acid as an example, write two equations to show that its monocarboxylate ion is an amphiprotic species.

\[
\begin{align*}
\text{HO}_2\text{CCH}_2\text{CO}_2^- + \text{H}^+ & \rightarrow \text{HO}_2\text{CCH}_2\text{CO}_2\text{H} \\
\text{HO}_2\text{CCH}_2\text{CO}_2^- + \text{OH}^- & \rightarrow ^{\text{O}}\text{O}_2\text{CCH}_2\text{CO}_2^- + \text{H}_2\text{O}
\end{align*}
\]
(iii) The pH-volume added curve when 55 cm$^3$ of 0.20 mol dm$^{-3}$ NaOH is added to 25 cm$^3$ of 0.20 mol dm$^{-3}$ oxalic acid is shown below.

![pH-volume added curve](image)

Calculate the pH of the curve at points X, Y and Z.

X - Initial pH = 0.974

\[
[H_3O^+]^2 = K_{a1}[\text{acid}] = (10^{-1.25})(0.20) = 0.01124 \text{ mol}^2 \text{ dm}^{-6}
\]

pH = – lg[H$_3$O$^+$] = – lg $\sqrt{(0.01124)} = 0.974$ (3 s. f.)

Y - pH at 1st equiv. point = $\frac{1}{2}(pK_{a1} + pK_{a2})= \frac{1}{2}(1.25 + 4.27) = 2.76$

(HO$_2$CCO$_2^-$ is an amphiprotic species)

Z - pH at MBC$_2$ (when [HO$_2$CCO$_2^-$] = [–O$_2$CCO$_2^–$]) = pK$_{a2}$ = 4.27

(c) Thermal decomposition of the calcium salt of oxalic acid, calcium oxalate, produces calcium oxide and oxides of carbon.

The graph below is an Ellingham diagram, which shows the variation in the standard Gibbs free energy change of formation, $\Delta G_f^\circ$, with temperature, T, for various oxides.
(i) Which oxide, calcium oxide, zinc oxide or silver(I) oxide, could be decomposed by heat at 1000 K? Explain your choice.

Silver(I) oxide
\[ \Delta G < 0 \text{ for the decomposition of } 2\text{Ag}_2\text{O} \rightarrow 4\text{Ag} + \text{O}_2 \]

(ii) What does the gradient of the graph in the Ellingham diagram represent? Hence, explain why the gradient for \(2\text{C} + \text{O}_2 \rightarrow 2\text{CO}\) is as shown.

Gradient represents \(-\Delta S^\theta\) (equation of line is \(\Delta G^\theta = -T\Delta S^\theta + \Delta H^\theta\)). A negative gradient implies that \(\Delta S^\theta\) is positive. An increase in disorderliness of the system (\(\Delta S^\theta > 0\)) is due to an increase in amount of gases (from 1 to 2 mol) as the reaction proceeds.

(iii) From the Ellingham diagram, find the \(\Delta G^\theta\) values of the following reactions at 1500 K.

\[
\begin{align*}
\text{I} & \quad 2\text{C}(s) + \text{O}_2(g) \rightarrow 2\text{CO}(g) \\
\text{II} & \quad 2\text{Zn}(s) + \text{O}_2(g) \rightarrow 2\text{ZnO}(s)
\end{align*}
\]

\[
\begin{align*}
\text{2C} + \text{O}_2 & \rightarrow \text{2CO} \quad \Delta G^\theta = -500 \text{ kJ mol}^{-1} \quad \cdots \cdots \ (1) \\
\text{2Zn} + \text{O}_2 & \rightarrow \text{2ZnO} \quad \Delta G^\theta = -300 \text{ kJ mol}^{-1} \quad \cdots \cdots \ (2)
\end{align*}
\]

(iv) Use your answer in (iii) to calculate \(\Delta G^\theta\) value for the reaction in which carbon reduces zinc oxide at 1500 K.

\[
2\text{ZnO} + 2\text{C} \rightarrow 2\text{Zn} + 2\text{CO}
\]
Hence, comment on the feasibility of the reaction at 1500 K.

\[2\text{ZnO} \rightarrow 2\text{Zn} + \text{O}_2 \quad \Delta G^\circ = +300 \text{ kJ mol}^{-1} \quad \ldots\ldots(3)\]

(1) + (3) gives \[2\text{ZnO} + 2\text{C} \rightarrow 2\text{Zn} + 2\text{CO} \quad \Delta G^\circ = -200 \text{ kJ mol}^{-1}\]

The reaction is thermodynamically feasible at 1500 K.

(d) In no more than 3 steps, suggest how each of the following transformations can be achieved. You are required to state the reagents and conditions for each step and give the structures of the intermediate compounds.

(i)

\[
\begin{align*}
\text{HO-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} & \quad \text{Excess conc H}_2\text{SO}_4 \quad 170^\circ \text{C} \\
& \rightarrow \text{HO-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br} \\
& \rightarrow \text{HO-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \\
& \rightarrow \text{HO-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \\
\end{align*}
\]

(ii)

\[
\begin{align*}
\text{CH}_3-\text{C}_6\text{H}_4-\text{NO}_2 & \quad \rightarrow \text{CH}_3-\text{C}_6\text{H}_4-\text{COOH} \\
\end{align*}
\]
CH$_3$NO$_2$COOH

H$_2$SO$_4$(aq), KMnO$_4$(aq), heat
concentrated HNO$_3$, concentrated H$_2$SO$_4$, >55°C

[5]
[Total: 20]
Magnesium carbonate occurs naturally in several forms. Due to its hygroscopic properties, anhydrous magnesium carbonate is used in organic reactions to remove moisture.

The decomposition temperature of magnesium carbonate is 540 °C. Explain how you would expect the decomposition temperature of barium carbonate to differ from magnesium carbonate.

Ba\(^{2+}\) ion has a smaller ionic radius compared to Mg\(^{2+}\). Ba\(^{2+}\) ion has a lower charge density and hence is less polarising/ lower polarising power. Ba\(^{2+}\) ion polarises and weakens the C-O bond in CO\(_3^{2-}\) to a smaller extent than Mg\(^{2+}\). Thus, the C-O bond in BaCO\(_3\) is stronger. More energy is required to break the bond and hence the decomposition temperature of barium carbonate would be higher.

The solubility of magnesium carbonate is 0.267 g dm\(^{-3}\).

(i) Calculate the solubility product, \(K_{sp}\), of magnesium carbonate.

\[
M_r \text{MgCO}_3 = 24.3 + 12.0 + 3(16.0) = 84.3
\]

Solubility = \(\frac{0.267}{84.3}\) = \(3.17 \times 10^{-3}\) mol dm\(^{-3}\)

\[K_{sp} = (3.17 \times 10^{-3})^2 = 1.00 \times 10^{-5}\] mol\(^2\) dm\(^{-6}\)

(ii) To a 1.0 dm\(^3\) saturated solution of magnesium carbonate, 50.0 cm\(^3\) of 1.00 mol dm\(^{-3}\) aqueous magnesium chloride was added. Find the mass of precipitate formed.

Let the solubility of MgCO\(_3\) in MgCl\(_2\) be \(s\) mol dm\(^{-3}\).

Total volume = 1.0 + 0.0500 = 1.05 dm\(^3\)

\[[\text{Mg}^{2+}] = s + \left(\frac{1 \times 50}{1000} / 1.05\right) = s + 0.04762\]

\[
s(s + 0.04762) = 1 \times 10^{-5}
\]

\[
s(0.04762) = 1 \times 10^{-5} \text{ (since } 0.04762 \gg s)\]

\[
s = 2.100 \times 10^{-4}\] mol dm\(^{-3}\)

Amount of MgCO\(_3\) extracted = \(3.17 \times 10^{-3}\) – \((2.100 \times 10^{-4} \times 1.05)\) = \(2.950 \times 10^{-3}\) mol

Mass extracted = \(2.950 \times 10^{-3} \times 84.3\) = 0.249 g
(c) Compound A (C_{11}H_{22}) decolourises aqueous bromine. Compound A was heated with a mixture of aqueous sodium hydroxide and potassium manganate(VII). After the reaction was completed (assuming 100% yield), the reaction mixture was extracted several times with an organic solvent.

The aqueous and organic layers were then collected separately. Acidification of the aqueous layer yielded compound B (M_r = 102), which rotated the plane of polarised light. Compound B produced a colourless gas with sodium metal.

(i) Use all of the information to determine the identity of functional group present in

I compound A
II compound B.

For each functional group you identify, explain how you came to your decision.

**Compound A contains an alkene.**
*It has one degree of unsaturation and undergoes electrophilic addition with aqueous bromine. A undergoes oxidative cleavage/ strong oxidation with KMnO_4.*

**Compound B contains a carboxylic acid.**
*Alkenes undergo oxidative cleavage/ strong oxidation to form carbon dioxide, ketones or carboxylic acids.*
*Only carboxylic acid can react with sodium metal via redox reaction.*

(ii) Deduce the molecular formula of compound B and hence, draw its displayed formula.

\[
\text{C}_5\text{H}_{10}\text{O}_2
\]

(iii) Explain why the salt of compound B was found in the aqueous layer after the separation of the reaction mixture.

**The carboxylate anion, produced by strong oxidation of alkene A, can form favourable ion-dipole interactions with water, and is hence highly soluble in water.**
The organic layer was then distilled to give compound C \((\text{C}_6\text{H}_{12}\text{O})\). Warming compound C with aqueous alkaline iodine, followed by controlled addition of concentrated hydrochloric acid produced compound B.

(iv) Propose the structure of compound C and give a balanced equation for its reaction with aqueous alkaline iodine.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH} - \\
\text{C} - \\
\text{CH} \\
\text{CH} - \\
\text{C} - \\
\text{CH}_3
\end{array}
+ 3\text{I}_2 + 4\text{OH}^- \rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{CH} - \\
\text{C} - \\
\text{CH} \\
\text{CH} - \\
\text{C} - \\
\text{CH}_3
\end{array}
+ \text{CH}_2 + 3\text{I}^- + 3\text{H}_2\text{O}
\]

(v) Hence or otherwise, deduce the structure of compound A.

Compound C was converted to compound E via the following reaction scheme.

\[
\text{Compound C} \quad \text{HCN(aq), NaCN, 10-20 °C} \rightarrow \text{Compound D}
\]

\[
\text{C}_6\text{H}_{12}\text{O} \quad \text{C}_7\text{H}_{14}\text{O}_3
\]

\[
\text{Compound D} \quad \text{H}_2\text{SO}_4\text{(aq), heat under reflux} \rightarrow \text{Compound E}
\]

\[
\text{C}_7\text{H}_{14}\text{O}_3 \quad \text{C}_{14}\text{H}_{24}\text{O}_4
\]
(vi) Draw the structures of compounds D and E.

\[ \text{OH} \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3 \]
\[ \text{C} \quad \text{C} \quad \text{CH} \]
\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_2 \quad \text{CH}_3 \]
\[ \text{D} \]

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \]
\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \quad \text{CH}_3 \]
\[ \text{E} \]

(vii) Describe a simple chemical test to distinguish between compounds C and D, clearly stating how each compound behaves in the test. You should not use any of the reagents and conditions outlined in this question.

**Test:** Aqueous sodium carbonate, room temperature. Bubble any gas evolved into limewater.

Observation for C: No effervescence observed.
Observation for D: Effervescence observed. Gas evolved forms a white precipitate with limewater.

**OR**

**Test:** 2, 4- dinitrophenylhydrazine, room temperature.
Observation for C: Orange precipitate/ orange crystalline solid observed.
Observation for D: No orange precipitate observed.

[13]

[Total: 20]

End of Paper
READ THESE INSTRUCTIONS FIRST

Do not use staples, paper clips, highlighters, glue or correction fluid. Write your name, class, centre number and index number on the Answer Sheet in the spaces provided.

There are forty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D. Choose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

This document consists of 16 printed pages.
Section A

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

1. Methane was burned with a faulty Bunsen burner. As a result, a mixture of carbon dioxide and carbon monoxide was produced in a ratio of 98:2, together with water vapour.

   What was the volume of oxygen gas used when \( y \) dm\(^3\) of methane was burned?

   A \( \frac{0.01}{2} \cdot y \) dm\(^3\)
   B \( 2y - 0.01y \) dm\(^3\)
   C \( y - 0.01y \) dm\(^3\)
   D \( y - 0.01y \) dm\(^3\)

2. An ion of metal \( M \) can be oxidised by potassium manganate(VII) in acid solution to form \( MO_3^- \). In an experiment, \( 1.25 \times 10^{-3} \) mol of the ion of \( M \) required 37.5 cm\(^3\) of 0.0200 mol dm\(^{-3}\) potassium manganate(VII) for complete reaction.

   What is the initial oxidation state of the ion of \( M \)?

   A +1
   B +2
   C +3
   D +4

3. Which of the following statements best explains why the boiling point of \( CH_3CH_2CH_2NH_2 \) is higher than that of \( (CH_3)_3N \)?

   A There are hydrogen bonds between \( CH_3CH_2CH_2NH_2 \) molecules but no hydrogen bonds between \( (CH_3)_3N \) molecules.
   B The covalent bonds between atoms in \( CH_3CH_2CH_2NH_2 \) are stronger than those between atoms in \( (CH_3)_3N \).
   C \( CH_3CH_2CH_2NH_2 \) molecule has a larger surface area than \( (CH_3)_3N \) molecule.
   D \( CH_3CH_2CH_2NH_2 \) molecule is polar but \( (CH_3)_3N \) molecule is not.
4 Which of the following electrostatic attraction is **not** present in a sample of CH$_3$F?
   A permanent dipole-permanent dipole interactions
   B instantaneous dipole-induced dipole interactions
   C hydrogen bonds
   D covalent bonds

5 Which of the following graph is obtained when density ($\rho$) is plotted against temperature ($T$) for an ideal gas under constant pressure?

![Graph options A, B, C, D]

6 Which of the following oxides is unlikely to dissolve in aqueous sodium hydroxide?
   A MgO
   B Al$_2$O$_3$
   C SiO$_2$
   D SO$_2$
Nitrogen dioxide decomposes on heating according to the following equation.

\[ 2\text{NO}_2(g) \rightleftharpoons 2\text{NO}(g) + \text{O}_2(g) \]

When 2 mol of nitrogen dioxide is placed in a 4 dm\(^3\) container and heated, the equilibrium mixture contained 0.8 mol of oxygen.

What is the numerical value of the equilibrium constant, \(K_c\), at the temperature of the experiment?

A  0.0889  
B  0.800  
C  3.20  
D  12.8

Which statement about the effect of a catalyst on a reversible reaction is correct?

A  It increases the yield of product in an equilibrium.  
B  It increases the equilibrium constant for the forward reaction.  
C  It increases the rate of the forward reaction and decreases the rate of the reverse reaction.  
D  It increases the rate constant for both the forward and the reverse reaction.

Which expression represents the solubility product of iron(III) hydroxide?

A  \([\text{Fe}^{3+}][\text{OH}^-]\)  
B  \([\text{Fe}^{3+}][\text{OH}^-]^3\)  
C  \([\text{Fe}^{3+}][3\text{OH}^-]\)  
D  \([\text{Fe}^{3+}][3\text{OH}^-]^3\)
10 \( \text{H}_2\text{SO}_4(\text{aq}) \) was added to \( \text{Ba(OH)}_2(\text{aq}) \) until the acid was in excess. Which graph shows the variation in the total number of ions in solution?

A  

B  

C  

D  

11 The product of the concentrations of \( X \) and \( Y \), \([X][Y]\), is plotted against time, \( t \), for the following second-order reaction.

\[ X + Y \rightarrow Z \]

Which graph would be obtained?

A  

B  

C  

D  

No. of ions  

V\(_{\text{acid}}\)  

No. of ions  

V\(_{\text{acid}}\)  

[X][Y]  

t  

[X][Y]  

t  

[X][Y]  

t  

[X][Y]  

t
12 Which one of the following elements has the same oxidation state in all of its known compounds?

A beryllium  B bromine  
C nitrogen  D sulfur

13 X is obtained by reacting aqueous cobalt(III) chloride with ammonia. The coordination number of cobalt is 6 and when the complex is treated with an excess of aqueous silver nitrate, only \( \frac{1}{3} \) of the total chloride is precipitated as AgCl.

What is the formula of X?

A \( \text{Co(NH}_3\text{)}_6\text{Cl}_3 \)  B \( \text{Co(NH}_3\text{)}_5\text{Cl}_3 \)  
C \( \text{Co(NH}_3\text{)}_4\text{Cl}_3 \)  D \( \text{Co(NH}_3\text{)}_3\text{Cl}_3 \)

14 Using relevant \( E^0 \) values from the Data Booklet, determine which of the following statements is correct.

A No reaction occurs when \( \text{V}^{3+}(aq) \) is added to \( \text{Fe}^{3+}(aq) \).
B \( \text{VO}^{2+}(aq) \) can reduce \( \text{Fe}^{2+}(aq) \) to \( \text{Fe}^{3+}(aq) \).
C \( \text{Zn}^{2+}(aq) \) can reduce \( \text{VO}^{2+}(aq) \) to \( \text{V}^{3+}(aq) \).
D \( \text{Zn}(s) \) can reduce \( \text{V}^{3+}(aq) \) to \( \text{V}^{2+}(aq) \).

15 A current of 8 A is passed for 100 min through molten aluminium oxide using inert electrodes.

What will be the approximate volume of gas liberated, measured at s.t.p.?

A 2.8 dm\(^3\)  B 3.0 dm\(^3\)  
C 11.2 dm\(^3\)  D 12.0 dm\(^3\)

16 Which one of the following products is not obtained commercially by the electrolysis of concentrated brine?

A chlorine  B oxygen  
C sodium chlorate(V)  D sodium hydroxide
17 Use of the Data Booklet is relevant to this question.

In the construction of pacemakers for the heart, a tiny magnesium electrode can be used to create an electrical cell with the inhaled oxygen. The relevant half-equations are as shown:

\[ \text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg} \]
\[ \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O} \]

In the body, a potential of 3.20 V is usually obtained. What is the best explanation for this e.m.f.?

A The small size of the magnesium electrode  
B The low concentration of Mg^{2+} surrounding the magnesium electrode  
C The high resistance of the body fluids surrounding the electrodes  
D The physiological pH of between 7 and 8 of the body fluid surrounding the electrodes

18 Use of the Data Booklet is relevant to this question.

The enthalpy changes for three reactions are given below:

\[ \text{Na}(s) \rightarrow \text{Na}(g) \quad \Delta H_1 = +107 \text{ kJ mol}^{-1} \]
\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_2 = -58 \text{ kJ mol}^{-1} \]
\[ 2\text{Na}^+(g) + 2\text{H}^+(aq) + 2e^- \rightarrow 2\text{Na}^+(aq) + \text{H}_2(g) \quad \Delta H_3 = -1700 \text{ kJ mol}^{-1} \]

What is the enthalpy change for the following reaction?

\[ \text{Na}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) + \frac{1}{2}\text{H}_2(g) \]

A $-191$ kJ mol^{-1}  
B $-307$ kJ mol^{-1}  
C $-685$ kJ mol^{-1}  
D $-1041$ kJ mol^{-1}

19 The bond dissociation energy of H–C{l} is 431 kJ mol^{-1}. In which of the following processes is 431 kJ of energy released?

A \( \text{HCl}(g) \rightarrow \text{H}(g) + \text{Cl}(g) \)
B \( \text{H}(g) + \text{Cl}(g) \rightarrow \text{HCl}(g) \)
C \( \text{HCl}(g) \rightarrow \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Cl}_2(g) \)
D \( \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{HCl}(g) \)
20 Vitamin E acts as an antioxidant as well as an enzymatic activity regulator. There are 8 forms of Vitamin E, of which \( \alpha \)-tocopherol is the most biologically active form. The diagram shows the structure of \( \alpha \)-tocopherol.

![Structure of \( \alpha \)-tocopherol]

How many chiral carbon centres are there in one molecule of \( \alpha \)-tocopherol?

A 2  B 3  C 4  D 5

21 Which of the following could be best used to distinguish between hex-1-ene and methylbenzene?

A acidified \( \text{K}_2\text{Cr}_2\text{O}_7 \)
B \( \text{Br}_2 \) in \( \text{CCl}_4 \)
C \( \text{I}_2 \) in \( \text{NaOH(aq)} \)
D concentrated sulfuric acid

22 Samples of the gases \( \text{CH}_3\text{Cl} \) and \( \text{Cl}_2 \) are mixed together and irradiated with light. Which compound is produced by a termination stage in the chain reaction?

A \( \text{HC}l \)  B \( \text{CH}_2=\text{CH}_2 \)
C \( \text{CH}_3\text{CH}_3 \)  D \( \text{CH}_2\text{Cl}_2 \)

23 Which hydrocarbon, on treatment with hot acidified potassium manganate(VII), would give ethanoic acid as one of the products?

A
![Cyclohexane]

B
![2-Methylhexene]

C
![5-Methyl-2-pentene]

D
![2,4-Dimethyl-2-pentene]
24 Which of the following compounds would undergo electrophilic substitution most readily?

A  

B  

C  

D  

25 A reaction sequence is given below.

\[ \text{CHBrCH}_3 \xrightarrow{\text{KCN, CH}_3\text{CH}_2\text{OH}} \text{P} \xrightarrow{\text{HC/(aq) Heat under reflux}} \text{Q} \]

Which of the following structures represents the product Q?

A  

B  

C  

D  
26 *Citronellol* is a colourless oily liquid with a rose-like smell. It is the active ingredient in over 30 essential oils and is a major component in perfumes, cosmetics and soaps. It may be prepared synthetically from compound **S** using reagent **T**.

![Citronellol](image)

Which of the following could **S** and **T** most likely be?

A. KOH in ethanol
B. aqueous NaOH
C. LiA/H₄ in dry ether
D. concentrated H₂SO₄ at 170 °C

27 One mole of compound **R** reacts with excess sodium metal to give one mole of hydrogen gas. One mole of ammonia gas is also evolved when one mole of compound **R** is heated with aqueous sodium hydroxide.

What is the identity of **R**?

A. HOCH₂CH(NH₂)CO₂H
B. HOCH₂CH(OH)CN
C. HOCH₂CH₂CONH₂
D. HOCH₂CH(NO₂)CO₂H
The reaction scheme below shows the formation of compound V.

What is the structure of V?

A

B

C

D

Which of the following statements explains why ethylamine has a lower $pK_b$ value than ammonia? ($pK_b$ of ethylamine = 3.2; $pK_b$ of ammonia = 4.8)

A. The nitrogen atom in ammonia is bonded to more hydrogen atoms than that in ethylamine.

B. The conjugate acid of ethylamine is less stable than that of ammonia.

C. Ethyl group in ethylamine increases the electron density of the nitrogen atom.

D. The lone pair on the nitrogen atom of ammonia is less delocalised than that on ethylamine.
Denaturation of proteins occurs due to the destruction of the tertiary structure where various R group interactions are disrupted by external factors such as extreme pH and heavy metal ions.

Which of the following **incorrectly** shows the R group interactions that will be affected by such external factors?

<table>
<thead>
<tr>
<th>R group interactions</th>
<th>External factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>hydrogen bonds</td>
</tr>
<tr>
<td>B</td>
<td>disulfide bridges</td>
</tr>
<tr>
<td>C</td>
<td>disulfide bridges</td>
</tr>
<tr>
<td>D</td>
<td>ionic interactions</td>
</tr>
</tbody>
</table>

extreme pH

heavy metal ions
Section B

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

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

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

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

31 Which statements about the electronegativity of elements in the Periodic Table are correct?

1 In Period 3, it decreases from sodium to chlorine.
2 In Group II, it decreases from beryllium to barium.
3 In Group VII, it decreases from fluorine to iodine.

32 When light is shown for a fixed period into a solution of \( \text{CH}_2\text{ICH}_2\text{I} \) and \( \text{I}_2 \) in tetrachloromethane at 100 °C, the following reaction occurs.

\[
\text{CH}_2\text{ICH}_2\text{I} \rightarrow \text{CH}_2=\text{CH}_2 + \text{I}_2
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Relative concentrations</th>
<th>Relative light intensity</th>
<th>Relative initial rate of formation of iodine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{CH}_2\text{ICH}_2\text{I} )</td>
<td>( \text{I}_2 )</td>
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<td>4</td>
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<td>2</td>
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</tbody>
</table>

From the data above, the rate of formation of iodine is

1 independent of the initial concentration of \( \text{I}_2 \)
2 proportional to the initial concentration of \( \text{CH}_2\text{ICH}_2\text{I} \)
3 proportional to the square root of light intensity
33 Why is the addition of concentrated sulfuric acid to solid potassium iodide **unsuitable** for the preparation of hydrogen iodide?

1 Hydrogen iodide is not displaced by sulfuric acid
2 Iodide ions are oxidised to iodine
3 The product is contaminated by sulfur-containing compounds

34 When a paramagnetic object is placed in a strong magnetic field, it is attracted to the field. Paramagnetism is associated with unpaired electrons, and many transition elements are often paramagnetic because they contain unpaired d-electrons.

Which of the following transition metal atoms or ions would you expect to be paramagnetic?

1 Cr
2 Mn
3 Cu⁺

35 The enthalpy changes of formation of carbon monoxide and carbon dioxide are given below.

\[ \Delta H_f (\text{CO}) = -110 \text{ kJ mol}^{-1} \]
\[ \Delta H_f (\text{CO}_2) = -393 \text{ kJ mol}^{-1} \]

Which of the following statements are correct?

1 The enthalpy change of combustion of carbon monoxide is exothermic.
2 Carbon dioxide is energetically more stable than carbon monoxide.
3 The enthalpy change of combustion of carbon is \(-110 \text{ kJ mol}^{-1}\).
36 What are the conditions usually quoted for the standard electrode potential of hydrogen to be 0.00 V?

1 temperature is 25 °C
2 pH of the acid solution is 1.0
3 atmospheric pressure is exactly 1 atm

37 Use of the Data Booklet is relevant to this question.
When nitric acid is added to iron filings, a brown gas that turns moist blue litmus red is observed.
Which statements are correct?

1 Iron acts as a reducing agent.
2 The standard cell potential of the reaction between iron filings and nitric acid is +0.04 V.
3 Addition of potassium cyanide to the reaction vessel of nitric acid and iron filings will result in a decrease in the standard cell potential.

38 By varying the conditions of the reaction between 1,2-dibromoethane and sodium hydroxide, which of the following compounds can be obtained?

<table>
<thead>
<tr>
<th>A</th>
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<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

1

2

3

C

OH

C

H

H

OH

H

H

Br

OH

C

H

H

Br
39 Ethanal can react with HCN in a nucleophilic addition reaction catalysed by NaCN. Which of the following statements about the reaction mechanism are true?

1. The shape of the intermediate is planar.
2. In the intermediate, the oxygen carries a negative charge.
3. A new carbon-carbon bond is formed.

40 In which of the following reactions is the inorganic reagent acting as a nucleophile?

1. \( \text{CH}_3\text{CH}_2\text{C}1 + \text{KCN} \rightarrow \text{CH}_3\text{CH}_2\text{CN} + \text{KC}1\)
2. \( \text{CH}_3\text{COCl} + \text{NH}_3 \rightarrow \text{CH}_3\text{CONH}_2 + \text{HC}1\)
3. \( \text{CH}_3\text{CH}_2\text{NH}_2 + \text{HC}1 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+\text{Cl}^-\)
Answer key for Prelim Paper 1

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<td>B</td>
<td>40</td>
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</table>
READ THESE INSTRUCTIONS FIRST

Write your name, class, Centre number and index number 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 all questions in the space provided.
A Data Booklet is provided. Do NOT write anything on it.

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

Calcium salts are used in many industrial processes. Calcium oxide is used in the production of cement while calcium nitrate is sometimes used to accelerate the setting of concrete.

Calcium oxide is a white hygroscopic solid. Calcium oxide can react with water and as such can cause severe irritation when in contact with skin, eyes or if inhaled.

Calcium nitrate is also a white hygroscopic solid. Calcium nitrate decomposes on heating to form the oxide, nitrogen dioxide and oxygen.

(a) Write a balanced equation, including state symbols, for the thermal decomposition of calcium nitrate.

………………………………………………………………… [1]

(b) Calculate the change in mass of the solid you would expect if 1.00 mol of calcium nitrate underwent thermal decomposition.

………………………………………………………………… [1]

(c) A container of calcium nitrate was contaminated with calcium oxide. Design an experiment to determine the percentage purity of calcium nitrate by a gravimetric method. You are provided with about 2 g of the impure calcium nitrate.

(In gravimetric methods, the objective is to form a thermally stable solid so that the mass can be determined accurately for analysis.)

Your plan should include the following:

- A full description of the procedure.
- Details of how you would calculate the percentage purity from the measurements made.

\[ M_r \text{ of } \text{Ca(NO}_3\text{)}_2 = 164 \]

………………………………………………………………… [1]

………………………………………………………………… [1]

………………………………………………………………… [1]
(d) State and explain clearly one precaution you would take to improve the accuracy of your results.

.......................................................................................................................................................... [8]

(e) Identify one potential safety hazard in this experiment and state how you would minimise the risk.

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

[Total: 12]
Titanium(IV) oxide, TiO₂, is the naturally occurring oxide of titanium. It is the main ingredient in sunscreen lotion due to its high refractive index and strong UV-light absorbing capability.

(a) Using the following information as well as relevant data from the *Data Booklet*, draw a Born-Haber cycle for the formation of TiO₂(s) and calculate the lattice energy of TiO₂(s).

| Standard enthalpy change of formation of TiO₂(s) | $-945 \text{ kJ mol}^{-1}$ |
| Standard enthalpy change of atomisation of Ti | $+471 \text{ kJ mol}^{-1}$ |
| 1st electron affinity of oxygen | $-142 \text{ kJ mol}^{-1}$ |
| 2nd electron affinity of oxygen | $+844 \text{ kJ mol}^{-1}$ |
(b) Crude titanium(IV) oxide is purified via the Chloride process. In this two-step process, the crude ore (containing at least 70% titanium(IV) oxide) is first reacted with carbon and chlorine, represented by the equation shown below.

\[
\text{TiO}_2(s) + \text{C}(s) + 2\text{Cl}_2(g) \rightarrow \text{TiCl}_4(l) + \text{CO}_2(g)
\]

| Standard enthalpy change of formation of TiCl₄(l) | -804 kJ mol⁻¹ |
| Standard enthalpy change of formation of CO₂(g)  | -394 kJ mol⁻¹ |
| Standard molar entropy of TiO₂(s)               | +49.9 J mol⁻¹ K⁻¹ |
| Standard molar entropy of C(s)                  | +5.7 J mol⁻¹ K⁻¹ |
| Standard molar entropy of Cl₂(g)               | +223 J mol⁻¹ K⁻¹ |
| Standard molar entropy of TiCl₄(l)              | +252 J mol⁻¹ K⁻¹ |
| Standard molar entropy of CO₂(g)               | +214 J mol⁻¹ K⁻¹ |

Using the above information, as well as relevant data from (a) and the Data Booklet, calculate, for the first step of the Chloride process,

(i) the standard enthalpy change of reaction,

(ii) the standard entropy change of reaction.

Note: \(\Delta S = \Sigma S_{(\text{products})} - \Sigma S_{(\text{reactants})}\)
(c) Using your answers in (b), determine if the first step of the Chloride process is spontaneous at 2000 K.

(d) The second step of the Chloride process involves the titanium(IV) chloride being distilled off and oxidised in a pure oxygen flame to give pure titanium(IV) oxide and chlorine gas.

Write an equation for the reaction in the second step.

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

[Total: 7]

3 Neidong Forest Recreation National Park, located in the Wulai District in Taipei, has the highest concentration of anions in Taiwan due to the numerous waterfalls and lush forestation in the park. Anions are said to help boost the immune system, among other health benefits.

(a) Bromide ions are thought to be one of the anions present in abundance. The concentration of bromide ions in the river waters can be used as an estimate of the concentration of the ions in the park.

A 25.0 cm$^3$ sample of river water was collected and 50.0 cm$^3$ of 1.00 mol dm$^{-3}$ Pb(NO$_3$)$_2$ was added. The precipitate formed was filtered off and 3.00 g of precipitate was collected. The filtrate can be regarded as a saturated solution of PbBr$_2$.

(i) Calculate the concentration of Pb$^{2+}$ ions in the filtrate.
(ii) Write an expression for the solubility product, $K_{sp}$, of PbBr$_2$.

\[
\text{..........................................................}\\
\]

(iii) The numerical value for the $K_{sp}$ of PbBr$_2$ is $3.9 \times 10^{-5}$. Determine the concentration of bromide ions in the sample of river water.

\[
\text{..........................................................}\\
\]

(b) Another anion, W, found in Neidong National Park can be formed when the oxide of a Period 3 element reacts with an alkali. When dilute nitric acid is added to a solution containing W, a colourless and pungent gas that turns acidified potassium dichromate(VI) from orange to green is evolved.

(i) Suggest an identity for anion W.

\[
\text{..........................................................}\\
\]

(ii) Write an equation for the formation of W from the reaction of a Period 3 oxide with an alkali.

\[
\text{..........................................................}\\
\]

[Total: 7]
4 The lead–acid accumulator is a storage battery used in cars because it can be recharged. It consists of a series of cells containing lead plate anodes, lead dioxide plate cathodes and an electrolyte of 6 mol dm$^{-3}$ sulfuric acid.

When it is operating, the reactions that occur at the electrodes are

\[
Pb^{2+}(aq) + 2e^− = Pb(s) \quad E = –0.13 \text{ V}
\]

\[
PbO_2(s) + 4H^+(aq) + 2e^- = Pb^{2+}(aq) + 2H_2O(l) \quad E = +1.47 \text{ V}
\]

(a) Write the overall equation for the reaction during discharge and calculate the voltage delivered by the battery.

Equation: ........................................................................................................................................

(b) However, it is noted that the actual voltage is 2.0 V as compared to the value that you have calculated in (a). Explain why the actual voltage differs from the calculated voltage.

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........................................................................................................................................
........................................................................................................................................ [2]

(c) Explain why the battery is rechargeable.

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........................................................................................................................................ [1]
(d) State one disadvantage of the lead-acid accumulator battery.

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

[Total: 6]

5 This question is about the chemistry of halogens and halide ions.

(a) Aqueous bromine is decolourised when added to aqueous sodium thiosulfate. When excess of aqueous barium nitrate is added to the resulting solution, a white precipitate is observed. This precipitate is filtered off, leaving a colourless filtrate.

(i) Write a balanced ionic equation for the reaction between bromine and sodium thiosulfate.

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

(ii) To the colourless filtrate in (i), aqueous silver nitrate is added, followed by concentrated ammonia solution.

Describe what is observed and write balanced equations for any reaction that occur.

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.......................................................................................................................... [4]
(b) In a separate experiment, aqueous bromine is added to aqueous potassium iodide. To the resulting mixture, an equal volume of an organic solvent is added.

What will be the colour of the organic layer? Write equations for any reactions that occur.

…………………………………………………………………………………………………… [2]

(c) Iodide ions react with peroxodisulfate ions in the presence of Fe$^{3+}$ catalyst. The overall equation for the reaction is shown below.

\[
2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)
\]

(i) Fe$^{3+}$ ions are added to lower the high activation energy so that the reaction can proceed at a higher rate. Explain why the activation energy is high for the reaction between the iodide and peroxodisulfate ions if no Fe$^{3+}$ ions are added.

…………………………………………………………………………………………………… [2]

(ii) With reference to the Data Booklet, suggest a mechanism for this reaction in the presence of Fe$^{3+}$.

[4]

[Total: 10]
6 Chromium is a hard grey metal which is widely used in the manufacture of stainless steel due to its good corrosion-resistant properties.

Calcium is a fairly soft, silvery grey metal which tarnishes quickly in air.

(a) The melting point of calcium is 843 °C while chromium melts at a much higher temperature of 1907 °C.

Explain this difference in terms of the type and strength of bonding in each metal.

…………………………………………………………………………………………………… [3]

(b) Write the electronic configuration of chromium atoms and chromium(III) ions.

Cr .................................................................
Cr3+ ................................................................. [2]

(c) When aqueous sodium hydroxide was added to aqueous chromium(III) nitrate, a blue-green precipitate was observed. Upon addition of excess aqueous sodium hydroxide, the precipitate dissolved to give a dark green complex.

When aqueous sodium carbonate was added to aqueous chromium(III) nitrate, effervescence was observed.

(i) State the formula of the blue-green precipitate.

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

(ii) Suggest a reason why effervescence was observed when aqueous sodium carbonate was added to aqueous chromium(III) nitrate.

…………………………………………………………………………………………………..
(iii) Given that the formula of the soluble dark green complex is \( \text{Na}_3\text{CrO}_6\text{H}_6 \), state the formula of the complex ion formed.

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

(iv) Draw the structure of the complex ion.

[4]

[Total: 9]
Hydrocarbons are commonly used as combustible fuel sources as well as feed materials in the petrochemical industry.

(a) Describe a simple chemical test to distinguish between but-1-ene and but-2-ene. State clearly what would be observed with each compound.

(b) But-2-ene is able to exist as 2 isomers.

(i) State the type of isomerism exhibited by but-2-ene.

(ii) Draw the displayed structural formulae for the 2 isomers of but-2-ene.
(c) Benzene is an aromatic hydrocarbon present in many compounds.

A reaction scheme involving benzene derivatives is given below. Draw the structures of A to D and give the reagents and conditions for steps I to IV.
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Step I: 

Step II: 

Step III: 

Step IV: 

[8]

[Total: 13]
8 Students often complain of headaches when faced with a tough problem they cannot solve. A very common over-the-counter drug to combat headaches is paracetamol. The synthesis of paracetamol is shown below:

(a) Draw the structure of compound X.

(b) Step I is actually a two-stage process. State the reagents and conditions for the two stages.

Stage 1: .................................................................

Stage 2: ................................................................. [2]

(c) Step II involves a condensation reaction. An organic side-product, Y, can be formed along with paracetamol.

(i) State the reagent for this step.

.......................................................................................... [2]

(ii) Suggest a structure for Y.
(d) Suggest the structures of all the organic products formed when paracetamol reacts with

(i) NaOH(aq) at room temperature

(ii) NaOH(aq) with heating

[3]

[Total: 8]
READ THESE INSTRUCTIONS FIRST

Write your name, class, Centre number and index number 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 all questions in the space provided. A Data Booklet is provided. Do NOT write anything on it.

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

For Examiner's Use

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This document consists of 18 printed pages.
1 Planning (P)

Calcium salts are used in many industrial processes. Calcium oxide is used in the production of cement while calcium nitrate is sometimes used to accelerate the setting of concrete.

Calcium oxide is a white hygroscopic solid. Calcium oxide can react with water and as such can cause severe irritation when in contact with skin, eyes or if inhaled.

Calcium nitrate is also a white hygroscopic solid. Calcium nitrate decomposes on heating to form the oxide, nitrogen dioxide and oxygen.

(a) Write a balanced equation, including state symbols, for the thermal decomposition of calcium nitrate.

\[
\text{Ca(NO}_3\text{)}_2(s) \rightarrow \text{CaO}(s) + 2\text{NO}_2(g) + \frac{1}{2}\text{O}_2(g)
\]

(b) Calculate the change in mass of the solid you would expect if 1.00 mol of calcium nitrate underwent thermal decomposition.

\[
\text{Loss in mass} = \text{Mass of NO}_2 \text{ and O}_2 = 2(14.0 + 2(16.0)) + \frac{1}{2}(2(16.0)) = 108 \text{ g}
\]

(c) A container of calcium nitrate was contaminated with calcium oxide. Design an experiment to determine the percentage purity of calcium nitrate by a gravimetric method. You are provided with about 2 g of the impure calcium nitrate.

(In gravimetric methods, the objective is to form a thermally stable solid so that the mass can be determined accurately for analysis.)

Your plan should include the following:

- A full description of the procedure.
- Details of how you would calculate the percentage purity from the measurements made.

\[
\text{Mr of Ca(NO}_3\text{)}_2 = 164
\]

1. Weigh accurately a clean and dry crucible (Accept: hard glass tube). Add the sample and weigh the crucible with its contents.
2. Heat the crucible strongly for about five minutes to decompose the calcium nitrate.
3. Place crucible in a dessicator to cool. Then weigh the crucible and its contents.
4. Repeat the heating, cooling and weighing process until the mass of the crucible and its contents is consistent within 0.05 g in difference.

\[
\text{Loss in mass} = \text{initial mass of crucible and contents} – \text{final mass of crucible and contents after final heating}
\]
(d) State and explain clearly one precaution you would take to improve the accuracy of your results.

Sample should be stored in dessicator while cooling to prevent absorption of water from the air. [1]

(e) Identify one potential safety hazard in this experiment and state how you would minimise the risk.

NO₂ is toxic. Perform experiment in fume cupboard.

OR

CaO causes skin / eye irritation / irritation if inhaled. Wear gloves, mask etc. [1]

[Total: 12]

2 Titanium(IV) oxide TiO₂ is the naturally occurring oxide of titanium. It is the main ingredient in sunscreen lotion due to its high refractive index and strong UV-light absorbing capability.

(a) Using the following information as well as relevant data from the Data Booklet, draw a Born-Haber cycle for the formation of TiO₂(s) and calculate the lattice energy of TiO₂(s).

| Standard enthalpy change of formation of TiO₂(s) | −945 kJ mol⁻¹ |
| Standard enthalpy change of atomisation of Ti | +471 kJ mol⁻¹ |
| 1ˢᵗ electron affinity of oxygen | −142 kJ mol⁻¹ |
| 2ⁿᵈ electron affinity of oxygen | +844 kJ mol⁻¹ |

\[
\begin{align*}
\text{Ti}(s) & \rightarrow \text{Ti}^{4+}(g) + 4e^- + 471 \\
\text{O}_2(g) & \rightarrow 2\text{O}^{2-}(g) + 142 \\
\text{Ti}^{4+}(g) + 2\text{O}^{2-}(g) & \rightarrow \text{TiO}_2(s) + 496 \\
\text{Lattice energy of TiO}_2 & \approx 945 \\
\end{align*}
\]
By Hess’ Law,

\[ -945 = +471 + (+661) + (+1310) + (+2720) + (+4170) + (+496) + \\ 2((-142) + (+844)) + LE(TiO_2) \]

\[ LE(TiO_2) = -12177 \text{ kJ mol}^{-1} \]

\[ = -1.22 \times 10^4 \text{ kJ mol}^{-1} \]

(b) Crude titanium(IV) oxide is purified via the Chloride process. In this two-step process, the crude ore (containing at least 70% titanium(IV) oxide) is first reacted with carbon and chlorine, represented by the equation shown below.

\[ TiO_2(s) + C(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + CO_2(g) \]

Using the above information, as well as relevant data from (a) and the *Data Booklet*, calculate, for the first step of the Chloride process,

(i) the standard enthalpy change of reaction,

\[
\text{Standard enthalpy change of reaction} = \left[ (-804) + (-394) \right] - \left[ (-945) + 0 + 2(0) \right] = -253 \text{ kJ mol}^{-1}
\]

(ii) the standard entropy change of reaction.

Note: \( \Delta S^\circ = \Sigma S\text{(products)} - \Sigma S\text{(reactants)} \)

\[
\text{Standard entropy change of reaction} = \left[ (+252) + (+214) \right] - \left[ (+49.9) + (+5.7) + 2(+223) \right] = -35.6 \text{ J mol}^{-1} \text{ K}^{-1}
\]

[2]
(c) Using your answers in (b), determine if the first step of the Chloride process is spontaneous at 2000 K.

\[ \Delta G = \Delta H - T\Delta S \]
\[ \Delta G = (-253) - (2000)(-35.6/1000) \]
\[ \Delta G = -182 \text{ kJ mol}^{-1} < 0 \]

Hence, the reaction is spontaneous at 2000 K. \[1\]

(d) The second step of the Chloride process involves the titanium(IV) chloride being distilled off and oxidised in a pure oxygen flame to give pure titanium(IV) oxide and chlorine gas.

Write an equation for the reaction in the second step.

\[ \text{TiCl}_4 + O_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2 \] \[1\]

[Total: 7]

3 Neidong Forest Recreation National Park, located in the Wulai District in Taipei, has the highest concentration of anions in Taiwan due to the numerous waterfalls and lush forestation in the park. Anions are said to help boost the immune system, among other health benefits.

(a) Bromide ions are thought to be one of the anions present in abundance. The concentration of bromide ions in the river waters can be used as an estimate of the concentration of the ions in the park.

A 25.0 cm\(^3\) sample of river water was collected and 50.0 cm\(^3\) of 1.00 mol dm\(^{-3}\) Pb(NO\(_3\))\(_2\) was added. The precipitate formed was filtered off and 3.00 g of precipitate was collected. The filtrate can be regarded as a saturated solution of PbBr\(_2\).

(i) Calculate the concentration of Pb\(^{2+}\) ions in the filtrate.

Amount of PbBr\(_2\) collected = \[ \frac{3.00}{207 + 2(79.9)} \]
\[ = 8.18 \times 10^{-3} \text{ mol} \]

Amount of Pb\(^{2+}\) in filtrate = \[ \frac{50}{1000} \times 1.00 \] \[ - (8.18 \times 10^{-3}) \]
\[ = 0.0418 \text{ mol} \]
(i) Write an expression for the solubility product, $K_{sp}$, of PbBr$_2$.

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

(ii) The numerical value for the $K_{sp}$ of PbBr$_2$ is $3.9 \times 10^{-5}$. Determine the concentration of bromide ions in the sample of river water.

$$[\text{Br}^-]_{\text{filtrate}} = \sqrt{\frac{3.9 \times 10^{-5}}{0.557}} = 8.37 \times 10^{-3} \text{ mol dm}^{-3}$$

Total amount of Br$^-$ in sample of river water

= Amount of Br$^-$ in filtrate + Amount of Br$^-$ in ppt

= $(8.37 \times 10^{-3} \times \frac{75}{1000}) + (8.18 \times 10^{-3} \times 2)$

= 0.0170 mol

$$[\text{Br}^-]_{\text{sample of river water}} = \frac{0.0170}{25} \times \frac{25}{1000} = 0.680 \text{ mol dm}^{-3}$$

(b) Another anion, W, found in Neidong National Park can be formed when the oxide of a Period 3 element reacts with an alkali. When dilute nitric acid is added to a solution containing W, a colourless and pungent gas that turns acidified potassium dichromate(VI) from orange to green is evolved.

(i) Suggest an identity for anion W.

SO$_3^{2-}$/HSO$_3^-$

(ii) Write an equation for the formation of W from the reaction of a Period 3 oxide with an alkali.

$$\text{SO}_2 + 2\text{OH}^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$$

OR $$\text{SO}_2 + \text{OH}^- \rightarrow \text{HSO}_3^-$$

[Total: 7]
4 The lead–acid accumulator is a storage battery used in cars because it can be recharged. It consists of a series of cells containing lead plate anodes, lead dioxide plate cathodes and an electrolyte of 6 mol dm$^{-3}$ sulfuric acid.

When it is operating, the reactions that occur at the electrodes are

\[
Pb^{2+}(aq) + 2e^- = Pb(s) \quad E = -0.13 \text{ V}
\]

\[
PbO_2(s) + 4H^+(aq) + 2e^- = Pb^{2+}(aq) + 2H_2O(l) \quad E = +1.47 \text{ V}
\]

(a) Write the overall equation for the reaction during discharge and calculate the voltage delivered by the battery.

\[
Pb(s) + PbO_2(s) + 4H^+(aq) \rightarrow 2Pb^{2+}(aq) + 2H_2O(l)
\]

\[
E_{\text{cell}} = 1.47 - (-0.13) = +1.60 \text{V}
\]

(b) However, it is noted that the actual voltage is 2.0 V as compared to the value that you have calculated in (a). Explain why the actual voltage differs from the calculated voltage.

During discharging, Pb$^{2+}$(aq) is removed as it precipitates out as PbSO$_4$(s). This causes the equilibrium position of \( PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 2H_2O \) to shift to the right, hence, \( E(PbO_2/Pb^{2+}) \) is more positive than +1.47 V.

On the other hand, as PbSO$_4$ is precipitated out, the equilibrium position of \( Pb^{2+} + 2e^- = Pb \) shifts to the left, resulting in \( E(Pb^{2+}/Pb) \) to be more negative than −0.13 V.

Hence actual voltage is 2.0V

(c) Explain why the battery is rechargeable.

When an external current is applied, it will recharge the battery by driving the cell reaction in the reverse direction.

(d) State one disadvantage of the lead-acid accumulator battery.

1) Rather large and heavy due to the lead, hence produces low power for its mass.
2) PbSO$_4$ deposits on the electrodes in a finely divided form during discharge. If a discharged battery stands for a long time, the small grains of PbSO$_4$ may grow into large crystals that fall from the electrodes. If too much PbSO$_4$ is lost, the cell cannot be recharged and results in a loss of capacity.

3) Lead is toxic.
This question is about the chemistry of halogens and the halide ions.

(a) Aqueous bromine is decolourised when added to aqueous sodium thiosulfate. When excess of aqueous barium nitrate is added to the resulting solution, a white precipitate is observed. This precipitate is filtered off, leaving a colourless filtrate.

(i) Write a balanced ionic equation for the reaction between bromine and sodium thiosulfate.

\[4\text{Br}_2 + \text{S}_2\text{O}_3^{2-} + 5\text{H}_2\text{O} \rightarrow 8\text{Br}^- + 2\text{SO}_4^{2-} + 10\text{H}^+\]

(ii) To the colourless filtrate in (i), aqueous silver nitrate is added, followed by concentrated ammonia solution.

Describe what is observed and write balanced equations for the reaction that occur.

Cream ppt formed when AgNO\textsubscript{3} is added.

Upon adding concentrated NH\textsubscript{3}, cream ppt is soluble in concentrated NH\textsubscript{3}.

\[\text{Ag}^+(\text{aq}) + \text{Br}^- (\text{aq}) \rightarrow \text{AgBr} (\text{s})\]

\[\text{AgBr} (\text{s}) + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Ag(NH}_3)_2]^+ (\text{aq}) + \text{Br}^- (\text{aq})\]

(b) In a separate experiment, aqueous bromine is added to aqueous potassium iodide. To the resulting mixture, an equal volume of an organic solvent is added.

What will be the colour of the organic layer? Write equations for any reactions that occur.

Colour: Purple

Equation: \[\text{Br}_2(\text{aq}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{KBr}(\text{aq}) + \text{I}_2(\text{aq})\]

(c) Iodide ions react with peroxodisulfate ions in the presence of Fe\textsuperscript{3+} catalyst. The overall equation for the reaction is shown below.

\[2\text{I}^- (\text{aq}) + \text{S}_2\text{O}_8^{2-} (\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{SO}_4^{2-} (\text{aq})\]

(i) Fe\textsuperscript{3+} ions are added to lower the high activation energy so that the reaction can proceed at a higher rate. Explain why the activation energy is high for the reaction between the iodide and peroxodisulfate ions if no Fe\textsuperscript{3+} ions are added.

Energy is required to overcome the repulsion between two reactant anions before the ions can react.

(ii) With reference to the Data Booklet, suggest a mechanism for
this reaction in the presence of Fe$^{3+}$.
\[ \text{S}_2\text{O}_8^{2-} (aq) + 2e^- = \text{SO}_4^{2-} (aq) \quad E_r = +2.01 \text{ V} \]
\[ \text{Fe}^{3+} (aq) + e^- = \text{Fe}^{2+} (aq) \quad E_r = +0.77 \text{ V} \]
\[ \text{I}_2 (aq) + 2e^- = 2\text{I}^- (aq) \quad E_r = +0.54 \text{ V} \]

Step 1:  $2\text{Fe}^{3+} (aq) + 2\text{I}^- (aq) \rightarrow 2\text{Fe}^{2+} (aq) + \text{I}_2 (aq)$
\[ E_{\text{cell}} = +0.77 - (+0.54) = +0.23 \text{ V} > 0 \text{ V} \]
Reaction in step 1 is energetically feasible.

Step 2:  $2 \text{Fe}^{2+} (aq) + \text{S}_2\text{O}_8^{2-} (aq) \rightarrow 2\text{Fe}^{3+} (aq) + 2\text{SO}_4^{2-} (aq)$
\[ E_{\text{cell}} = +2.01 - (+0.77) = +1.24 \text{ V} > 0 \text{ V} \]
Reaction in step 2 is energetically feasible.

6 Chromium is a hard grey metal which is widely used in the manufacture of stainless steel due to its good corrosion-resistant properties.

Calcium is a fairly soft, silvery grey metal which tarnishes quickly in air.

(a) The melting point of calcium is 843 °C while chromium melts at a much higher temperature of 1907 °C.

Explain this difference in terms of the type and strength of bonding in each metal.

Both elements have metallic bonding. In Cr, both the 4s and 3d electrons can be contributed to form mobile charge cloud as they are very close in energy. The resulting chromium ion has a higher positive charge and a smaller ionic radius. This leads to stronger metallic bonds in Cr as compared to Ca, which only contributes 2 valence electrons per Ca atom to form Ca$^{2+}$.

(b) Write the electronic configuration of chromium atoms and chromium(III) ions.
Cr: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^5 \ 4s^1$
Cr$^{3+}$: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^3$

(c) When aqueous sodium hydroxide was added to aqueous chromium(III) nitrate, a blue-green precipitate was observed. Upon addition of excess sodium hydroxide, the precipitate dissolved to give a dark green complex.
When aqueous sodium carbonate was added to aqueous chromium(III) nitrate, effervescence was observed.

(i) State the formula of the blue-green precipitate.

\[ \text{Cr(OH)}_3 \]

(ii) Suggest a reason why effervescence was observed when aqueous sodium carbonate was added to aqueous chromium(III) nitrate.

Aqueous chromium(III) solutions are acidic (and an acid-carbonate reaction occurred forming carbon dioxide).

(iii) Given that the formula of the soluble dark green complex is \( \text{Na}_3\text{CrO}_6\text{H}_6 \), state the formula of the complex ion formed.

\[ [\text{Cr(OH)}_3]^{3-} \]

(iv) Draw the structure of the complex ion.

![Complex ion structure]

7 Hydrocarbons are commonly used as combustible fuel sources as well as feed materials in the petrochemical industry.

(a) Describe a simple chemical test to distinguish between but-1-ene and but-2-ene. State clearly what would be observed with each compound.

Heat with acidified \( \text{KMnO}_4 \) and test the gas evolved with \( \text{limewater} \).

But-1-ene would (turn purple \( \text{KMnO}_4 \) colourless and) produce a gas that forms a white ppt with \( \text{limewater} \), while but-2-ene (would turn purple \( \text{KMnO}_4 \) colourless but) would not produce a gas.

(b) But-2-ene is able to exist as 2 isomers.

(i) State the type of isomerism exhibited by but-2-ene.
**Geometric(al) isomerism / cis-trans isomerism**

(ii) Draw the displayed structural formulae for the 2 isomers of but-2-ene.

![Structural formulae of but-2-ene isomers](image)

(c) Benzene is an aromatic hydrocarbon present in many compounds.

A reaction scheme involving benzene derivatives is given below. Draw the structures of A to D and give the reagents and conditions for steps I to IV.
<table>
<thead>
<tr>
<th>A:</th>
<th>B:</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure A" /></td>
<td><img src="image2" alt="Chemical Structure B" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C:</th>
<th>D:</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image3" alt="Chemical Structure C" /></td>
<td><img src="image4" alt="Chemical Structure D" /></td>
</tr>
</tbody>
</table>

**Step I**: NaOH(aq)/KOH(aq), heat under reflux

**Step II**: acidified K$_2$Cr$_2$O$_7$(aq), heat and distil

**Step III**: alcoholic NaOH/KOH, heat under reflux

**Step IV**: I$_2$, NaOH(aq), warm
8. Students often complain of headaches when faced with a tough problem they cannot solve. A very common over-the-counter drug to combat headaches is paracetamol. The synthesis of paracetamol is shown below:

![Paracetamol synthesis diagram]

(a) Draw the structure of compound X.

(b) Step I is actually a two-stage process. State the reagents and conditions for the two stages.

Stage 1: …………………………………………………………………........
Sn, conc. HCl, heat

Stage 2: …………………………………………………………………........
NaOH(aq)

(c) Step II involves a condensation reaction. An organic side-product, Y, can be formed along with paracetamol.

(i) State the reagent for this step.
CH$_3$COCl

(ii) Suggest a structure for the side-product, Y.
(d) Suggest the structures of all the organic products formed when paracetamol reacts with

(i) NaOH(aq) at room temperature

(ii) NaOH(aq) with heating

and CH$_3$COO$^-$.Na$^+$

[Total: 8]
READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of 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.
Begin each question on a fresh sheet of paper.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

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

1 (a) One common characteristic of transition elements is the ability to form complexes. Transition elements react with carbon monoxide to form a class of complexes known as metal carbonyls. One aspect of metal carbonyls that is unusual for metallic compounds is that they are often volatile.

Nickel carbonyl was first synthesised in 1890 by Ludwig Mond by passing carbon monoxide over nickel metal. Nickel carbonyl has a boiling point of 43 °C and is extremely poisonous.

(i) Draw the ‘dot-and-cross’ diagram of carbon monoxide.

(ii) Explain in terms of structure and bonding why nickel carbonyl has a low boiling point.

(iii) A 2.00 g sample of nickel carbonyl was vaporised and found to occupy a volume of 314 cm$^3$ at 50 °C and 1 atmosphere pressure.

Determine the $M_r$ of nickel carbonyl.

(iv) Nickel carbonyl has the general formula Ni(CO)$_x$. Using the answer in (iii), determine the coordination number of nickel in nickel carbonyl and suggest the shape of the complex. [7]

(b) Transition metal compounds are often coloured.

(i) Explain why transition metal compounds are often coloured.

(ii) When a solution of dilute sulfuric acid was electrolysed using copper electrodes, a blue solution was obtained. On heating this solution to dryness, an anhydrous white solid was eventually obtained.

When concentrated hydrochloric acid was electrolysed using copper electrodes in a separate experiment, a yellow solution was obtained. On adding water, the colour of the solution turned from yellow to green and eventually blue.

Explain these observations. State clearly the formula of any coloured species. [9]
(c) Menthol, menthone and limonene are members of a class of compounds called isoprenoids which are derived from isoprene, \( \text{CH}_2=\text{C(\text{CH}_3)\text{CH}=\text{CH}_2} \).

Limonene and menthone are intermediates in the biosynthesis of menthol. The many reactions in the biosynthesis of menthol are catalysed by different enzymes. In the laboratory, transition metal catalysts can be used to catalyse many of these reactions instead of enzymes.

![Chemical structures of limonene, menthone, and menthol](image)

Describe how you would distinguish these three compounds by means of simple chemical tests. [4]

[Total: 20]
2 (a) Hydrocarbons like alkanes are commonly used for fuels. Increasingly, biofuels are gaining increased public and scientific attention, driven by concerns over oil prices and greenhouse gas emission. Biofuels, like methanol and butan-1-ol, which can be produced by the fermentation of biomass, are increasingly being used for fuels over hydrocarbons.

(i) Using common oxidation numbers for H and O, calculate the oxidation number of carbon in methanol, CH₃OH.

(ii) Using only the elements C, H and O, suggest the structural formulae of two compounds, each containing a single carbon atom with an oxidation number of zero and +2 respectively.

In an experiment to determine the standard enthalpy change of combustion of butan-1-ol, \( \Delta H^\circ_c \), a quantity of the fuel was burned underneath a 200 g copper can containing 515 g of water. It was found that the temperature of water rose from 23 °C to 58 °C after 2.30 g of butan-1-ol has been burned completely.

(iii) Write an equation for the complete combustion of butan-1-ol.

(iv) Using the experimental results and relevant data from the Data Booklet, calculate the apparent \( \Delta H^\circ_c \) of butan-1-ol. You can ignore the heat capacity of the copper can.

(v) The true value of \( \Delta H^\circ_c \) of butan-1-ol is \(-2670 \text{ kJ mol}^{-1}\). Compare this value to the one you have calculated in (iv) and suggest a reason for the discrepancy. [7]

(b) The following table compares the \( pK_a \) values of two dicarboxylic acids.

<table>
<thead>
<tr>
<th>acid</th>
<th>formula</th>
<th>( pK_1 )</th>
<th>( pK_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>propanedioic acid</td>
<td>HO₂C(CH₂)n-CO₂H</td>
<td>2.85</td>
<td>5.70</td>
</tr>
<tr>
<td>butanedioic acid</td>
<td>HO₂CCH₂CH₂CO₂H</td>
<td>4.20</td>
<td>5.60</td>
</tr>
</tbody>
</table>

(i) Suggest a reason why the \( pK_1 \) value of propanedioic acid is so much less than the \( pK_1 \) of butanedioic acid.

(ii) Suggest a reason why the \( pK_2 \) value of propanedioic acid is higher than its \( pK_1 \) value.

(iii) Calculate the pH of 0.25 mol dm\(^{-3}\) of butanedioic acid (ignoring the effect of \( pK_2 \) on the pH).
(iv) Sketch the pH-volume added curve you would expect to obtain when 60 cm$^3$ of 0.25 mol dm$^{-3}$ NaOH is added to 20 cm$^3$ of 0.25 mol dm$^{-3}$ butanedioic acid. On your curve, include all relevant information and highlight any buffer regions. [7]

(c) When chlorine gas is passed over heated aluminium in a hard glass tube, a vapour is produced which condenses to a yellow-white solid. At low temperatures, the vapour has the empirical formula AlCl$_3$ and an $M_r$ of 267.

(i) Suggest the molecular formula of the vapour, and draw a ‘dot-and-cross’ diagram to describe the bonding.

The yellow-white solid reacts with water in two different ways. When a few drops of water are added to the solid, steamy white fumes are evolved and a white solid remains, which is insoluble in water. When a large volume of water is added to the solid, a clear, weakly acidic solution is produced.

(ii) Write equations, including state symbols, for these two reactions and explain the observations. [6]

[Total: 20]
3 Alcohols and ketones are two classes of organic compounds with great importance in both industrial processes and in biological systems.

(a) The iodination of propanone under acidic conditions is shown by the following equation:

\[ \text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{I}(\text{aq}) + \text{H}^+(\text{aq}) + \text{I}^-(\text{aq}) \]

The rate of the reaction was studied via a colorimetric method, in which the colour intensity of iodine was measured at regular intervals. Three sets of separate experiments were performed in which the initial concentration of iodine, propanone and acid was varied in turn, with the other two being kept constant. The results are shown in Graphs 1 and 2 below:

**Graph 1**

- \([\text{CH}_3\text{COCH}_3] = 0.10 \text{ mol dm}^{-3}\)
- \([\text{CH}_3\text{COCH}_3] = 0.17 \text{ mol dm}^{-3}\)
- \([\text{CH}_3\text{COCH}_3] = 0.25 \text{ mol dm}^{-3}\)

**Graph 2**

- \([\text{H}^+] = 0.20 \text{ mol dm}^{-3}\)
- \([\text{H}^+] = 0.40 \text{ mol dm}^{-3}\)
- \([\text{H}^+] = 0.60 \text{ mol dm}^{-3}\)
(i) Suggest another method, other than a colorimetric method, that can be used to investigate the rate of the reaction. Include the variables to be measured.

(ii) Using the graphs above, deduce the orders of reaction with respect to propanone, iodine and H⁺.

(iii) Hence, write the rate equation for this reaction.

A mechanism for the reaction is suggested as below:

\[
\begin{align*}
\text{CH}_3\text{COCH}_3 & \xrightarrow{\text{H}^+ \text{ as catalyst}} \text{CH}_2\text{C(OH)}\text{CH}_3 \\
\text{stage 1} & \xrightarrow{\text{I}_2 \text{ stage 2}} \text{CH}_3\text{COCH}_2\text{I}
\end{align*}
\]

(iv) From your answers from (iii), what can be deduced about the relative rate of the two stages given in the mechanism above? Explain your answer. [8]

(b) Ketone bodies are three water-soluble organic compounds that are produced as by-products when fatty acids are broken down for energy in the liver. The three ketone bodies found in humans are propanone, 3-oxobutanoic acid and 3-hydroxybutanoic acid.

![Chemical structures of 3-oxobutanoic acid and 3-hydroxybutanoic acid]

(i) 3-oxobutanoic acid can be converted to 3-hydroxybutanoic acid in a chemistry laboratory. State the reagents required for this conversion and the type of reaction undergone.

(ii) Under suitable conditions, 3-hydroxybutanoic acid can be converted to 3-bromobutanoic acid. Compare the acid strength of 3-bromobutanoic acid and butanoic acid. Explain your answer.

(iii) The accumulation of ketone bodies in blood can cause an alarming decrease in the pH of blood. Suggest how this is prevented in the human body. [5]
(c) Compound P is a drug used to treat narcolepsy, a condition where a person falls asleep uncontrollably. P has a molecular formula of C₄H₆O₃ and is structurally related to one of the ketone bodies. P can be oxidised to give compound Q, which then reacts with alkaline copper(II) ions to give a brick-red precipitate and the salt of an acid, R. 1 mole of P and R will each react with sodium metal to produce 1 mole of hydrogen gas.

When P is warmed with a few drops of concentrated sulfuric acid, a neutral compound S, with the molecular formula C₄H₆O₂, can be isolated.

Deduce the structures of P, Q, R and S. Explain your reasoning. [7]

[Total: 20]
Organic compounds containing halogens are widely used in industry and society as flame retardants, refrigerants, propellants, solvents and pharmaceuticals.

(a) Methylbenzene can be converted to 1-chloro-2-methylbenzene.

(i) State the reagents and conditions required for the conversion.

(ii) State the type of reaction and describe the mechanism for the conversion of methylbenzene to 1-chloro-2-methylbenzene.

(iii) Calculate the percentage yield of the conversion given that 92.4 g of 1-chloro-2-methylbenzene was obtained from 118 g of methylbenzene.

(iv) Another mono-chlorinated compound was also formed in significant amounts. Suggest the structure of this other compound.

(b) Suggest a two-step synthesis to convert 1-chloropropane to butanoic acid, giving the structure of the intermediate.

(c) Compound A is an optically active compound with molecular formula C_{10}H_{13}Br. When heated with aqueous sodium hydroxide, compound A gives compound B which forms a yellow precipitate when warmed with alkaline iodine.

When compound A is heated under reflux with sodium hydroxide dissolved in ethanol, it forms compound C which has molecular formula C_{10}H_{12}. When cold, alkaline potassium manganate(VII) is added to compound C, compound D with molecular formula, C_{10}H_{10}O_{2}, is formed. On the other hand, when compound C is heated with acidified potassium manganate(VII), the products are compound E with molecular formula, C_8H_6O_4, and ethanoic acid.

Deduce the structures of compounds A, B, C, D and E. Explain the chemistry of the reactions involved.
Sulfur is a chemical element with the symbol S and an atomic number of 16. It is an abundant, multivalent non-metal. It can be found in amino acids and as a precursor to other chemicals such as H₂SO₄. H₂SO₄ is a common mineral acid with many uses. It can be used as an electrolyte and an oxidising agent.

(a) Anodising is a process used to increase the thickness of the natural oxide, on the surface of metal parts. Aluminium is a common metal which can be anodised as aluminium is a reactive metal and is readily oxidised by oxygen in air. This forms a layer of aluminium oxide (Al₂O₃), making it resistant to corrosion.

(i) Using H₂SO₄(aq) as the electrolyte and an inert electrode, draw an electrolysis set-up to show how an iPod Nano®, which is made of Al, can be anodised.

(ii) Write chemical equations to show the reactions at the anode and cathode during anodisation.

(iii) The iPod Nano® has a surface area of 29.21 cm² which can be anodised. How long will it take to form a 0.2 mm protective layer of Al₂O₃ on the iPod Nano® if a current of 2.0 A is passed through the set-up?

\[
\text{density of Al₂O₃ is } 3.95 \text{ g cm}^{-3}\]

[10]

(b) Heating solid halides with concentrated H₂SO₄ is one of the ways to obtain hydrogen halides. However, the halides have different reactivity with concentrated H₂SO₄.

(i) Write an equation to show the reaction of NaCl with concentrated H₂SO₄.

(ii) With reference to the Data Booklet, explain why chlorine cannot be isolated by the action of concentrated sulfuric acid with sodium chloride.

[3]
(c) Sulfur is an essential element for all life, and is widely used in biochemical processes. Sulfur is a component of some amino acids such as cysteine.

(i) Using the cysteine residue, as shown in the diagram below, construct an equation to show the formation of the disulfide bridge between two cysteine residues.

\[
\begin{align*}
\text{H} & \quad \text{CH}_2\text{SH} \\
\text{-----N--CH--C-----} & \\
\text{O} & \\
\end{align*}
\]

(ii) Denaturation of proteins involves the disruption and possible destruction of the tertiary structure of the protein. Addition of heavy metal ions can cause denaturation through the disruption of R group interactions.

State and explain, in chemical terms, how R group interactions are disrupted by the addition of heavy metal ions. [4]

(d) Group II elements are shiny, silvery-white reactive metals. Down the group, reactivity of the elements changes.

(i) With reference to the Data Booklet, state and explain the trend in reactivity, in terms of reducing power, from Mg to Ba.

(ii) State the differences in reactivity of Mg and Ba with water. [3]

[Total: 20]
H2 Chemistry (9647) Prelims 2012 Paper 3

1 (a) (i) \[
\begin{array}{c}
\text{C} \\
\text{O}
\end{array}
\]

(ii) Nickel carbonyl has a simple covalent structure with weak intermolecular forces which require little energy to overcome.

(iii) \[
\begin{align*}
M_r &= \frac{2.00 \times 8.31 \times (273 + 50)}{1.01 \times 10^5 \times 314 \times 10^{-6}} \\
&= 169
\end{align*}
\]

(iv) \[
\begin{align*}
58.7 + (12.0 + 16.0)x &= 169 \\
x &= \frac{169 - 58.7}{12.0 + 16.0} \\
&= 3.93 \\
&= 4 \text{ (nearest whole number)}
\end{align*}
\]

Coordination number is 4

Tetrahedral (accept “square planar”) [7]

(b) (i) In transition metal compounds, the presence of ligands causes the 3d orbitals to split into 2 sets of non-degenerate orbitals. The difference in energies (\(\Delta E\)) between these 2 sets of 3d orbitals is small and radiation from the visible region of the electromagnetic spectrum is absorbed when an electron moves from a lower energy d-orbital to another unfilled/partly-filled d orbital of higher energy. The colour observed correspond to the complement of the absorbed colours. Hence, transition metal compounds are often coloured. [3]

(ii) Blue solution \([\text{Cu(H}_2\text{O)}_6]^2+\]

Yellow solution \(\text{CuCl}_4^{2-}\)

Blue solution was formed from the oxidation of Cu (to \(\text{Cu}^{2+}(\text{aq})\)).

Blue solution formed a white solid on heating to due to loss of water ligands. / Splitting of 3d orbitals into 2 sets of different energy no longer occurs.

\[
\text{CuCl}_4^{2-} + 6\text{H}_2\text{O} = [\text{Cu(H}_2\text{O)}_6]^2+ + 4\text{Cl}^- 
\]

On addition of water, position of equilibrium of \(\text{CuCl}_4^{2-} + 6\text{H}_2\text{O} = [\text{Cu(H}_2\text{O)}_6]^2+ + 4\text{Cl}^-\) shifts to the right, forming blue \([\text{Cu(H}_2\text{O)}_6]^2+\) [6]
(c) Limonene:
  aqueous bromine
  cold alkaline KMnO₄
Menthone:
  2,4-DNPH
Menthol:
  PCl₅ / SOCl₂
  Acidified potassium dichromate, heat

Acidified KMnO₄, heat; followed by test with limewater

2 (a) (i) Oxidation number = 0 – (−2) – 4(+1)
       = −2

(ii) Zero

(iii) CH₃CH₂CH₂CH₂OH(l) + 6O₂(g) → 4CO₂(g) + 5H₂O(l)

(iv) Temperature increase = 58 − 23
     = 35 °C
Heat evolved = 35 × 515 × 4.18
       = 7.53 × 10⁴ J
Amount of butan-1-ol = 2.30 ÷ (4 × 12.0 + 10 × 1.0 + 16.0)
       = 3.11 × 10⁻² mol

\[\Delta H_c = \frac{7.53 \times 10^4}{3.11 \times 10^{-2}}\]
       = −2.42 × 10⁶ J mol⁻¹
\[ = -2.42 \times 10^3 \text{ kJ mol}^{-1} \]

(v) The calculated value is less negative (less exothermic) than the true value as there is heat loss to the surroundings and copper can calorimeter.

(b) (i) Propanedioic acid is a stronger acid than butanedioic acid due to the stabilisation of the anion by hydrogen bonding with the unionised $-\text{CO}_2\text{H}$ group.

\[
\text{HO}_2\text{C} = \text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{C} = \text{O} + \text{H}_3\text{O}^+ \\
\text{H}_2\text{C} = \text{O}^\text{2-} + \text{H}_3\text{O}^+ \\
\text{A}
\]

(ii) Removal of $\text{H}^+$ from an anion (A) that already carries a negative charge is electrostatically unfavourable.

OR

The stabilising hydrogen bonding would be destroyed by the ionisation of the second $-\text{CO}_2\text{H}$ group.

(iii) Let the acid be HA and the concentration of $\text{H}^+(\text{aq})$ be $x$.

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

\[
10^{-4.20} = \frac{x^2}{0.25 - x}
\]

Since $x$ is small,

\[
10^{-4.20} = \frac{x^2}{0.25}
\]

\[x = 3.97 \times 10^{-3} \text{ mol dm}^{-3}\]

\[\text{pH} = -\log (3.97 \times 10^{-3}) \]

\[= 2.40\]
(iv) 

\[
\text{Al}_2\text{Cl}_6(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Al(OH)}_3(s) + 3\text{HCl}(g)
\]

OR 
\[
2\text{AlCl}_3(s) + 3\text{H}_2\text{O}(l) \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{HCl}(g)
\]

(When a few drops of water is added, AlCl₃ undergoes hydrolysis to form white fumes of HCl(g) and white insoluble solid of Al(OH)₃.)

\[
\text{AlCl}_3(s) + 6\text{H}_2\text{O}(l) \rightarrow [\text{Al(H}_2\text{O})_6]^{3+}(aq) + 3\text{Cl}^-(aq)
\]

\[
[\text{Al(H}_2\text{O})_6]^{3+}(aq) + \text{H}_2\text{O}(l) = [\text{Al(OH)(H}_2\text{O})_5]^{2+}(aq) + \text{H}_3\text{O}^+(aq)
\]

AlCl₃ undergoes dissolves readily in water to form hydrated/aqueous Al³⁺ / Al²⁺(aq) ions which undergoes hydrolysis due to the high charge density of the polarising cation to give a weakly acidic solution.
3 (a) (i) Determine the \([I_2]\) at regular time intervals by quenching the sample of the solution and titrating with aqueous sodium thiosulfate. 

**OR** Measure the electrical conductivity of solution at different time intervals.

**OR** Measure the pH of the solution at regular time intervals using a pH meter.

(ii) The graph of \([I_2]\) against time is a straight line, indicating that rate is constant despite decreasing \([I_2]\). Hence, the reaction is zero order with respect to iodine.

From graph 1, when \([CH_3COCH_3]\) is increased from 0.10 mol dm\(^{-3}\) to 0.25 mol dm\(^{-3}\), gradient/rate of reaction is increased from \(1.0 \times 10^{-4}\) mol dm\(^{-3}\) min\(^{-1}\) to \(2.5 \times 10^{-4}\) mol dm\(^{-3}\) min\(^{-1}\). Gradient/rate is 2.5 times the original gradient/rate when \([CH_3COCH_3]\) is 2.5 times the original concentration. Hence, the reaction is first order with respect to propanone.

From graph 2, when \([H^+]\) is doubled from 0.20 mol dm\(^{-3}\) to 0.40 mol dm\(^{-3}\), gradient/rate of reaction is also doubled from \(1.67 \times 10^{-4}\) mol dm\(^{-3}\) min\(^{-1}\) to \(3.33 \times 10^{-4}\) mol dm\(^{-3}\) min\(^{-1}\). Hence, the reaction is first order with respect to \(H^+\).

(iii) Rate = \(k[CH_3COCH_3][H^+]\)

(iv) Stage 1 is relatively slower than stage 2. / Stage 1 is the slow step. / Stage 1 is the rate determining step.

Rate equation suggests that the slow step/ rate determining step involves only one molecule of propanone and a \(H^+\) ion.

(b) (i) \(NaBH_4\) (in aqueous ethanol) OR \(H_2, Ni, (heat)\)

Reduction

(ii) The **electron-withdrawing bromine** atom in 3-bromobutanoate ion **disperses the negative charge on the COO\(^-\) group**, making the 3-bromobutanoate ion **more stable** than the butanoate ion. Hence, **3-bromobutanoic acid is a stronger acid**.

(iii) An increase in concentration of 3-oxobutanoic acid and 3-hydroxybutanoic acid is buffered by the \(CO_2/HCO_3^-\) buffer system present in blood. **OR**

Excess ketone bodies are excreted from the human body in urine (since they are water-soluble).

(c) \(P\) undergoes oxidation to give \(Q\), which **is further oxidised by Fehling’s solution/gives positive Fehling’s test** to form the salt of \(R\).
Q is an aldehyde and P is a primary alcohol.

Both P and R undergoes acid-metal reaction with sodium to give 1 mole of hydrogen gas

Both P and R contain 2 O–H groups.

P undergoes (intramolecular) condensation when warmed with concentrated sulfuric acid to produce S ⇒ S is a (cyclic) ester.

Structures:

P:

\[
\text{HO} - \text{CH} = \text{CH} - \text{CH} - \text{CH} - \text{CH} = \text{O} - \text{OH}
\]

Q:

\[
\text{H} - \text{CH} = \text{CH} - \text{CH} - \text{CH} = \text{O} - \text{OH}
\]

R:

\[
\text{HO} - \text{CH} = \text{CH} - \text{CH} - \text{CH} = \text{O} - \text{OH}
\]

S:

\[
\text{O} - \text{O}
\]

4  (a)  

(i)  \( Cl_2, AlCl_3 \)

OR

\( Cl_2, FeCl_3 \)

OR

\( Cl_2, Fe \)

(ii)  Electrophilic substitution

\( Cl_2 + AlCl_3 \rightarrow Cl^+ + AlCl_4^- \)
(iii) Amount of methylbenzene in 118 g
\[ = 118 \div (7 \times 12.0 + 8 \times 1.0) \]
\[ = 1.28 \text{ mol} \]
Amount of 1-chloro-2-methylbenzene produced
\[ = 92.4 \div (7 \times 12.0 + 7 \times 1.0 + 35.5) \]
\[ = 0.730 \text{ mol} \]
Percentage yield \[= \frac{0.730}{1.28} \times 100 \]
\[= 57.0\% \]

(iv)

(b) \[\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{KCN(aq)}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CN} \xrightarrow{\text{dilute H}_2\text{SO}_4(aq)} \text{CH}_3\text{CH}_2\text{COOH}\]

(c) Compound A is optically active
\[\Rightarrow\] compound A contains chiral carbon
C:H ratio in Compound A is close to 1:1
\[\Rightarrow\] compound A contains benzene ring
Compound A undergoes nucleophilic substitution with NaOH(aq) to form compound B
\[\Rightarrow\] compound B is an alcohol
\[\Rightarrow\] compound A is an alkyl bromide/alkyl halide
Positive iodoform test with Compound B
⇒ compound B contains –CH(OH)CH₃

Compound A undergoes elimination to form compound C
⇒ compound A is an alkyl bromide/alkyl halide
⇒ compound C contains C=C bond / alkene functional group

Compound C undergoes mild oxidation to form compound D
⇒ compound D is a diol

Compound C undergoes vigorous oxidation to form compound E and ethanoic acid
⇒ compound C is not a terminal alkene
Reactions at anode:
\[ 2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \]
\[ 2\text{Al}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{Al}_2\text{O}_3(s) \]

Reaction at cathode:
\[ 2\text{H}^+(aq) + 2\text{e}^- \rightarrow \text{H}_2(g) \]

(iii) Volume of \( \text{Al}_2\text{O}_3 \) layer = 29.21 \times 0.02 = 0.584 cm\(^3\)

Mass of \( \text{Al}_2\text{O}_3 \) = 3.95 \times 0.584 = 2.31 g

Amount of \( \text{Al}_2\text{O}_3 \) = \( \frac{2.31}{2 \times 27.0 + 3 \times 16.0} \)
= 0.0226 mol

Amount of \( \text{O}_2 \) = 0.0226 \times 3/2
= 0.0339 mol

Amount of electrons passed through the cathode = 0.0339 \times 4
= 0.136 mol

\[ \text{Q} = 0.136 \times 96500 \]
= 13100 C

Time needed = 13100 ÷ 2.0
= 6550 s

(b) (i) \( \text{NaC}/(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{NaHSO}_4(s) + \text{HCl}(g) \)
(State symbols not required)

(ii) \(2\text{Cl}^- + \text{SO}_4^{2-} + 4\text{H}^+ \rightarrow \text{Cl}_2 + \text{SO}_2 + 2\text{H}_2\text{O}\)

\[ E_{\text{cell}} = +0.17 - (+1.36) \]

\[ = -1.19 \text{ V} \]

As \( E_{\text{cell}} < 0 \text{ V} \), reaction is energetically non-feasible.

(c) (i)

(ii) Heavy metal ions form ionic interactions with –COO\(^-\), which brings about the formation of insoluble protein salts (i.e. precipitation of protein). This disrupts the ionic interactions in the tertiary structure, and hence leads to denaturation.

Heavy metal ions have a high affinity for sulfur and will bind tightly to the –SH group. This disrupts the disulfide bridges in the tertiary structure, and hence leads to denaturation.

(d) (i)

<table>
<thead>
<tr>
<th>Electrode reaction</th>
<th>( E(\text{M}^{2+}/\text{M})/ \text{ V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}^{2+} + 2\text{e}^- = \text{Mg} )</td>
<td>(-2.38)</td>
</tr>
<tr>
<td>( \text{Ca}^{2+} + 2\text{e}^- = \text{Ca} )</td>
<td>(-2.87)</td>
</tr>
<tr>
<td>( \text{Ba}^{2+} + 2\text{e}^- = \text{Ba} )</td>
<td>(-2.90)</td>
</tr>
</tbody>
</table>

Down the group, \( E(\text{M}^{2+}/\text{M}) \) becomes more negative. Therefore, the reducing power increases from Mg to Ba.

<table>
<thead>
<tr>
<th>Element</th>
<th>1(^{\text{st}}) IE/ kJ mol(^{-1})</th>
<th>2(^{\text{nd}}) IE/ kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**OR Quote 1\textsuperscript{st} and 2\textsuperscript{nd} IE values**

This is because the atomic radius increases from Mg to Ba and as a result, ionisation energy decreases. Thus, reducing power increases from Mg to Ba.

(ii) Mg reacts with cold water slowly/Mg reacts with steam readily while Ba reacts with cold water vigorously.
ST ANDREW’S JUNIOR COLLEGE

JC2 Preliminary Examinations

Chemistry
Higher 2 9647/01
Paper 1 Multiple Choice 19 September 2012
1 hour

Additional Materials: Multiple Choice Answer Sheet, Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil. Do not use staples, paper clips, highlighters, glue or correction fluid.

There are 40 questions on this paper. Answer all questions. For each question there are four possible answers A, B, C and D. Chose the one you consider correct and record your choice in soft pencil on the separate Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.

This document consists of 22 printed pages including this page.
Section A

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

1. Group I and Group II ionic hydrides react with water.
   \[ \text{H}^+ + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2 \]

   In an experiment, 1 g of a sample of an ionic hydride is dissolved in excess \( \text{H}_2\text{O} \). The resulting solution required 24.00 cm\(^3\) of a 2.0 mol dm\(^{-3}\) \( \text{HCl} \) solution for complete neutralisation.

   What is the formula of the hydride?

   A. \( \text{LiH} \)
   B. \( \text{NaH} \)
   C. \( \text{MgH}_2 \)
   D. \( \text{CaH}_2 \)

2. Which species is oxidised and which species is reduced in the following reaction?

   \[ 4\text{TiCr}_2\text{O}_4 + 8\text{Rb}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Rb}_2\text{CrO}_4 + 2\text{Ti}_2\text{O}_3 + 8\text{CO}_2 \]

<table>
<thead>
<tr>
<th>Species oxidised</th>
<th>Species reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Chromium only</td>
</tr>
<tr>
<td>B</td>
<td>Chromium only</td>
</tr>
<tr>
<td>C</td>
<td>Chromium and titanium</td>
</tr>
<tr>
<td>D</td>
<td>Chromium and titanium</td>
</tr>
<tr>
<td></td>
<td>Carbonate ion only</td>
</tr>
<tr>
<td></td>
<td>Carbonate ion and oxygen</td>
</tr>
<tr>
<td></td>
<td>Oxygen only</td>
</tr>
<tr>
<td></td>
<td>Carbonate ion and oxygen</td>
</tr>
</tbody>
</table>
3. The graph below shows how pressure varies with temperature when 1 mole of helium is heated in an enclosed volume.

![Graph showing pressure vs. temperature for helium.]

Similar relationship between pressure and temperature was examined for 1 mole of gaseous $\text{XY}_2$ which dissociates according to the following equation.

$$\text{XY}_2 (g) \xrightleftharpoons{} \text{X} (g) + \text{Y}_2 (g) \Delta H > 0$$

Which graph best represents how pressure varies with temperature of the gas?

A  

B  

C  

D
4. Which of the following particles has a half-filled p subshell after losing two electrons?

A  Ga<sup>-</sup>
B  As<sup>2+</sup>
C  Se<sup>-</sup>
D  Te<sup>+</sup>

5. Which of the following isomers is likely to have the highest boiling point?

A

B

C

D

6. In which of the following reactions is the H–N–H bond angle in ammonia smaller than that in the product?

A  \(2\text{NH}_3(l) + 2\text{Na}(s) \rightarrow 2\text{NaNH}_2(s) + \text{H}_2(g)\)
B  \(\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)\)
C  \(2\text{NH}_3(g) \rightarrow \text{H}_2\text{N}–\text{NH}_2(l) + \text{H}_2(g)\)
D  \(2\text{NH}_3(g) + \text{O}_2(g) \rightarrow 2\text{NH}_2\text{OH}(l)\)
7. When water vaporises, 51.6 kJ mol\(^{-1}\) of heat enthalpy is required. What is the entropy change when 54 g of water boils at 1 atm?

A  + 138 J K\(^{-1}\)
B  + 415 J K\(^{-1}\)
C  + 516 J K\(^{-1}\)
D  + 1548 J K\(^{-1}\)

8. Ellingham diagrams are plots of \(\Delta G\) against temperature, T. An Ellingham diagram for two reactions involving the oxidation of S and SO\(_2\) is as shown below:

Given that, \(\Delta G = \Delta H - T\Delta S\), which of the following correctly shows the two reactions corresponding to reactions I and II in the above Ellingham diagram?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2S + 3O(_2) (\uparrow) 2SO(_3)</td>
<td>2SO(_2) + O(_2) (\uparrow) 2SO(_3)</td>
</tr>
<tr>
<td>B</td>
<td>2SO(_2) + O(_2) (\uparrow) 2SO(_3)</td>
<td>S + O(_2) (\uparrow) SO(_2)</td>
</tr>
<tr>
<td>C</td>
<td>S + O(_2) (\uparrow) SO(_2)</td>
<td>2S + 3O(_2) (\uparrow) 2SO(_3)</td>
</tr>
<tr>
<td>D</td>
<td>2SO(_2) + O(_2) (\uparrow) 2SO(_3)</td>
<td>2S + 3O(_2) (\uparrow) 2SO(_3)</td>
</tr>
</tbody>
</table>
9. In the conversion of compound X into compound Z, it was found that the reaction proceeded according to the rate equation below:

\[
\text{Rate} = k [X]
\]

The intermediate Y can be isolated. Which reaction profile fits these data?
10. A solution of vanadium (V) ions in 1 mol dm$^{-3}$ H$_2$SO$_4$ slowly oxidises arsenic (III) oxide to arsenic (V) oxide, according to the following equation.

$$\text{As}_2\text{O}_3 + 4 \text{VO}_2^+ + 4 \text{H}^+ \rightleftharpoons \text{As}_2\text{O}_5 + 4 \text{VO}^{2+} + 2 \text{H}_2\text{O}$$

To find the rate equation for the above reaction, two experiments were carried out, starting with different concentrations of arsenic (III) oxide and the concentration of VO$_2^+$ was monitored.

The rate equation is most likely to be

A  $\text{rate} = k [\text{As}_2\text{O}_3][\text{VO}_2^+]$

B  $\text{rate} = k [\text{As}_2\text{O}_3][\text{VO}_2^+]^2$

C  $\text{rate} = k [\text{As}_2\text{O}_3]^2[\text{VO}_2^+]$

D  $\text{rate} = k [\text{As}_2\text{O}_3]$
11. The graphs below show the variation of the percentage of gaseous products present at equilibrium, with pressure and two temperatures, $T \, ^\circ\text{C}$ and $(T + z) \, ^\circ\text{C}$.

Which one of the following systems could the graphs represent?

A $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ \hspace{1cm} $\Delta H = - 92 \text{ kJ mol}^{-1}$

B $3\text{O}_2(g) + 4\text{NH}_3(g) \rightleftharpoons 2\text{N}_2(g) + 6\text{H}_2\text{O}(g)$ \hspace{1cm} $\Delta H = - 1248 \text{ kJ mol}^{-1}$

C $2\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{N}_2\text{O} \, (g)$ \hspace{1cm} $\Delta H = + 82 \text{ kJ mol}^{-1}$

D $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO} \, (g)$ \hspace{1cm} $\Delta H = + 173 \text{ kJ mol}^{-1}$

12. Solutions E, F, G and H contain a strong monobasic acid, a weak monobasic acid $\text{HX}$, a strong base and a salt of $\text{HX}$, but not necessarily in the same order. The concentration and pH for each solution are shown below.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration /mol dm$^{-3}$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>F</td>
<td>1.0</td>
<td>9.4</td>
</tr>
<tr>
<td>G</td>
<td>0.01</td>
<td>12.0</td>
</tr>
<tr>
<td>H</td>
<td>0.01</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Which one of the following statements is false?

A $\text{E}$ contains a weak acid while $\text{H}$ contains a strong acid.

B Mixing 10 cm$^3$ of $\text{E}$ and 50 cm$^3$ of $\text{G}$ produces a buffer solution.

C Mixing 10 cm$^3$ of $\text{E}$ and 50 cm$^3$ of $\text{H}$ produces a buffer solution.

D Mixing 10 cm$^3$ of $\text{F}$ and 1 dm$^3$ of $\text{H}$ produces an acidic solution.
13. At a temperature $T$ K, 0.60 mol $\text{dm}^{-3}$ of CO and 0.30 mol $\text{dm}^{-3}$ of O₂ were introduced into a 5 $\text{dm}^3$ vessel and allowed to reach equilibrium.

\[ 2 \text{CO (g)} + \text{O}_2 (g) \rightleftharpoons 2\text{CO}_2 (g) \quad \Delta H < 0 \]

The graph below shows the changes in the concentration of CO and CO₂ in the system with time. A change was made to the system at time, $t_1$ and $t_2$.

What were the changes made at time, $t_1$ and $t_2$?

<table>
<thead>
<tr>
<th></th>
<th>$t_1$</th>
<th>$t_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A catalyst was added</td>
<td>Volume of the system is increased</td>
</tr>
<tr>
<td>B</td>
<td>The temperature was increased</td>
<td>Volume of the system is decreased</td>
</tr>
<tr>
<td>C</td>
<td>More CO₂ was added</td>
<td>An inert gas was added at constant volume</td>
</tr>
<tr>
<td>D</td>
<td>The temperature was decreased</td>
<td>More O₂ was added</td>
</tr>
</tbody>
</table>
14. *Use of the data booklet is relevant to this question.*

Two cells are connected in series as shown in the diagram where **P**, **Q**, **R** and **S** are electrodes. Which of the following correctly shows the products formed at each electrode?

![Diagram of a cell with electrodes P, Q, R, and S connected in series.](image)

<table>
<thead>
<tr>
<th></th>
<th><strong>P</strong></th>
<th><strong>Q</strong></th>
<th><strong>R</strong></th>
<th><strong>S</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cu$^{2+}$</td>
<td>H$_2$</td>
<td>O$_2$</td>
<td>Fe$^{2+}$</td>
</tr>
<tr>
<td>B</td>
<td>O$_2$</td>
<td>Cu</td>
<td>SO$_2$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>C</td>
<td>Cl$_2$</td>
<td>H$_2$</td>
<td>O$_2$</td>
<td>Fe</td>
</tr>
<tr>
<td>D</td>
<td>Cu$^{2+}$</td>
<td>Cu</td>
<td>SO$_2$</td>
<td>Fe$^{2+}$</td>
</tr>
</tbody>
</table>

15. *Use of the data booklet is relevant to this question.*

Ladles are often made from sterling silver. Which aqueous solution should not be stirred with a silver ladle because a reaction could occur?

A  KC\textsubscript{1}  
B  (NH\textsubscript{4})\textsubscript{2}S\textsubscript{4}O\textsubscript{6}  
C  Na\textsubscript{2}SO\textsubscript{4}  
D  PbBr\textsubscript{4}  

[Turn Over]
16. The oxide and chloride of an element F are separately mixed with water. The two resulting solutions have the same effect on methyl orange and can also be used to dissolve BeO. What is element F?

A  Magnesium  
B  Aluminium  
C  Silicon  
D  Phosphorus

17. Which of the following statements about the elements strontium and barium is correct?

A  The elements react with cold water liberating hydrogen gas.  
B  Aqueous solutions of their chlorides have a pH greater than 7.  
C  The hydroxide of barium is less stable to heat.  
D  The enthalpy change of hydration of the cations becomes less endothermic from strontium to barium.

18. Which statement is likely to be true for astatine which is below iodine in group VII of the Periodic Table?

A  Potassium astatide and hot dilute sulfuric acid react to form astatine.  
B  Silver astatide reacts with excess dilute aqueous ammonia to form a soluble complex.  
C  Sodium astatide and hot concentrated phosphoric acid react to form white fumes of hydrogen astatide.  
D  Hydrogen astatide is stable to heat.
19. Transition metals such as iron are often used as a catalyst in reactions such as the Haber process. Which of the following statements best explains the role of transition metals in this use?

A Transition metals have good electrical conductivity as both 4s and 3d electrons are involved in metallic bonding.
B Transition metals have available and partially filled 3d orbitals for adsorption of reactant molecules.
C Transition metals form coloured ions due to the absorption of energy in the visible light region to promote an electron from a lower to a higher energy 3d orbital.
D Transition metals can exhibit variable oxidation states due to the close proximity in energy between the 3d and 4s electrons.

20. X is a transition metal. In aqueous solution, it forms the coloured complex ion, \([X(H_2O)_6]^{3+}\). On oxidation of \([X(H_2O)_6]^{3+}\) to \([X(H_2O)_6]^{5+}\), the solution turned colourless. Which of the following is the electronic configuration of the transition metal X?

A \([\text{Ar}]\ 3d^2\ 4s^2\)
B \([\text{Ar}]\ 3d^3\ 4s^2\)
C \([\text{Ar}]\ 3d^5\ 4s^1\)
D \([\text{Ar}]\ 3d^{10}\ 4s^2\)

21. How many cyclic hydrocarbons are there with the molecular formula \(C_4H_6\)?

A 3
B 4
C 5
D 6
22. Warfarin is used as a pesticide against rodents. The structural formula of warfarin is given below.

Which of the following reactants will not react with warfarin?

A  Alkaline aqueous iodine
B  Acidified potassium manganate (VII)
C  Ethanoyl chloride
D  Neutral FeCl₃

23. In which of the following reactions would the intermediate behave as a nucleophile?

- Reaction 1: CH₃CH₂CHO $\overset{\text{intermediate}}{\longrightarrow}$ CH₃CH₂CH(OH)(CN)
- Reaction 2: C(CH₃)₃Cl $\overset{\text{intermediate}}{\longrightarrow}$ C(CH₃)₃NH₂
- Reaction 3:

A  Reaction 1
B  Reactions 1 and 2
C  Reaction 2
D  Reactions 2 and 3
24. Which of the following reaction scheme is able to prepare compound G from methylbenzene?

\[
\text{NH}_2 \\
\text{O} \\
\text{O} \\
\text{NH}_2
\]

Compound G

A  Nitration, Side-chain oxidation, Condensation
B  Nitration, Reduction, Side-chain oxidation, Condensation
C  Side-chain oxidation, Condensation, Nitration
D  Side-chain oxidation, Condensation, Nitration, Reduction

25. Diels-Alder reaction is a conjugate addition reaction which is best exemplified by the reaction below.

\[
\text{Cyclopentene} + \text{Ethene} \rightarrow \text{Compound H}
\]

Which of the following pairs of starting materials will give the following compound H?

\[
\text{Compound H}
\]

A  Cyclopentene and ethene
B  Cyclobutene and ethene
C  Cyclopentadiene and ethene
D  Cyclobutadiene and ethene
26. Which of the following compounds is formed when compound M is dissolved in aqueous sodium hydroxide under standard conditions?

![Compound M](image)

**A**  
\[
\begin{align*}
O^+Na^+ &\quad NH_2 \\
O^+Na^+ &\quad OCOCH_2OH
\end{align*}
\]

**B**  
\[
\begin{align*}
O^+Na^+ &\quad NHCOCH_3 \\
O^+Na^+ &\quad OCOCH_2O^+Na^+
\end{align*}
\]

**C**  
\[
\begin{align*}
O^+Na^+ &\quad NH_2 \\
O^+Na^+ &\quad OCOCH_2OH
\end{align*}
\]

**D**  
\[
\begin{align*}
O^+Na^+ &\quad NHCOCH_3 \\
O^+Na^+ &\quad OCOCH_2OH
\end{align*}
\]

27. In which sequence is it correctly stated that the value of pKₐ decreases continuously?

A  \[CH_3CH_2CONHCH_3, CH_3CH_2NH_2, CH_2C(CH_2NH_2), C_6H_5NH_2\]

B  \[CH_3CH_2CONHCH_3, C_6H_5NH_2, CH_2C(CH_2NH_2), CH_3CH_2NH_2\]

C  \[CH_3CH_2NH_2, CH_2C(CH_2NH_2), C_6H_5NH_2, CH_3CH_2CONHCH_3\]

D  \[CH_2C(CH_2NH_2), CH_3CH_2NH_2, C_6H_5NH_2, CH_3CH_2CONHCH_3\]
28. Compound J exhibits the following characteristics:

- 1 mol of J reacts with excess sodium metal to form 1 mol of hydrogen gas.
- Yellow precipitate is formed when J reacts with aqueous alkaline iodine.
- Orange precipitate is formed when J reacts with 2,4-DNPH, but no reaction with alkaline silver diammine solution.
- J rotates plane-polarised light.

What could compound J be?

A

B

C

D

29. Which one of the following alcohols will give the most number of products when it is heated with concentrated H₂SO₄ at 170°C?

A  CH₃CH₂CH₂OH
B  C(CH₃)₂OH
C  CH₃CH₂CH(OH)CH₃
D  CH₃CH₂C(CH₃)₂OH
30. Polypeptides can be enzymatically hydrolysed to form shorter peptide chains. When a nanopeptide was hydrolysed by enzymes, the following tripeptides were obtained.

- gly-ala-leu
- tyr-ser-leu
- leu-gly-tyr
- lys-gly-ala
- ser-leu-gly

Which of the following could this nanopeptide be?

A  lys-gly-ala-leu-gly-tyr-ser-leu-gly
B  gly-ala-leu-gly-tyr-ser-leu-gly-tyr
C  lys-gly-ala-tyr-ser-leu-gly-tyr-ser
D  gly-ala-leu-gly-ser-tyr-leu-gly-tyr
Section B

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct. Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31. For the elements R and S with atomic number 14 and 15 respectively, which of the following statements are true?

1. The fifth ionisation energy of R is higher than that of S.
2. They can form RC\textsubscript{4} and SC\textsubscript{5} respectively.
3. The atomic radius of R is smaller than that of S.

32. For the following chlorine-containing species, IC\textsubscript{2}\textsuperscript{-}, C\textsubscript{5}F\textsubscript{3}, C\textsubscript{3}O\textsubscript{3}\textsuperscript{-}

Which of the following statements is correct?

1. All atoms achieve stable octet configuration.
2. IC\textsubscript{2}\textsuperscript{-} is linear, C\textsubscript{5}F\textsubscript{3} is T-shaped while C\textsubscript{3}O\textsubscript{3}\textsuperscript{-} is trigonal pyramidal.
3. The bond angles increase in the order of C\textsubscript{5}F\textsubscript{3}, C\textsubscript{3}O\textsubscript{3}\textsuperscript{-}, IC\textsubscript{2}\textsuperscript{-}
When a few drops of calcium nitrate solution is added to a saturated calcium hydroxide solution, a white precipitate is observed. Which of the following provides the correct explanation?

1. [Ca^{2+}] and [OH^-] are high enough such that the ionic product exceeds the $K_{sp}$.
2. The precipitate is formed because of the common ion, NO$_3^-$, and its effect on the equilibrium.
3. The $K_{sp}$ has decreased due to the addition of calcium nitrate.

When a current of 2.05 A was passed through J(NO$_3$)$_3$ (aq) for 1 hour and 13 minutes, 1.73 g of metal J was deposited at the cathode. Which of the following statements about the above electrolysis are correct?

1. J is iron.
2. A colourless gas, which turned acidified KMnO$_4$ from purple to colourless, was evolved at the anode.
3. Increasing the [NO$_3^-$] decreased the rate of formation of J.

Which of the following can act as ligands?

1. BF$_4^-$
2. CH$_3$CH$_2$NH$_2$
3. H$_2$S
No other combination of statements is used as a correct response.

36. In black and white photographic film, light converts silver chloride into metallic silver. After the film has been produced, the unreacted silver chloride is removed by reaction with sodium thiosulfate. Given that the function of the thiosulfate ion is similar to that of ammonia, what are the functions of the thiosulfate ion?

1 To oxidise the chloride ions to chlorine.
2 To form complexes with silver ions.
3 To lower the concentration of silver ions.

37. Salbutamol is used in the treatment of asthma.

Salbutamol

Which of the following statements about salbutamol are correct?

1 It reacts with SOCl₂ to form a product with three Cl atoms.
2 It has one chiral carbon.
3 One mole of salbutamol reacts with four moles of ethanoyl chloride.
No other combination of statements is used as a correct response.

38. Saffron and vanilla beans are often used to flavour foods. Safranal and vanillin are organic molecules which are responsible for the aromas of saffron and vanilla beans respectively.

Which of the following reagents show identical observations when reacted with both compounds?

1. Aqueous bromine
2. Ammonical silver nitrate
3. Acidified potassium dichromate (VI)
No other combination of statements is used as a correct response.

39. Which of the following statements are true for all amino acids from natural sources?

1. They can undergo condensation with one another to form peptide linkages.
2. They can exist as zwitterions which have high melting points.
3. When placed in buffer solutions with pH lower than their isoelectric points, amino acids will move towards the negative plate when electricity is applied.

40. Collagen is the main component of connective tissues in our body. The more common amino acids in collagen are listed in the table below.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>R-group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>-H</td>
</tr>
<tr>
<td>Alanine</td>
<td>-CH₃</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>-CH₂CH₂COOH</td>
</tr>
<tr>
<td>Arginine</td>
<td>-CH₂CH₂CH₂NHC(NH₂) = NH</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>-CH₂COOH</td>
</tr>
</tbody>
</table>

Which of the following statements about collagen are true?

1. pH changes will denature collagen.
2. Hydrogen bonds are responsible for forming the secondary and tertiary structures in collagen.
3. The R-groups of alanine and arginine interact with each other through induced dipole-induced dipole interactions.
<p>| | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D</td>
<td>2</td>
<td>C</td>
<td>3</td>
<td>D</td>
<td>4</td>
<td>C</td>
<td>5</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>7</td>
<td>B</td>
<td>8</td>
<td>C</td>
<td>9</td>
<td>A</td>
<td>10</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>D</td>
<td>12</td>
<td>C</td>
<td>13</td>
<td>B</td>
<td>14</td>
<td>A</td>
<td>15</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>D</td>
<td>17</td>
<td>A</td>
<td>18</td>
<td>C</td>
<td>19</td>
<td>B</td>
<td>20</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>C</td>
<td>22</td>
<td>D</td>
<td>23</td>
<td>A</td>
<td>24</td>
<td>B</td>
<td>25</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>D</td>
<td>27</td>
<td>B</td>
<td>28</td>
<td>C</td>
<td>29</td>
<td>C</td>
<td>30</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>B</td>
<td>32</td>
<td>C</td>
<td>33</td>
<td>D</td>
<td>34</td>
<td>D</td>
<td>35</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>C</td>
<td>37</td>
<td>C</td>
<td>38</td>
<td>C</td>
<td>39</td>
<td>A</td>
<td>40</td>
<td>A</td>
<td></td>
</tr>
</tbody>
</table>
Candidates answer in the spaces provided on the question paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST
Write in dark blue or black pen.
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 all questions.
You are reminded of the need for good English and clear presentation in your answers.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner’s Use:

<table>
<thead>
<tr>
<th>Question</th>
<th>Marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
</tr>
</tbody>
</table>
1 Planning (P)

Four aqueous solutions are provided. Each solution contains one of the following:
Aluminium bromide, Zinc sulfate, Silver nitrate, Barium hydroxide

You are to plan a series of test-tube experiments using only the four solutions and solid potassium carbonate, in order to deduce which compound is present.

**No other reagents should be used.**

You should commence your plan by adding potassium carbonate to each of the solutions. Your completed plan should include observations, deductions and balanced equations for positive tests.

<table>
<thead>
<tr>
<th>No.</th>
<th>Experiment</th>
<th>Observations</th>
<th>Deductions with relevant balanced equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Add ½ spatula of solid potassium carbonate to each separate samples (1 cm³) of the 4 solutions in clean, dry test tubes.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2 (a) Transition metals are often used to produce ornamental stained-glass windows. Iron–based colours and pigments have been used since ancient times for stained-glass windows in European churches.

(i) Explain why iron compounds are usually coloured.

(ii) Explain why the melting point of iron is significantly higher than that of calcium.

Stained-glass windows are darkened from corrosion and age. Microprobe analysis showed that the tiny cracks and defects on the glass surface were enriched with insoluble MnO₂.

(iii) Using the Data Booklet, suggest a suitable reducing agent to dissolve MnO₂ without reducing iron (III) to iron (II).
2 (b) Iron (III) chloride is often used as a catalyst in the conversion of benzene to produce carbonyl compounds.

\[
\text{CO / HCl} \quad \text{FeCl}_3 \quad \text{CHO}
\]

(i) Write an equation to show the generation of the electrophile to form benzaldehyde.

(ii) Explain why iron (III) chloride must be anhydrous in order to generate the electrophile.
2 (c) By making use of the reaction in 2(b) and suitable starting materials, suggest a synthetic pathway (in no more than 4 steps) to convert benzene into the following compound. State clearly the reagents and conditions for each stage, and draw the structural formulae of every intermediate formed.
Iron (III) chloride can also be used in the alkylation of benzene to yield alkyl benzene, for example methylbenzene (toluene). Toluene is less toxic than benzene, and thus can replace benzene as an aromatic solvent in chemical preparation.

Using the following data,

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H^\circ / \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy change of formation of ( \text{CO}_2 ) (g)</td>
<td>-393.5</td>
</tr>
<tr>
<td>Enthalpy change of formation of ( \text{H}_2\text{O} ) (l)</td>
<td>-285.8</td>
</tr>
<tr>
<td>Enthalpy change of combustion of ( \text{C}_6\text{H}_5\text{CH}_3 ) (l)</td>
<td>-3910</td>
</tr>
<tr>
<td>Enthalpy change of vaporisation of ( \text{C}_6\text{H}_5\text{CH}_3 ) (l)</td>
<td>+38</td>
</tr>
</tbody>
</table>

(i) Calculate the standard enthalpy change of formation of toluene, \( \Delta H^\circ_{\text{C}_6\text{H}_5\text{CH}_3} \).

(ii) Using your answer to 2 (d)(i), relevant data from the table above and the Data Booklet, draw an appropriate energy cycle to determine the enthalpy change of formation of benzyl radical \( \text{C}_6\text{H}_5\text{CH}_2^\cdot \).
2 (d) (iii) Hence, deduce the thermodynamic stability of the product, benzyl radical C₆H₅CH₂• as compared to its reactants. Explain.

__________________________________________________________________________

__________________________________________________________________________

__________________________________________________________________________

[7]
[Total: 21 marks]

3 (a) Chelation is the formation of coordinate bonds between a ligand and a single central atom or metal ion. The ethanedioate ion (C₂O₄²⁻) is an example of a chelating ligand. Two complexes which are successfully synthesised are [A/(C₂O₄)₃]³⁻ and [A/(C₂O₄)₂]⁻.

(i) Draw a dot-and-cross diagram for C₂O₄²⁻. Hence, suggest the bond angle about either carbon atom.

__________________________________________________________________________

(ii) State the coordination number of aluminium in the complex [A/(C₂O₄)₃]³⁻.

__________________________________________________________________________

[3]
Aluminium is able to form ethanedioate complex such as \( K_{2n-3}[A/(C_2O_4)_n] \). To determine the identity of the complex, the complex is first decomposed in an acidic solution to give ethanedioic acid and then titrated against potassium manganate (VII).

\[
\begin{align*}
\text{Al}(C_2O_4)_n^{(3-2n)} + n \text{H}_2\text{SO}_4 & \rightarrow n \text{H}_2\text{C}_2\text{O}_4 + \text{Al}^{3+} + n \text{SO}_4^{2-} \quad (n = 2 \text{ or } 3) \\
2 \text{H}^+ + 2 \text{CO}_2 + 2 \text{e}^{-} & = \text{H}_2\text{C}_2\text{O}_4 \\
E & = -0.49 \text{ V}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Volumetric Analysis for ethanedioate content</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step 1</strong></td>
</tr>
<tr>
<td>Weigh 1.77 g of the complex, ( K_{2n-3}[A/(C_2O_4)_n] ), in a 50 cm(^3) beaker.</td>
</tr>
<tr>
<td><strong>Step 2</strong></td>
</tr>
<tr>
<td>Dissolve it in deionised water and transfer to a 250 cm(^3) volumetric flask and top up to the mark with deionised water.</td>
</tr>
<tr>
<td><strong>Step 3</strong></td>
</tr>
<tr>
<td>Pipette 25.0 cm(^3) of the solution into a conical flask and add about 40 cm(^3) of aqueous ( \text{H}_2\text{SO}_4 ).</td>
</tr>
<tr>
<td><strong>Step 4</strong></td>
</tr>
<tr>
<td>Warm the solution to about 50 °C.</td>
</tr>
<tr>
<td><strong>Step 5</strong></td>
</tr>
<tr>
<td>Titrate the contents of the flask with potassium manganate (VII) from a burette until the first pink colour appears.</td>
</tr>
</tbody>
</table>

(i) Use the *Data Booklet* to explain how the results of titration would differ when \( \text{HCl} \) is used instead of \( \text{H}_2\text{SO}_4 \) in **Step 3**.

(ii) By using collision theory of reaction kinetics, explain why the solution needs to be warmed in **Step 4**.
3 (b) (iii) Given that 27.50 cm$^3$ of 0.0213 mol dm$^{-3}$ potassium manganate (VII) is needed to reach equivalence point, calculate the % by mass of ethanedioate ion in the aluminium complex.

(iv) Hence, determine the value of $n$. 
3 (c) Other chelating ligands such as $\text{F}^-$, $\text{H}_2\text{O}$ and $\text{NH}_3$ can also be used to form cobalt complexes.

The UV-visible absorption spectra of the three aqueous solutions are shown below:

(i) With the aid of the spectrum above, account for the difference in the wavelength for each complex.

(ii) With the addition of another chelating ligand such as $\text{EDTA}^{4-}$ to $[\text{Co(H}_2\text{O)}_6]^{2+}$, $[\text{CoEDTA}]^{2-}$ complex is formed according to the following equation:

$$[\text{Co(H}_2\text{O)}_6]^{2+}(\text{aq}) + \text{EDTA}^{4-}(\text{aq}) \rightleftharpoons [\text{CoEDTA}]^{2-}(\text{aq}) + 6\text{H}_2\text{O} \ (l)$$

Explain why this reaction is spontaneous at all temperatures.
4 (a) Acetal is relatively inert and can be made from a carbonyl compound. The carbonyl functional group may be restored by adding aqueous acid.

Formation of Acetal

Carbonyl functional group is restored by adding aqueous H^+

(i) Suggest the type of reaction which occurs in Step I.

(ii) Suggest why OH^- catalyst is needed in Step I.

(iii) Outline a mechanism for Step I. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons.
4 (a) (iv) Explain why anhydrous calcium chloride is added after Step II.

(b) Thiols (RSH) are sulfur analogs of alcohols.

\[
\text{HS} \xrightarrow{\text{CH}_3\text{SH}} \xrightarrow{\text{H}^+ \text{catalyst}} \text{Final organic product, X}
\]

(i) Compound X has the following composition by mass.
C: 51.2%; H: 7.7%; S: 27.4%; O: 13.7%

Using the given data, calculate the empirical formula of the final organic product X.

(ii) When a sample of 0.219 g of compound X was vaporised using a suitable apparatus, the vapour occupied 38.2 cm³ at 95 °C and 150 kPa.
Calculate the Mr of compound X.

[Total: 10 marks]
5 (a) The rate of the reaction between A and Cl₂ (i) has the following rate law:
\[ \text{Rate} = k[A]^m [Cl₂] \]

Where A = [Diagram of A] and k is the rate constant with units of mol⁻²dm⁶s⁻¹.

Two experiments to study the kinetics of this reaction were carried out and the data obtained are tabulated below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [A] / mol dm⁻³</th>
<th>[Cl₂] / mol dm⁻³</th>
<th>Initial rate / mol dm⁻³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.40</td>
<td>0.08</td>
<td>R</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>y</td>
<td>½ R</td>
</tr>
</tbody>
</table>

(i) What is the value of y in Experiment 2?

(ii) Given that the half-life of Cl₂ in Experiment 1 was 4.5 seconds, predict a value for the half-life of Cl₂ in Experiment 2, giving your reasoning.

(b) (i) Predict the products formed when BaCl₂ reacts with concentrated H₂SO₄.
5 (b) (ii) Hence, identify the structural formula for the organic product formed when

\[ \text{organic product} \]

reacts with \( \text{BaCl}_2 \) and concentrated \( \text{H}_2\text{SO}_4 \). 

(c) The reaction scheme below shows how an ester is generated from

\[ \text{organic product} \]

Complete the reaction scheme below by writing the structural formulae of the organic products and the reagents and conditions in the spaces provided.

\[ \text{Organic product} \xrightarrow{\text{I}} \text{A} \xrightarrow{\text{hot alumina}} \text{B} \xrightarrow{\text{II}} \xrightarrow{\text{III}} \text{C} \xrightarrow{\text{IV}} \text{D} \]

\[ \text{Organic product} \xrightarrow{\text{NaBH}_4} \text{in methanol} \]
<table>
<thead>
<tr>
<th>Step</th>
<th>Reagents and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td></td>
</tr>
</tbody>
</table>

[Total: 13]
<table>
<thead>
<tr>
<th>No.</th>
<th>Experiment</th>
<th>Observation</th>
<th>Deductions with relevant equation</th>
</tr>
</thead>
</table>
| 1.  | Add ½ spatula of solid potassium carbonate to each separate samples (1 cm³) of the 4 solutions in clean, dry test tubes. | Effervescence OR gas evolved. White precipitate formed | \[
\begin{align*}
\text{Al}(\text{H}_2\text{O})_6^{3+}(\text{aq}) & \leftrightarrow \text{Al}[(\text{OH})(\text{H}_2\text{O})_3]^{2+}(\text{aq}) + \text{H}^+(\text{aq}) \\
2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) & \rightarrow \text{H}_2\text{O}(l) + \text{CO}_2 (g)
\end{align*}
\] A/Br$_3$ identified ZnCO$_3$, Ag$_2$CO$_3$, CaCO$_3$

| 2.  | Add each unknown sample to 1 cm³ of A/Br$_3$ solution till excess in clean, dry test tubes. | No precipitate formed Off-white precipitate formed White precipitate formed White ppt soluble in excess | ZnSO$_4$ identified Ag$^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(s)$ AgNO$_3$ identified \[
\begin{align*}
\text{Al}^{3+}(\text{aq}) + 3 \text{OH}^-(\text{aq}) & \rightarrow \text{Al}[(\text{OH})_3](\text{s}) \\
\text{Al}[(\text{OH})_3](\text{s}) + \text{OH}^-(\text{aq}) & \rightarrow \text{Al}[(\text{OH})_4]^- (\text{aq}) \\
\text{Ba}[(\text{OH})_2] & \text{identified}
\end{align*}
\] Ba(OH)$_2$ identified

| 3.  | Add Ba(OH)$_2$ dropwise till excess to 1 cm³ of the last unknown solution | White precipitate formed | Ba$^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$ ZnSO$_4$ identified |
### 2(a)

<table>
<thead>
<tr>
<th>(i)</th>
<th>The iron ion has incompletely filled d-orbitals.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In the isolated gas phase atoms, all 5 d orbitals of the iron ion are degenerate.</td>
</tr>
<tr>
<td></td>
<td>In forming complexes, the d orbitals split into 2 groups with a small energy gap between them.</td>
</tr>
<tr>
<td></td>
<td>When a d-electron from the lower energy group is promoted to the higher energy group, energy from the visible region is absorbed.</td>
</tr>
<tr>
<td></td>
<td>The light energy not absorbed will be seen as the colour of the complex.</td>
</tr>
</tbody>
</table>

### 2(b)

<table>
<thead>
<tr>
<th>(i)</th>
<th>CO + HCl + FeCl₃ $\rightarrow$ CHO + FeCl₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeCl₃ will hydrolyse with water to yield $[Fe(H₂O)₅(OH)]^{2+}$ and Cl⁻ ions. OR dissolve in water to form $[Fe(H₂O)₅]^{3+}$. Fe in $[Fe(H₂O)₅(OH)]^{2+}$ or Fe in $[Fe(H₂O)₅]^{3+}$ has no vacant d-orbitals to accept electron pair from Cl⁻ to generate the electrophile.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(ii)</th>
<th>FeCl₂ + e $\rightarrow$ Fe²⁺ +0.77V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MnO₂ + 4H⁺ + 2e $\rightarrow$ Mn²⁺ + H₂O +1.23V</td>
</tr>
<tr>
<td>Ag metal</td>
<td>Student can choose any reducing agent as long as the electrode potential is +0.77V &lt; x &lt; +1.23V.</td>
</tr>
<tr>
<td></td>
<td>OR student show calculation of Ecell</td>
</tr>
<tr>
<td></td>
<td>Ecell &gt;0 for Ag/MnO₂.</td>
</tr>
<tr>
<td></td>
<td>Ecell = 1.23- 0.80 = + 0.43V &gt;0 reaction is feasible.</td>
</tr>
<tr>
<td></td>
<td>Ecell of Ag/Fe³⁺ &lt; 0V, no reaction, Ag only reduces MnO₂.</td>
</tr>
<tr>
<td></td>
<td>Ecell = 0.77 -0.80</td>
</tr>
<tr>
<td></td>
<td>= -0.03V &lt;0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(ii)</th>
<th>The melting point of iron is significantly higher than that of calcium due to the stronger metallic bonding present in iron and thus more energy needed which is attributed to the following reasons:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- more delocalised electrons contributed from 3d and 4s electrons</td>
</tr>
<tr>
<td></td>
<td>- higher charge density</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(iii)</th>
<th>Fe³⁺ + e $\rightarrow$ Fe²⁺ +0.77V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MnO₂ + 4H⁺ + 2e $\rightarrow$ Mn²⁺ + H₂O +1.23V</td>
</tr>
<tr>
<td>Ag metal</td>
<td>Student can choose any reducing agent as long as the electrode potential is +0.77V &lt; x &lt; +1.23V.</td>
</tr>
</tbody>
</table>
(c) (i) 

\[
\text{Heat with reflux}
\]

\[
\text{CHO} + \text{LiAIH}_4 \text{ in dry ether}
\]

\[
\text{CH}_2\text{OH} \rightarrow \text{PCl}_3, \text{r.t.p}
\]

\[
\text{PCl}_3 \text{ r.t.p}
\]

\[
\text{OR} \rightarrow \text{SOCl}_2 \text{ r.t.p}
\]

\[
\Delta H = \sum n \Delta H_{\text{formation}}(\text{products}) - \sum n \Delta H_{\text{formation}}(\text{reactants})
\]

\[
\Delta H_{\text{f \text{C}_6\text{H}_5\text{CH}_3}} = +12.3 \text{ kJ/mol}
\]

(d) (i) 

\[
\Delta H_{\text{C}_6\text{H}_5\text{CH}_3} = \sum n \Delta H_{\text{formation}}(\text{products}) - \sum n \Delta H_{\text{formation}}(\text{reactants})
\]

\[
- (-3910) = 7 (-393.5) + 4 (-285.8) - \Delta H_{\text{f \text{C}_6\text{H}_5\text{CH}_3}}
\]

\[
\Delta H_{\text{f \text{C}_6\text{H}_5\text{CH}_3}} = +12.3 \text{ kJ/mol}
\]

(ii) 

\[
\Delta H_{\text{f \text{C}_6\text{H}_5\text{CH}_2\bullet}} = +242 \text{ kJ/mol}
\]

\[
\Delta H_{\text{vapouration}} = +38.00
\]

\[
\text{B.E. (H-H)} = +218
\]

\[
\Delta H_{\text{f \text{C}_6\text{H}_5\text{CH}_2\bullet}} = +12.3 + 38 + 410 - 218
\]

\[
= +242.3 \text{ kJ/mol}
\]

\[
= +242 \text{ kJ/mol}
\]
### 3(a)

(i) Benzyl radical \( \text{C}_6\text{H}_5\text{CH}_2\cdot \) is less stable than its reactant, \( \Delta H_{f} \) \( \text{C}_6\text{H}_5\text{CH}_2\cdot \) (g) is endothermic. The radical is very reactive as it requires only 1 more electron to form a stable configuration.

(ii) Coordination no: 6

![Coordination no: 6](image)

(iii) 120°

### 3(b)

(i)  
\[
\text{Cl}_2^- + 2e^- \rightarrow 2\text{Cl}^- + 1.36V \\
\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 1.52V
\]

\( \text{MnO}_4^- \) is able to oxidise \( \text{Cl}^- \) to \( \text{Cl}_2^- \). \( \text{E}_{\text{cell}} = +0.16V \), reaction is feasible. Hence more \( \text{MnO}_4^- \) will be used for the titration.

(ii) When temperature is increased, the molecules gain kinetic energy and move about faster. This increases the number of molecules having energy \( E \geq E_A \). Thus, the frequency of effective collisions increases. Reaction rate increases.

(iii) Calculation of % weight of \( \text{C}_2\text{O}_4^{2-} \) ion Al complex

\[
\text{H}^+ + 2\text{CO}_2 + 2e^- \rightarrow \text{H}_2\text{C}_2\text{O}_4
\]

\[
5\text{H}_2\text{C}_2\text{O}_4 \equiv 2\text{MnO}_4^- \\
\text{Amt of MnO}_4^- = 27.50/1000 \times 0.0213 = 5.86 \times 10^{-4} \text{ mol}
\]

\[
\text{Amt of H}_2\text{C}_2\text{O}_4 \text{ in 25 ml} = 5.86 \times 10^{-4} \times 5/2 = 1.466 \times 10^{-3} \text{ mol}
\]

\[
\text{Amt of H}_2\text{C}_2\text{O}_4 \text{ in 250 ml} = 1.466 \times 10^{-3} \times 10 = 1.466 \times 10^{-2} \text{ mol}
\]

\[
\text{Mass C}_2\text{O}_4^{2-} = 1.466 \times 10^{-2} \times 88.0 = 1.29 \text{ g}
\]

\[
\% \text{ of C}_2\text{O}_4^{2-} \text{ in complex} = 1.29/1.77 \times 100\% = 72.9\%
\]

(iv) If \( n = 2 \), \( K[A/ (\text{C}_2\text{O}_4)_2] \)

\[
\% \text{ of C}_2\text{O}_4^{2-} \text{ in complex} = 176/242.1 \times 100\% = 72.7\%
\]

If \( n = 3 \), \( K_3[A/ (\text{C}_2\text{O}_4)_3] \)

\[
\% \text{ of C}_2\text{O}_4^{2-} \text{ in complex} = 264/408.3 \times 100\% = 64.7\%
\]

Since the value obtained is closer to \( n = 2 \), the complex is \( K[A/ (\text{C}_2\text{O}_4)_2] \)

### 3(c)

(i) Due to the presence of different ligand, the d orbitals are split to different extent/energy gap, \( \Delta E \).

Rank of the d-orbital splitting \( \text{NH}_3 > \text{H}_2\text{O} > \text{F}^- \)
(ii) Since EDTA is able to displace H₂O, hence it will form a stronger dative bond to Co²⁺. Hence, ∆H is negative. ∆S is positive as there is an increase in entropy due to more molecules at the product side, 7 molecules vs 2 molecules. Using ∆G = ∆H - T∆S, since ∆S > 0 and ∆H is < 0, -T∆S would always be < 0 ∆G would be always < 0 at all temperature.

<table>
<thead>
<tr>
<th>4(a) (i)</th>
<th>Nucleophilic addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ii)</td>
<td>OH⁻ will react with ethanol to generate a stronger nucleophile CH₃CH₂O⁻.</td>
</tr>
</tbody>
</table>

(iii) **Nucleophilic addition**

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{O}^- + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{O}^- + \text{H}^+
\]

- Generation of Nucleophile
- Slow
- Intermediate
- Arrow
- Partial charges + lone pair

(iv) An Acetal

Calcium chloride is a drying agent, which help to remove water. Hence the position equilibrium will shift right to increase the yield of the product.

<table>
<thead>
<tr>
<th>4(b) (i)</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage by mass / %</td>
<td>51.2</td>
<td>7.7</td>
<td>13.7</td>
<td>27.4</td>
</tr>
<tr>
<td>Mole ratio</td>
<td>4.3</td>
<td>7.7</td>
<td>0.86</td>
<td>0.85</td>
</tr>
<tr>
<td>Simplest ratio</td>
<td>5</td>
<td>9</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Empirical formula = C₅H₉OS
Using the ideal gas equation, 
\[ pV = nRT = (m/Mr)RT \]
\[ Mr = \frac{(mRT)}{pV} \]
\[ = \frac{[0.219 \times 8.31 \times (95 + 273)]}{(150 \times 10^3 \times 38.2 \times 10^{-6})} = 116.9 \]

(ii) Experiment 2: 18 seconds.
Since \( r = k' [\text{Cl}_2] \), hence \( t_{1/2} = \frac{\ln 2}{k'} \).

Where \( k' = k [\text{Cl}_2]^2 \), thus when \( \text{Cl}_2 \) halves, the time \( x 4 \).

(b) (i) \( \text{HCl} + \text{BaSO}_4 \) or \( \text{HCl} + \text{Ba(HSO}_4)_2 \)

(ii) 

(c)

<table>
<thead>
<tr>
<th>Step</th>
<th>Reagents and conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>( X_2 ) (aq)</td>
</tr>
<tr>
<td>II</td>
<td>Ethanoic KCN heat with reflux</td>
</tr>
<tr>
<td>III</td>
<td>Aqueous ( \text{H}_2\text{SO}_4 ), heat with reflux</td>
</tr>
<tr>
<td>IV</td>
<td>( \text{PCl}_5 ) or ( \text{SOCl}_2 ) (with pyridine) or ( \text{PCl}_3 ) (heat)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>D</td>
</tr>
</tbody>
</table>
ST ANDREW’S JUNIOR COLLEGE

JC2 Preliminary Examinations

Chemistry

Higher 2 9647/03
Paper 3 18 September 2012
2 hours

Candidates answer on separate paper.

Additional Materials: Writing paper, Data Booklet

READ THESE INSTRUCTIONS FIRST:

Write your name and civics group on all the work you hand in.

Write in dark blue or black pen.

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.

You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of 12 printed pages including this page.

[Turn Over
Answer any 4 questions.

1. Paracetamol and aspirin are well known drugs to treat pain and to reduce fever.

(a) The following are structures of paracetamol and aspirin:

\[
\text{Paracetamol} \quad \text{Aspirin}
\]

\[
\begin{array}{c}
\text{HO} \\
\text{H} \\
\text{N} \\
\text{C} \\
\text{CH}_3 \\
\text{O} \\
\end{array} \quad \begin{array}{c}
\text{COOH} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{CH}_3 \\
\end{array}
\]

\[
\begin{array}{c}
\text{pK}_a = 9.5 \\
\text{Mr} = 151.0 \\
\end{array} \quad \begin{array}{c}
\text{pK}_a = 3.5 \\
\text{Mr} = 180.0 \\
\end{array}
\]

(i) Explain the difference in the pK\textsubscript{a} values of aspirin and paracetamol.

(ii) Phenacetin is an analgesic whose use has largely declined due to its carcinogenic properties. Starting from paracetamol, show the steps involved in the synthesis of phenacetin. In your answer, include the reagents and conditions required for each step, as well as the structure of the intermediate involved.

\[
\text{Phenacetin}
\]

(iii) Salicin is an anti-inflammatory agent that is closely related in chemical make-up to aspirin. Suggest a chemical test that could be used to distinguish salicin from aspirin. Write a balanced equation for the reaction that occurred.

\[
\text{Salicin}
\]
1. (a) (iv) Aspirin is supplied as a crystalline solid. A standard solution of aspirin may be made by dissolving aspirin in an organic solvent. Explain why water is not used as a suitable solvent.

   [9]

(b) (i) Write an expression for the acid dissociation constant, $K_a$, of aspirin.

(ii) A tablet of aspirin is swallowed into the stomach. Given that the pH of the stomach is 1, calculate the percentage of aspirin molecules that remain undissociated in the stomach.

   [3]

(c) 0.270 g of aspirin and 0.121 g of paracetamol are dissolved in 30 cm$^3$ of ethanol and titrated against 0.100 mol dm$^{-3}$ aqueous sodium hydroxide, using 1 to 2 drops of two indicators, methyl red and phenolphthalein.

$x$ cm$^3$ of aqueous sodium hydroxide is required to change the colour of the methyl red and a further $y$ cm$^3$ of aqueous sodium hydroxide is needed to change the colour of phenolphthalein.

(i) Explain why both indicators are added in small amounts.

(ii) Calculate the initial pH of the mixture, assuming the initial pH is from aspirin only.

(iii) Calculate the values of $x$ and $y$.

(iv) Sketch the shape of the pH curve during this titration.

   [8]

[Total 20]
2. (a) In an effort to provide a sustainable system for waste treatment and energy production, scientists are currently working in the area of microbial fuel cell (MFC) technology. MFC is a device that converts chemical energy to electrical energy by the catalytic reaction of microorganisms such as bacteria. A typical microbial fuel cell consists of an anode and a cathode separated by a cation exchange membrane which only allows cations to pass through. Copper has been used extensively as electrodes in MFCs as shown in the following diagram.

![Diagram of a microbial fuel cell](image)

On the anode side, bacteria grow and proliferate, forming a dense cell aggregate known as a biofilm that adheres to the MFC’s anode. In the course of their microbial metabolism, the bacteria act as catalysts for converting the organic substrate such as sucrose, C\text{12}H\text{22}O\text{11}, into carbon dioxide. At the cathode, in the presence of air, steam is produced.

(i) Write balanced half-equations, occurring at each electrode, when the MFC discharges.

(ii) Given the electromotive force of the MFC is 1.25 V, calculate the reduction potential of the carbon dioxide / sucrose half-cell.

(iii) Suggest with a reason, the effect on the standard cell potential if the pH of the electrolyte at the cathode is increased.

[5]
2. (b) Copper reacts with 50% nitric (V) acid, HNO₃, to give a blue solution, containing complex ion A and a brown gas B. If the solution containing A is diluted and sodium hydroxide solution added cautiously, a gelatinous blue precipitate C is obtained, which if heated, forms a black solid D.

Addition of concentrated aqueous ammonia solution to A gives a deep blue solution that contains the ion E. Addition of concentrated hydrochloric acid to E gives a yellow solution of the ion F, which on dilution with water gives a solution containing the same ion A.

If the brown gas B is passed into water, a mixture of acids G and H is formed in a disproportionation reaction.

(i) Identify A – H. Construct balanced equations, with state symbols, for the formation of C, D, E and F.

(ii) Draw a dot-and-cross diagram of nitric (V) acid, HNO₃. With reference to the Valence Shell Electron Repulsion theory, explain the shape about the nitrogen atom.

[15]
[Total 20]
3. Hydrazine, N₂H₄, is a colourless, volatile and corrosive liquid with an ammonia-like odour. It is well known for its use in various rocket fuels and to prepare gas precursors used in air bags.

(a) Hydrazine decomposes thermally, liberating a large amount of heat and a large volume of gaseous products in the following ways:

\[ 3 \text{N}_2\text{H}_4 (l) \xrightarrow{\text{thermally}} 4\text{NH}_3 (g) + \text{N}_2 (g) \quad \Delta H_r = +111.8 \text{kJ mol}^{-1} \]

\[ \text{N}_2\text{H}_4 (l) \xrightarrow{\text{thermally}} \text{N}_2 (g) + 2\text{H}_2 (g) \quad \Delta H_r = z \text{kJ mol}^{-1} \]

(i) Write the equation that corresponds to the enthalpy change of formation of ammonia.

(ii) Hence, using your answer to (a)(i), the above reactions and relevant data from the Data Booklet, construct an energy cycle to calculate \( z \).

[3]

(b) Hydrazine can be synthesised by the Raschig process, where Cl₂ gas and NH₃ gas are heated under certain conditions in the presence of sodium hydroxide.

(i) State the change in oxidation number of nitrogen atom during the Raschig process.

(ii) Predict the product of Cl₂ in the process.

(iii) Construct an ionic equation for the Raschig process.

[3]
3. (c) The **Wolff–Kishner reduction** is a chemical reaction that reduces a carbonyl compound (ketone or aldehyde) to its corresponding alkane. Condensation of the carbonyl compound with hydrazine forms a hydrazone intermediate, and treatment with a base induces the formation of the corresponding alkane.

Below shows the synthesis of propane from propanone via the **Wolff-Kishner reduction**.

![Chemical reaction diagram]

Carbonyl compounds A and B both undergo the **Wolff-Kishner reduction** separately forming ethylbenzene.

**A** is found to give a silver mirror with Tollen’s reagent but **B** does not.

Draw the displayed formulae of **A**, **B** and the hydrazone intermediate formed with **A**.

[3]
3. (d) Ethylbenzene undergoes the following reaction scheme producing C.

\[
\begin{align*}
\text{Step I} & \quad \text{HNO}_3 + \text{BF}_3 \\
\text{Step II} & \quad \text{NO}_2 \\
\text{Step III} & \quad \text{NH}_2
\end{align*}
\]

For Step I,
(i) outline the mechanism of the reaction.
(ii) with reference to the structure of BF\(_3\), explain how BF\(_3\) helps in the mechanism.

For Step II,
(iii) state the reagents and conditions required.

For Step III,
(iv) an intermediate is involved. Draw the structure of the intermediate.
(v) state the reagents and conditions required to form the intermediate.
(vi) name the two types of reactions involved.
(vii) explain why the yield of C is low.

[11]

[Total 20]
4.  (a) A 25.0 cm$^3$ solution containing 0.00500 mol dm$^{-3}$ of potassium chloride, KCl, and 0.800 mol dm$^{-3}$ of potassium chromate (VI), K$_2$CrO$_4$, was titrated against 0.100 mol dm$^{-3}$ aqueous silver nitrate. White precipitate was first formed.

When $v$ cm$^3$ of aqueous silver nitrate was added, a trace amount of red precipitate, Ag$_2$CrO$_4$, was observed.

\[ K_{sp} \text{ for } AgCl = 1.6 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} \]
\[ K_{sp} \text{ for } Ag_2CrO_4 = 9.0 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9} \]

(i) Assuming no dilution was caused by the addition of aqueous silver nitrate, calculate the concentration of chloride present in the mixture when the first trace of red precipitate was observed.

(ii) Calculate the percentage of chloride precipitated when the first trace of red precipitate was observed.

Hence, suggest the role of potassium chromate (VI) in the solution.

[4]

Potassium chlorate (I), KClO, and potassium chlorate (V), KClO$_3$, can be easily made by the electrolysis of saturated potassium chloride solution under different conditions.

During the electrolysis, inert electrodes are used and the products at the electrodes are allowed to mix.

(b)  (i) Using the Data booklet, describe and explain the reactions occurring at the cathode and the anode.

(ii) Write a balanced equation to show the formation of KClO$_3$.

(iii) How do you ensure that potassium chlorate (I), KClO, is not formed.

(iv) A current of 3 A was passed through the electrolytic cell. Calculate the time required to obtain 30 g of KClO$_3$.

[9]
4. (c) 2.12 g of potassium chlorate, KC/Oₓ, was heated and decomposed completely to give oxygen gas and potassium chloride as shown in the diagram below.

The oxygen gas produced was collected over water at 22 °C at a total pressure of 100525 Pa. The volume of gas collected was 650 cm³, and the vapour pressure of water at 22 °C is 2800 Pa.

(i) Write the balanced equation, with state symbols, of the decomposition reaction of KC/Oₓ.

(ii) Calculate the amount of O₂ produced. Hence, deduce the value of x in KC/Oₓ.

(d) Compare and explain the ease of decomposition between KBrOₓ and KC/Oₓ.

[Total 20]
The following information was taken from the side of a carton of milk.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>How long does your milk keep?</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C</td>
<td>½ day</td>
</tr>
<tr>
<td>18°C</td>
<td>1 day</td>
</tr>
<tr>
<td>5°C</td>
<td>4 days</td>
</tr>
</tbody>
</table>

(a) (i) The souring of milk is a chemical reaction. How is the rate of this reaction related to the length of time the milk keeps?

(ii) Explain how this rate varies with temperature. Draw an energy distribution diagram to illustrate your answer.

(b) (i) For each of the following cases, explain with the help of a diagram, how the following types of side chain interactions are affected during each denaturation process.

I. AgNO₃ is used as disinfectants to prevent gonorrhea infections in the eyes of new born infants.

II. Ethanol solutions are used as disinfectants on the skin as it can penetrate the bacterial cell wall and denature the proteins inside the cell.
5. **(b) (ii)** Which of the treatments, AgNO₃ in case I or ethanol in case II, is likely to affect the alpha helix structure? Explain.  

[6]

**(c)** Compound B (C₁₀H₁₄O₂) is optically active and does not react with aqueous sodium carbonate. However, it dissolves slowly in aqueous sodium hydroxide.

B reacts with hydrogen bromide but will not decolourise acidified potassium dichromate (VI). B decolourises aqueous bromine to form white precipitate C (C₁₀H₁₂O₂Br₂), together with dense white fumes.

Upon treatment with concentrated sulfuric acid at 170°C, B gives compound D (C₁₀H₁₂O) which exists as a pair of geometric isomers. D gives compound E (C₁₀H₁₄O₃) on addition of cold, dilute alkaline potassium manganate (VII) solution.

E reacts with phosphorus pentachloride to give copious fumes and compound F (C₁₀H₁₂OCl₂).

Suggest a structure for each lettered compound, B – F, and explain the reactions involved.

[10]

[Total 20]

~~~ END ~~~

[Turn Over]
<table>
<thead>
<tr>
<th>No.</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(a)(i)</td>
<td>Aspirin has a lower pKa hence a higher Ka thus aspirin is a stronger acid. Aspirin has a RCOOH group and the conjugate base that is formed is more stable as the negative charge on the carboxylate ion is delocalised over O-C-O bond (charge delocalised over two oxygen atoms) by resonance effect. The conjugate base of phenol is less stable as the negative charge (lone pair of electrons on O) of the phenoxide ion is only delocalised into the benzene ring.</td>
</tr>
<tr>
<td>(ii)</td>
<td>![Diagram of Aspirin to Phenacetin reaction]</td>
</tr>
</tbody>
</table>
| (iii) | Add aqueous sodium carbonate / sodium hydrogen carbonate. Aspirin gives bubbles that will form white ppt. with aqueous calcium hydroxide. Salicin does not give white ppt or bubbles.  
\[
2 \text{OC-CH}_3 + \text{Na}_2\text{CO}_3 \rightarrow 2 \text{OCOCCH}_3 + \text{H}_2\text{O} + \text{CO}_2
\]  
OR  
K$_2$Cr$_2$O$_7$ (aq), aq H$_2$SO$_4$, heat OR Add aqueous KMnO$_4$ (aq), aq H$_2$SO$_4$, heat. Salicin decolourises purple KMnO$_4$ OR turns K$_2$Cr$_2$O$_7$ from orange to green. Aspirin remains purple OR remains orange. |
| (iv) | Water is not a suitable solvent as the solute-solvent interaction (pd-pd, id-id, H-bonding) cannot overcome the H-bonding between water and id-id between aspirin. |
| (b)(i) | $K_a = \frac{[H^+][A^-]}{[HA]}$ |
Where \(HA=\text{COO}^-\) and \(A^-=\text{COO}^-\)

(ii) \(10^{-3.5} = \frac{[A^-]}{[HA]}\)
Hence, \([A^-] = 3.16 \times 10^{-3}\)
Percentage ionised = \((3.16 \times 10^{-3} / 1) \times 100\% = 0.316\%
Percentage unionised = 100 – 0.316 = 99.7\%

(c)(i) Indicators are weak acids hence if added in large amount, the amount of NaOH required will be higher than expected / titration is inaccurate.

(ii) \([\text{aspirin}] = \frac{270 \times 10^{-3}}{50} = 0.05 \text{ mol dm}^{-3}\)
Using \(K_a = \frac{[H^+]^2}{[\text{aspirin}]^2}\)
\([H^+]^2 = 3.98 \times 10^{-3}\)
\(pH = 2.40\)

(iii) Using \([\text{aspirin}] = 0.05 \text{ mol dm}^{-3}\)
\(x = \frac{0.05 \times 50}{1000} \times 1000 = 15.00 \text{ cm}^3\)
\([\text{paracetamol}] = \frac{151 \times 10^{-3}}{10} = 0.0267 \text{ mol dm}^{-3}\)
\(y = \frac{0.0267 \times 50}{1000} \times 1000 = 8.00 \text{ cm}^3\)

(iv) 2(a)(i) Cathode: \(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\)
Anode: \(13H_2O + C_{12}H_{22}O_{13} \rightarrow 12CO_2 + 48H^+ + 48e^-\)

(ii) Using data booklet: \(E^0 O_2 + 4H^+ + 4e^- \rightarrow 2H_2O + 1.23 \text{ V}\)
Using \(E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} + 1.25 = +1.23 - (E^0_{\text{anode}})\)
\(E^0_{\text{cathode}} = -0.02 \text{ V}\)
(iii) \[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O} + 1.23 \text{ V} \]
When the pH increases, the cathodic reaction shifts to the left to replenish \( \text{H}^+ \). Hence, the \( E^{\text{cell}} \) becomes more negative.

(b)(i) 
<table>
<thead>
<tr>
<th>A: ([\text{Cu(H}_2\text{O)}_6]^{2+})</th>
<th>B: (\text{NO}_2)</th>
<th>C: (\text{Cu(OH)}_2)</th>
<th>D: (\text{CuO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>E: ([\text{Cu(NH}_3\text{)}_4(\text{H}_2\text{O)}_2]^{2+})</td>
<td>F: ([\text{CuCl}_4]^{2-})</td>
<td>G/H: (\text{HNO}_2) and (\text{HNO}_3)</td>
<td></td>
</tr>
</tbody>
</table>

Equations:
- C: \([\text{Cu(H}_2\text{O)}_6]^{2+}\) (aq) + 2OH\(^-\) (aq) \rightleftharpoons \text{Cu(OH)}_2 (s) + 6\text{H}_2\text{O} (l)
  OR \text{Cu(NO}_3\text{)}_2 (aq) + 2\text{NaOH} (aq) \rightleftharpoons \text{Cu(OH)}_2 (s) + 2\text{NaNO}_3 (aq)
- D: \text{Cu(OH)}_2 (s) \rightleftharpoons \text{CuO} (s) + \text{H}_2\text{O} (l)/ (g)
- E: \([\text{Cu(H}_2\text{O)}_6]^{2+}\) (aq) + 4\text{NH}_3 (aq) \rightleftharpoons \text{[Cu(NH}_3\text{)}_4(\text{H}_2\text{O)}_2]^{2+}\) (aq) + 4\text{H}_2\text{O} (l)
- F: \([\text{Cu(NH}_3\text{)}_4(\text{H}_2\text{O)}_2]^{2+}\) (aq) + 4\text{HCl} (aq) \rightleftharpoons \text{[CuCl}_4]^{2-}\) (aq) + 2\text{H}_2\text{O} (l) + 4\text{NH}_4^+ (aq)
  OR \text{[Cu(NH}_3\text{)}_4(\text{H}_2\text{O)}_2]^{2+}\) (aq) + 4\text{Cl}^- (aq) \rightleftharpoons \text{[CuCl}_4]^{2-}\) (aq) + 2\text{H}_2\text{O} (l) + 4\text{NH}_3 (aq)

(ii) 

3 bond pairs of electrons repel each other equally OR \( \text{lp-lp} > \text{lp-bp} > \text{bp-bp} \)

Hence, the shape is trigonal planar.

3(a)(i) \( \frac{1}{2} \text{N}_2 (g) + \frac{3}{2} \text{H}_2 (g) \rightleftharpoons \text{NH}_3 (g) \)

(ii) 

\[ \begin{align*}
3\text{N}_2\text{H}_4 (l) & \rightleftharpoons 4\text{NH}_3 (g) + \text{N}_2 (g) \\
3z & \downarrow \\
3\text{N}_2 (g) + 6\text{H}_2 (g) & \downarrow \ y
\end{align*} \]

Using bond energy from the data booklet:
\[ y = [2\text{BE (N} \equiv \text{N}) + 6\text{BE (H-H)}] - 12 \text{ BE (N-H)} \]
\[ y = -76 \text{ kJ mol}^{-1} \]

Using energy cycle:
\[ 3z + y = 111.8 \]
\[ Z = +62.6 \text{ kJ mol}^{-1} \]

(b)(i) 
-3 to -2

(ii) \( \text{N} \) is oxidised, \( \text{Cl}^- \) is formed or \( \text{NaCl} \) where \( \text{Cl}_2 \) must be reduced.
Note: \( \text{HCl} \) not accepted given that \( \text{NaOH} \) is the medium.

(iii) \( 2\text{OH}^- + 2\text{H}_3\text{O}^+ + \text{Cl}_2 \rightleftharpoons \text{N}_2\text{H}_4 + 2\text{Cl}^- + 2\text{H}_2\text{O} \)
Note: No spectator ions.
4. SAJC PRELIM 2012 P3 solutions

(c) A: \[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{H} \\
\text{H}
\end{array}
\]

B: \[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

Hydrazone: \[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

3(d)(i) \[
\begin{align*}
\text{HNO}_3 + \text{BF}_3 & \rightleftharpoons \text{NO}_2^- + [\text{BF}_3\text{OH}] \\
\text{CH}_2\text{CH}_3 & \rightarrow \text{NO}_2^+ \text{slow} \rightarrow \text{CH}_3\text{CH}_3 \rightarrow \text{H}^+ + [\text{BF}_3\text{OH}] & \rightarrow \text{BF}_3 + \text{H}_2\text{O}
\end{align*}
\]

(ii) B has an empty orbital. Hence, B can accept a lone pair of electrons from OH\(^-\) via dative bonding.

(iii) Sn and concentrated HCl with heat followed by aq NaOH

(iv) \[
\begin{array}{c}
\text{H} \\
\text{CH}_2 \text{CH}_2 \text{Cl} \\
\text{H}_2\text{O}
\end{array}
\]

(v) Limited chlorine gas / in CCl\(_4\) + UV OR by heating.

(vi) Free radical substitution
Nucleophilic substitution

(vii) Difficult to control the position and number of substitution by Cl during FRS.
OR difficult to control NS.

4(a)(i) Using Ksp for Ag\(_2\)CrO\(_4\) = [Ag\(^+\)]\(^2\)[CrO\(_4\)\(^2-\)] = 9 \times 10\(^{-12}\)
[Ag\(^+\)] needed to form the red ppt = [(9 \times 10\(^{-12}\))/(0.8)]\(^{1/2}\) = 3.35 \times 10\(^{-6}\) mol dm\(^{-3}\)
Using Ksp for AgCl = [Ag\(^+\)][Cl\(^-\)] = 1.6 \times 10\(^{-6}\)
[Cl\(^-\)] = (1.6 \times 10\(^{-10}\))/(3.35 \times 10\(^{-6}\)) = 4.78 \times 10\(^{-5}\) mol dm\(^{-3}\)

(ii) Percentage of Cl\(^-\) precipitated = \[
\frac{0.005 - 4.776 \times 10^{-5}}{0.005} \times 100\% = 99.0\% \]
Since almost all of the Cl\(^-\) is precipitated when the first trace of red ppt appears, CrO\(_4\)\(^2-\) acts as an indicator for the titration.

(b)(i) At the cathode (negative electrode),
K\(^+\) and H\(_2\)O compete to be reduced.
K\(^+\) + e \rightleftharpoons K \quad -2.92 \text{ V}
2H\(_2\)O + 2e \rightleftharpoons H\(_2\) + 2OH\(^-\) \quad -0.83 \text{ V}
Since the E\(^0\) (H\(_2\)O/OH\(^-\)) = - 0.83 V is more positive than E\(^0\) (K\(^+\)/K) = - 2.92 V
H\(_2\)O is preferentially reduced.
Cathode: 2H\(_2\)O + 2e \rightleftharpoons H\(_2\) + 2OH\(^-\)

At the anode (positive electrode),
Cl\(^-\) and H\(_2\)O compete to be oxidised.
Cl\(_2\) + 2e \rightleftharpoons Cl\(^+\) + 1.36 V
O₂ + 4H⁺ + 4e⁻ ⇌ 2H₂O +1.23 V

Although the \( E^{\circ} (\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V} \) is more positive than \( E^{\circ} (\text{O}_2/\text{H}_2\text{O}) = +1.23 \text{ V} \)

\( \text{Cl}^- \) is preferentially oxidised due to its high concentration.

Anode: \( 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \)

(ii) \( 3\text{Cl}_2 + 6\text{KOH} \rightarrow \text{KClO}_3 + 5\text{KCl} + 3\text{H}_2\text{O} \)

Note: Ionic eqn accepted.

(iii) High temperature of electrolyte must be used.

(iv) \( \text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 6\text{H}^+ + 6e^- \)

OR Thus, 1 mole of \( \text{ClO}_3^- \) is formed from 6F.

122.6 g of \( \text{KClO}_3 = 1 \) mole of \( \text{KClO}_3 = 579,000 \) C

30 g of \( \text{KClO}_3 = 0.245 \) moles = 141,680 C

Using \( Q = It \) \n
\[ t = \frac{(141,680)}{3} = 47,227 \text{ seconds OR } 13.1 \text{ hours.} \]

(c)(i) \( \text{KClO}_x \rightarrow \text{KCl} (s) + x/2 \text{O}_2 (g) \)

(ii) \( P_{\text{oxygen gas}} = P_{\text{total}} - P_{\text{water vapour}} = 100,525 - 2800 = 97,725 \text{ Pa} \)

Using \( PV = nRT \)

\[ 97,725 \times 650 \times 10^{-6} = n_{\text{oxygen}} \times 8.314 \times (22 + 273) \]

\[ n_{\text{oxygen}} = 0.0260 \text{ mol.} \]

\[ \frac{n_{\text{KClO}_3}}{n_{\text{O}_2}} = \frac{\frac{x}{2}}{0.0260} = \frac{1}{x} \]

\[ x = 2.99 \approx 3 \]

(d) \( \text{KBrO}_3 \) is more easily decomposed than \( \text{KClO}_3 \) OR \( \text{KBrO}_3 \) is thermally less stable.

\( \text{BrO}_3^- \) has a larger electron cloud than \( \text{ClO}_3^- \) hence \( K^+ \) is more able to polarise the larger electron cloud more easily due to weakening of Br-O bond.

5(a)(i) Rate \( \alpha \frac{1}{\text{time}} \)

(ii) \( \frac{\text{Fraction of molecules having energy } E}{\text{Total number of molecules}} \)

When temperature is increased, the molecules gain kinetic energy and move about faster. This increases the number of molecules having energy \( E \geq E_a \). As a result, the frequency of effective collisions increases. Reaction rate thus increases.
b(i)  I. $\text{Ag}^+$ will compete with the cation of lysine to form ionic interaction with the anion of glutamic acid. OR $\text{NO}_3^-$ will compete with the anion of glutamic acid to form ionic interaction with the cation of lysine.

II. A polar solvent such as ethanol will disrupt the ion dipole interactions between Asp and Tyr to form ion-dipole interaction with the anion of aspartic acid OR hydrogen bonding with tyrosine.

(ii) Ethanol in case II.
Ethanol can disrupt the hydrogen bonding between peptide linkages which maintain the alpha helix structure OR by forming hydrogen bonds with the peptide linkages.
Note: OR ethanol can form hydrogen bonding with the secondary structure.
B is optically active.  
- B has a chiral carbon.

B dissolves slowly in aq. NaOH  
- B has phenol.
- B undergoes neutralisation.

B reacts with HBr  
- B undergoes N.S.
- B forms alkyl bromide.
- B has alcohol group.

B does not decolourise potassium dichromate.  
- B is a tertiary alcohol.

B decolourises aq. Bromine to form white ppt.  
- B is a phenol.  
- B undergoes E.S.
- From molecular formula of C, one of the 2,4 or 6 positions is occupied.

B reacts with concentrated sulfuric acid at 170°C  
- B undergoes elimination.
- D is an alkene.

D reacts with cold alkaline KMnO$_4$  
- D undergoes mild oxidation.
- D forms a diol.

E reacts with PCl$_5$ to give white fumes  
- E undergoes N.S.

ES substn at 2, 4 or 6.
READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, FIN/NRIC and class in the spaces provided.
Shade correctly your class and FIN/NRIC number.
Eg. If your NRIC is S9306660Z, shade S9306660Z for the item “index number”.

There are forty 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.
Section A

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

1  To determine the percentage of nitrogen present in a snack, 1.0 g of the snack was boiled with concentrated sulphuric acid to convert all the nitrogen into ammonium sulphate. The ammonium salt obtained was then boiled with excess aqueous sodium hydroxide to liberate the ammonia, which was passed into 25.0 cm$^3$ of 0.20 mol dm$^{-3}$ hydrochloric acid. The unreacted hydrochloric acid required 20.0 cm$^3$ of 0.10 mol dm$^{-3}$ aqueous sodium hydroxide for complete neutralisation.

What is the percentage by mass of nitrogen in the snack?

A  2.8%  B  4.2%  C  7.2%  D  8.4%

2  In an experiment, 25.0 cm$^3$ of 0.20 mol dm$^{-3}$ solution of K$_2$AO$_4$ reacted exactly with 25.0 cm$^3$ of 0.10 mol dm$^{-3}$ aqueous sodium sulfate(IV). The half-equation for the oxidation of the sulfate(IV) ion is shown below.

$$\text{SO}_3^{2-} (aq) + \text{H}_2\text{O (l)} \rightarrow \text{SO}_4^{2-} (aq) + 2\text{H}^+ (aq) + 2\text{e}^-$$

Calculate the final oxidation state of A.

A  +2  B  +3  C  +4  D  +5

3  Two elements D and E have the following properties.

- D and E form ionic compounds Na$_2$D and Na$_2$E respectively.
- Element E forms $\text{E}_6$ molecules whereas D is not able to do so.

Which pair of electronic configurations for D and E is correct?

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[He] 2s$^2$ 2p$^2$</td>
<td>[Ne] 3s$^2$ 3p$^4$</td>
</tr>
<tr>
<td>B</td>
<td>[He] 2s$^2$ 2p$^2$</td>
<td>[Ne] 3s$^2$ 3p$^2$</td>
</tr>
<tr>
<td>C</td>
<td>[He] 2s$^2$ 2p$^4$</td>
<td>[Ne] 3s$^2$ 3p$^2$</td>
</tr>
<tr>
<td>D</td>
<td>[He] 2s$^2$ 2p$^4$</td>
<td>[Ne] 3s$^2$ 3p$^4$</td>
</tr>
</tbody>
</table>
The diagram below shows liquid trichloromethane and liquid benzene flowing from burettes 1 and 2 respectively.

What would happen to the flow of the liquids trichloromethane and benzene when a negatively-charged rod is brought near to each of them?

<table>
<thead>
<tr>
<th></th>
<th>Liquid trichloromethane</th>
<th>Liquid benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Deflected towards the rod</td>
<td>Deflected towards the rod</td>
</tr>
<tr>
<td>B</td>
<td>Undeflected</td>
<td>Deflected towards the rod</td>
</tr>
<tr>
<td>C</td>
<td>Deflected towards the rod</td>
<td>Undeflected</td>
</tr>
<tr>
<td>D</td>
<td>Undeflected</td>
<td>Undeflected</td>
</tr>
</tbody>
</table>
5 The value of $pV$ is plotted against $p$ for two gases, \textit{G} and \textit{H}, where $p$ is the pressure and $V$ is the volume of the gas.

![Graph of $pV$ vs $p$ for gases G and H]

Which of the following could be the identities of the gases?

<table>
<thead>
<tr>
<th>Gas G</th>
<th>Gas H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0.5 mol of H$_2$ at 25 ºC</td>
<td>0.5 mol of H$_2$ at 50 ºC</td>
</tr>
<tr>
<td>B 0.5 mol of H$_2$ at 25 ºC</td>
<td>1 mol of SO$_2$ at 25 ºC</td>
</tr>
<tr>
<td>C 0.5 mol of SO$_2$ at 25 ºC</td>
<td>0.5 mol of SO$_2$ at 50 ºC</td>
</tr>
<tr>
<td>D 0.5 mol of SO$_2$ at 25 ºC</td>
<td>1 mol of H$_2$ at 25 ºC</td>
</tr>
</tbody>
</table>

6 During an inspection, a small spacecraft of capacity 20 m$^3$ was connected to another of capacity 50 m$^3$. Before connection, the pressure inside the smaller craft was 40 atm and that inside the larger one was 150 atm.

Given that all measurements were made at the same temperature, What is the pressure of the system after the connection?

| A 78 atm | B 95 atm | C 119 atm | D 190 atm |
7 In which of the following pairs of compounds will compound II have a higher boiling point than compound I?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Br</td>
<td>Cl</td>
</tr>
<tr>
<td>B</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
<td>C(CH₃)₄</td>
</tr>
<tr>
<td>C</td>
<td>CH₃CH₂CH₂COOH</td>
<td>CH₂CH₂CH₂OH</td>
</tr>
<tr>
<td>D</td>
<td>CH₂Cl₂C≡C CH₂Cl₂H</td>
<td>CH₂Cl₂C≡C CH₂Cl₂H</td>
</tr>
</tbody>
</table>

8 The conversion of compound X into Z was exothermic and proceeded by two steps, where Y was the intermediate. The steps involved were:

Step 1: X → Y

Step 2: Y → Z

It was found that Step 1 is the rate-determining step. Which diagram represents the energy level diagram for the reaction?
9 Pure nitrosyl chloride, NOCl gas, was heated at 320°C in a 2.0 dm³ vessel. At equilibrium, 30% of the NOCl gas had dissociated according to the equation below and the total pressure was $p$ atm.

\[
2\text{NOCl} (g) \rightleftharpoons 2\text{NO} (g) + \text{Cl}_2 (g)
\]

What is value of the equilibrium constant, $K_p$?

A \[ \frac{17.9}{p} \]  
B \[ \frac{41.7}{p} \]  
C \[ 0.0120p \]  
D \[ 0.0130p \]

10 The pH change when 0.10 mol dm⁻³ CH₃COOH is added drop-wise to 10.0 cm³ of 0.10 mol dm⁻³ NaOH (aq) is shown below.

At which point on the graph does pH = $pK_a$, where $K_a$ is the acid dissociation constant of the weak acid?
11 In an experiment, 70 cm$^3$ of water at 25ºC was brought to boiling point by burning butane in excess oxygen. Given that the standard enthalpy change of combustion of butane is $-2877$ kJ mol$^{-1}$, calculate the volume of butane needed if this process is only 85% efficient.

Assume that the specific heat capacity of water is $4.2$ J g$^{-1}$ K$^{-1}$ and that 1 mole of gas occupies 24 dm$^3$ under the given conditions.

A $0.0721$ dm$^3$  B $0.156$ dm$^3$  C $0.184$ dm$^3$  D $0.216$ dm$^3$

12 Which of the following changes does not alter the $E^0$ value measured for a $Cl_2/Cl^-$ half-cell that is under standard conditions?

A Adding water into the half-cell.
B Placing the half-cell in an ice bath.
C Adding copper(II) ions into the half-cell.
D Introducing an inert gas into the half-cell at a pressure of 1 atm through a separate inlet from the $Cl_2$ gas inlet.

13 Which statement concerning the chlorine-containing compounds of elements in the third period, sodium to argon, is correct?

A $NaCl$ dissolves easily in water due to favourable ion-dipole interactions and the compound with the highest electrical conductivity in molten state is $A/Cl_3$.
B $PCl_3$ and $Cl_2O_7$ are both acidic in nature due to hydration of the compounds in water.
C The low boiling points of $PCl_3$ and $Cl_2O_7$ are due to the weak bond energies involved in the P-Cl bonds and the Cl-O bonds.
D The different oxidation states of chlorine in $NaCl$ and $Cl_2O_7$ are due to the relative electronegativities of the pairing element and chlorine.
The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.

The sketches below represent another two properties of the elements.

What are properties J and K?

<table>
<thead>
<tr>
<th>property J</th>
<th>property K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A third ionisation energy</td>
<td>electronegativity</td>
</tr>
<tr>
<td>B number of valence electrons</td>
<td>boiling point</td>
</tr>
<tr>
<td>C ionic radius</td>
<td>nuclear charge</td>
</tr>
<tr>
<td>D electrical conductivity</td>
<td>atomic radius</td>
</tr>
</tbody>
</table>
15. Which of the following is true about the thermal decomposition of magnesium nitrate?

A. Sodium nitrate is thermally unstable as compared to magnesium nitrate.
B. Every 1 mol of magnesium nitrate burnt gives 2.5 mol of gaseous products.
C. The decomposition temperature of magnesium nitrate is higher than that of barium nitrate.
D. The solid product of the thermal decomposition of magnesium nitrate readily dissolves in water to give an alkaline solution.

16. Which of the following gives the best description of the reactions of Group II metals and their compounds?

A. All Group II metals react with steam to give hydrogen gas.
B. Barium oxide is stored in oil due to its explosive reaction with oxygen gas in air.
C. All Group II oxides undergo neutralisation with hot acids to give a salt and water.
D. Beryllium hydroxide is amphoteric due to the high charge density of the Be\(^{2+}\) ion.

17. The table below shows the results of experiments in which the halogens, P\(_2\), Q\(_2\) and R\(_2\) were added to separate aqueous solutions containing P\(^-\), Q\(^-\) and R\(^-\) ions.

<table>
<thead>
<tr>
<th></th>
<th>P(^-) (aq)</th>
<th>Q(^-) (aq)</th>
<th>R(^-) (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(_2)</td>
<td>no reaction</td>
<td>no reaction</td>
<td>R(_2) formed</td>
</tr>
<tr>
<td>Q(_2)</td>
<td>P(_2) formed</td>
<td>no reaction</td>
<td>R(_2) formed</td>
</tr>
<tr>
<td>R(_2)</td>
<td>no reaction</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

In which sequence is the solubility of the silver halides in aqueous ammonia arranged in increasing order?

A. AgP < AgQ < AgR
B. AgQ < AgP < AgR
C. AgQ < AgR < AgP
D. AgR < AgP < AgQ
Aqueous sodium hydroxide was added to a pale green solution of a mixture of two metal cations. The resulting precipitate was treated with excess ammonia solution giving an intense deep blue mixture. The mixture was filtered giving a reddish-brown residue and a deep blue filtrate. The residue was washed with deionised water and treated with excess acidified ammonium thiocyanate giving a blood red solution.

Which of the following substances best explains these observations?

<table>
<thead>
<tr>
<th>reddish-brown residue</th>
<th>deep blue filtrate</th>
<th>blood-red solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ( \text{Fe(OH)}_2 )</td>
<td>( \text{Cu(OH)}_2 )</td>
<td>( [\text{Fe(H}_2\text{O)}_6]^{2+} )</td>
</tr>
<tr>
<td>B ( \text{Fe(OH)}_3 )</td>
<td>( [\text{Cu(NH}_3)_4]^{2+} )</td>
<td>( [\text{Fe(H}_2\text{O)}_6]^{3+} )</td>
</tr>
<tr>
<td>C ( \text{Fe(OH)}_2 )</td>
<td>( [\text{Cu(H}_2\text{O)}_6]^{2+} )</td>
<td>( [\text{Fe(H}_2\text{O)}_5\text{SCN}]^{2+} )</td>
</tr>
<tr>
<td>D ( \text{Fe(OH)}_3 )</td>
<td>( [\text{Cu(NH}_3)_4]^{2+} )</td>
<td>( [\text{Fe(H}_2\text{O)}_5\text{SCN}]^{2+} )</td>
</tr>
</tbody>
</table>

19 Rhodium and its compounds are used as catalysts in many important reactions. Which of the following properties makes rhodium a suitable heterogeneous catalyst?

A Rhodium has vacant d orbitals of suitable energy.
B Rhodium exhibits variable oxidation states.
C Rhodium is able to form stable complexes.
D Rhodium is able to form coloured compounds.

20 Compound S was used in the following synthesis route.

\[ \text{Compound S} \xrightarrow{\text{HCN, trace KCN}} \text{Compound T} \xrightarrow{\text{Br}_2 (aq)} \text{Compound U} \]

What are the respective numbers of \( sp, sp^2 \) and \( sp^3 \) hybridised carbon atoms in compound U?

A 0, 6, 4
B 0, 7, 3
C 1, 6, 3
D 1, 7, 2
21 Carvone is the main active ingredient found in spearmint and has the following structure.

![Carvone structure](image)

Carvone can be reduced to compound V by heating with hydrogen gas in the presence of nickel.

How many stereoisomers do the molecules of carvone and V each have?

<table>
<thead>
<tr>
<th>Carvone</th>
<th>Compound V</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
</tr>
</tbody>
</table>

22 How many alcohols (including both structural isomers and stereoisomers) can have the molecular formula C₄H₁₀O?

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

23 A sample of ethene was added to a solution of Br₂ (aq) and NaCl (aq). Which of the following products is not likely to be found in the reaction mixture?

| A | CH₂(OH)CH₂Br |
| B | CH₂BrCH₂Cl   |
| C | CH₂(OH)CH₂Cl |
| D | CH₂BrCH₂Br   |
24 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.

Which of the following statements about hydrocortisone is true?

A  When treated with an excess of hot concentrated acidified KMnO₄, it forms a compound containing seven carbonyl groups.

B  When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

C  When treated with cold dilute KMnO₄, it forms a compound containing two hydroxy groups.

D  When treated with NaBH₄ in the presence of methanol, it forms a compound containing five hydroxy groups.
25 Deuterium, D, is an isotope of hydrogen, $^2H$.

Which of the following is the product formed when the above compound reacts with hot $\text{K}_2\text{Cr}_2\text{O}_7$ in aqueous $\text{D}_2\text{SO}_4$ under controlled conditions?

A

B

C

D

26 Which of the following shows the correct sequence in order of increasing ease of hydrolysis for the compounds below?

A  $X < W < Y < Z$

B  $Z < X < W < Y$

C  $Z < Y < X < W$

D  $W < X < Y < Z$
27. Which of the following statements about compound A is true?

![Compound A](image)

A. When treated with alkaline Tollens' reagent, it forms a compound with molecular formula, C_{15}H_{13}O_{5}Cl.

B. When reacted with PCl₅, 1 mole of HCl (g) is formed.

C. When heated with H₂ (g) in the presence of Ni catalyst, it forms a compound containing three hydroxy groups.

D. When treated with sodium hydroxide, hydrolysis occurs.

28. What is the ratio of sodium iodide formed when each of the three compounds reacts with alkaline aqueous iodine?

![Compounds](image)

A. 1:1:1

B. 5:0:6

C. 5:0:3

D. 1:1:2
Compound B can be converted to compound C as shown below.

\[ \text{Compound B} \rightarrow \text{X} \rightarrow \text{Y} \rightarrow \text{Compound C} \]

Which of the following statements is correct with regards to the given reaction scheme?

A. Step I may involve the use of \( \text{PCl}_5 \).

B. Step I may involve the use of hot acidified potassium manganate(VII).

C. Step III may involve the use of aqueous sodium hydroxide.

D. Step III may involve the use of hot concentrated sulfuric acid.

A polypeptide was partially hydrolysed using two different enzymes and the fragments were separated. Analysis of the fragments gave the following results:

Using enzyme D:
- glu-val-phe
- glu-asp-leu
- ala-ser
- val-ala

Using enzyme E:
- val-phe
- ala-glu-asp
- val
- ser-glu
- leu-ala

What is the amino acid sequence of the polypeptide?

A. leu-ala-ser-glu-val-phe-val-ala-glu-asp

B. ala-glu-asp-leu-ala-ser-glu-val-phe-val

C. glu-val-phe-ala-glu-asp-leu-ala-ser-val

D. val-ala-glu-asp-leu-ala-ser-glu-val-phe
Section B

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:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 The compound ammonium sulfate is primarily used as a fertiliser for alkaline soils. Which type(s) of bonding is/are found in the compound?

1 ionic

2 covalent

3 dative bond

32 The rate of reaction of a strip of magnesium ribbon and 45 cm$^3$ of 1.5 mol dm$^{-3}$ HNO$_3$ is determined at 25 °C. Which of the following cases would both conditions contribute to an increase in the rate of reaction?

1 Mg powder and 90 cm$^3$ of 1.5 mol dm$^{-3}$ HNO$_3$

2 Mg powder and 45 cm$^3$ of 2.0 mol dm$^{-3}$ HNO$_3$

3 45 cm$^3$ of 2.0 mol dm$^{-3}$ HNO$_3$ at 35°C

33 Which of the following statements is/are correct for the following equilibrium?

$$3\text{H}_2 (g) + \text{N}_2 (g) \rightleftharpoons 2\text{NH}_3 (g) \quad \Delta H < 0$$

<table>
<thead>
<tr>
<th>Condition</th>
<th>Position of equilibrium</th>
<th>$K_p$</th>
<th>Rate of formation of NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Increase in pressure</td>
<td>Right</td>
<td>No change</td>
<td>Increase</td>
</tr>
<tr>
<td>2 Decrease in temperature</td>
<td>Right</td>
<td>Increase</td>
<td>Decrease</td>
</tr>
<tr>
<td>3 Addition of catalyst</td>
<td>Left</td>
<td>No change</td>
<td>Increase</td>
</tr>
</tbody>
</table>
34 Which of the following indicators can be used for the titration between ethylamine and hydrochloric acid?

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH transition range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtholphthalein</td>
<td>7.3 – 8.7</td>
</tr>
<tr>
<td>Congo red</td>
<td>3.0 – 5.0</td>
</tr>
<tr>
<td>Azolitmin</td>
<td>4.5 – 8.3</td>
</tr>
</tbody>
</table>

35 In which of the following pairs will compound I and compound II give the same number of cis-trans isomers after reaction with hot ethanolic potassium hydroxide?

1

\[
\text{I} \quad \text{II}
\]

\[
\begin{align*}
1 & \quad \text{Br} \quad \text{CH}_2\text{CHCH}_3 \\
& \quad \text{Br} \\
2 & \quad \text{Br} \quad \text{C} \quad \text{CH}_2\text{CH}_3 \\
& \quad \text{Br} \quad \text{CH}_3 \\
3 & \quad \text{Br} \quad \text{Br} \\
& \quad \text{BrCH}_2\text{C} \quad \text{CH}_2\text{CH}_2\text{Br} \\
& \quad \text{H}
\end{align*}
\]

36 Which of the following processes lead(s) to an increase in entropy?

1 Diffusion of CFCs into the stratosphere.
2 Combustion of a piece of charcoal to form CO\(_2\) (g) and H\(_2\)O (g).
3 Desalination of sea water by reverse osmosis (solvent passes from a more concentrated solution to a more dilute solution).
37 The diagram shows the structure of salicylic acid:

![Salicylic acid structure](image)

Which compound(s) give(s) salicylic acid on acidic hydrolysis?

1. CO$_2$CH$_3$
2. CONH$_2$
3. COCl

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>
38 In which of the following sequences does the value of $pK_b$ decrease?

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

![Chemical structures]

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

A student set up an electrolytic cell for the purpose of purifying copper metal. However, the set-up did not lead to successful purification of copper.

Which of the following could explain the failure of the set-up?

1. The electrolyte used was aqueous chromium(III) chloride.
2. The impure copper was used as the cathode and the anode was made of pure copper metal.
3. The $E^{\circ}$ cell for the reaction is a negative value.

40 Vanadium has the electronic structure $1s^22s^22p^63s^23p^63d^34s^2$. Which of the following vanadium compounds is/are likely to exist?

1. $\text{V}_2\text{O}_5$
2. $\text{VOCl}$
3. $\text{K}_2\text{V}_2\text{O}_7$
READ THESE INSTRUCTIONS FIRST

On the separate multiple choice OMS given, write your name, FIN/NRIC and class in the spaces provided.
Shade correctly your class and FIN/NRIC number.
Eg. If your NRIC is S9306660Z, shade S9306660Z for the item “index number”.

There are forty 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.
Section A
Answer all questions

1. To determine the percentage of nitrogen present in a snack, 1.0 g of the snack was boiled with concentrated sulphuric acid to convert all the nitrogen into ammonium sulphate. The ammonium salt obtained was then boiled with excess aqueous sodium hydroxide to liberate the ammonia, which was passed into 25.0 cm$^3$ of 0.20 mol dm$^{-3}$ hydrochloric acid. The unreacted hydrochloric acid required 20.0 cm$^3$ of 0.10 mol dm$^{-3}$ aqueous sodium hydroxide for complete neutralisation.

What is the percentage by mass of nitrogen in the snack?

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.8%</td>
<td>4.2%</td>
<td>7.2%</td>
<td>8.4%</td>
</tr>
</tbody>
</table>

Answer: B

\[
\text{Amt of NH}_3 = \left( \frac{25}{1000} \times 0.20 \right) - \left( \frac{20}{1000} \times 0.10 \right) = 0.003 \text{ mol}
\]

\[
2\text{NH}_3 \equiv \text{1(NH}_4\text{)}_2\text{SO}_4 \equiv 2\text{N}
\]

\[
\text{Mass of nitrogen in snack} = 0.003 \times 14.0 = 0.042 \text{ g}
\]

\[
\% \text{ by mass} = \frac{0.042}{1} \times 100 = 4.2\%
\]

2. In an experiment, 25.0 cm$^3$ of 0.20 mol dm$^{-3}$ solution of K$_2$AO$_4$ reacted exactly with 25.0 cm$^3$ of 0.10 mol dm$^{-3}$ aqueous sodium sulfate(IV). The half-equation for the oxidation of the sulfate(IV) ion is shown below.

\[
\text{SO}_3^{2-} (aq) + \text{H}_2\text{O (l)} \rightarrow \text{SO}_4^{2-} (aq) + 2\text{H}^+ (aq) + 2\text{e}^-
\]

Calculate the final oxidation state of A.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+2</td>
<td>+3</td>
<td>+4</td>
<td>+5</td>
</tr>
</tbody>
</table>

Answer: D

\[
2\text{K}_2\text{AO}_4 \equiv \text{SO}_3^{2-}
\]

No. of e gained by A in K$_2$AO$_4$ = No. of e lost by S in SO$_3^{2-}$ = 2e

\[
2\text{A}^{n+} + 2e^{-} \rightarrow 2\text{A}^{n+}
\]

\[
12 - 2 = 2n
\]

\[n = +5\]
Two elements D and E have the following properties.

- D and E form ionic compounds Na₂D and Na₂E respectively.
- Element E forms EF₆ molecules whereas D is not able to do so.

Which pair of electronic configurations for D and E is correct?

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[He] 2s² 2p²</td>
<td>[Ne] 3s² 3p⁴</td>
</tr>
<tr>
<td>B</td>
<td>[He] 2s² 2p²</td>
<td>[Ne] 3s² 3p²</td>
</tr>
<tr>
<td>C</td>
<td>[He] 2s² 2p⁴</td>
<td>[Ne] 3s² 3p²</td>
</tr>
<tr>
<td>D</td>
<td>[He] 2s² 2p⁴</td>
<td>[Ne] 3s² 3p⁴</td>
</tr>
</tbody>
</table>

Answer: D

The diagram below shows liquid trichloromethane and liquid benzene flowing from burettes 1 and 2 respectively.

What would happen to the flow of the liquids trichloromethane and benzene when a negatively-charged rod is brought near to each of them?

<table>
<thead>
<tr>
<th></th>
<th>Liquid trichloromethane</th>
<th>Liquid benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Deflected towards the rod</td>
<td>Deflected towards the rod</td>
</tr>
<tr>
<td>B</td>
<td>Undelected</td>
<td>Deflected towards the rod</td>
</tr>
<tr>
<td>C</td>
<td>Deflected towards the rod</td>
<td>Undelected</td>
</tr>
<tr>
<td>D</td>
<td>Undelected</td>
<td>Undelected</td>
</tr>
</tbody>
</table>

Answer: C

Liquid trichloromethane is polar. The partial positive charge can be attracted by the negatively charged rod.

Benzene is non-polar and does not have partial charges.
5  The value of \( pV \) is plotted against \( p \) for two gases, \( G \) and \( H \), where \( p \) is the pressure and \( V \) is the volume of the gas.

Which of the following could be the identities of the gases?

<table>
<thead>
<tr>
<th></th>
<th>Gas G</th>
<th>Gas H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5 mol of ( H_2 ) at 25 °C</td>
<td>0.5 mol of ( H_2 ) at 50 °C</td>
</tr>
<tr>
<td>B</td>
<td>0.5 mol of ( H_2 ) at 25 °C</td>
<td>1 mol of ( SO_2 ) at 25 °C</td>
</tr>
<tr>
<td>C</td>
<td>0.5 mol of ( SO_2 ) at 25 °C</td>
<td>0.5 mol of ( SO_2 ) at 50 °C</td>
</tr>
<tr>
<td>D</td>
<td>0.5 mol of ( SO_2 ) at 25 °C</td>
<td>1 mol of ( H_2 ) at 25 °C</td>
</tr>
</tbody>
</table>

Answer: D

Amount of gas \( H \) should be twice the amount of gas \( G \).
According to the shape of the curves, gas \( G \) should be a less ideal gas than gas \( H \).

6  During an inspection, a small spacecraft of capacity 20 m\(^3\) was connected to another of capacity 50 m\(^3\). Before connection, the pressure inside the smaller craft was 40 atm and that inside the larger one was 150 atm.

Given that all measurements were made at the same temperature, What is the pressure of the system after the connection?

<table>
<thead>
<tr>
<th></th>
<th>78 atm</th>
<th>B</th>
<th>95 atm</th>
<th>C</th>
<th>119 atm</th>
<th>D</th>
<th>190 atm</th>
</tr>
</thead>
</table>
| Answer: C

Amt of gas in small spacecraft = \[ \frac{pV}{RT} = \frac{(40)(20)}{RT} = \frac{800}{RT} \]

Amt of gas in large spacecraft = \[ \frac{pV}{RT} = \frac{(150)(50)}{RT} = \frac{7500}{RT} \]

total amt of moles of gas = \[ \frac{800 + 7500}{RT} = \frac{8300}{RT} \]

Pressure in the combined arrangement = \[ \frac{nRT}{V} = \frac{(8300/RT)RT}{(20 + 50)} = 119 \text{ atm} \]
In which of the following pairs of compounds will compound II have a higher boiling point than compound I?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image1.png" alt="Image" /> Br</td>
<td><img src="image2.png" alt="Image" /> Cl</td>
</tr>
<tr>
<td>B</td>
<td>CH₃CH₂CH₂CH₂CH₃</td>
<td>C(CH₃)₄</td>
</tr>
<tr>
<td>C</td>
<td>CH₃CH₂CH₂COOH</td>
<td>CH₃CH₂CH₂OH</td>
</tr>
<tr>
<td>D</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>

**Answer: D**

A: I has higher Mr than II and hence has more extensive intermolecular VDW forces of attraction and a higher boiling point.

B: I is linear and II is branched and hence has more extensive intermolecular VDW forces of attraction and a higher boiling point.

C: I has more extensive intermolecular hydrogen bonding than II and hence a higher boiling point.

D: I is non-polar and has temporary dipole-induced dipole interactions while II is polar and has permanent dipole-dipole interactions. Hence II has a higher boiling point.
The conversion of compound **X** into **Z** was exothermic and proceeded by two steps, where **Y** was the intermediate. The steps involved were:

**Step 1:** \( X \rightarrow Y \)

**Step 2:** \( Y \rightarrow Z \)

It was found that Step 1 is the rate-determining step. Which diagram represents the energy level diagram for the reaction?

<table>
<thead>
<tr>
<th>Answer: A</th>
</tr>
</thead>
</table>

![Diagram A](image1)

![Diagram B](image2)

![Diagram C](image3)

![Diagram D](image4)
Pure nitrosyl chloride, NOCl, gas, was heated at 320°C in a 2.0 dm³ vessel. At equilibrium, 30% of the NOCl gas had dissociated according to the equation below and the total pressure was P atm.

\[2\text{NOCl} (g) \rightleftharpoons 2\text{NO} (g) + \text{Cl}_2 (g)\]

What is the value of the equilibrium constant, \(K_p\)?

<table>
<thead>
<tr>
<th>A</th>
<th>17.9 (\frac{p}{p})</th>
<th>B</th>
<th>41.7 (\frac{p}{p})</th>
<th>C</th>
<th>0.0120p</th>
<th>D</th>
<th>0.0130p</th>
</tr>
</thead>
</table>

**Answer:** C

**\[2\text{NOCl} (g) \rightleftharpoons 2\text{NO} (g) + \text{Cl}_2 (g)\]**

<table>
<thead>
<tr>
<th>Initial partial pressure/atm</th>
<th>0.7x</th>
<th>0.3x</th>
<th>0.15x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change in partial pressure / atm</td>
<td>-0.3x</td>
<td>+0.3x</td>
<td>+0.15x</td>
</tr>
<tr>
<td>Equilibrium partial pressure / atm</td>
<td>0.6087p</td>
<td>0.2609p</td>
<td>0.1304p</td>
</tr>
</tbody>
</table>

0.7x + 0.3x + 0.15x = p

x = 0.8696p

\[
K_p = \left( \frac{0.2609p \cdot 0.1304p}{0.6087p^2} \right)^2
\]

= 0.01197

= 0.0120p
The pH change when 0.100 mol dm\(^{-3}\) \(\text{CH}_3\text{COOH}\) is added drop-wise to 10.0 cm\(^3\) of 0.100 mol dm\(^{-3}\) NaOH (aq) is shown below.

At which point on the graph does pH = p\(K_a\), where \(K_a\) is the acid dissociation constant of the weak acid?

Answer: D

Regions C and D are where there is an excess of weak acid \(\text{CH}_3\text{COOH}\) as well as the salt \(\text{CH}_3\text{COO}^-\text{Na}^+\) that is formed. Hence, buffer region.

At Region D,

\[
\text{Amt of CH}_3\text{COO}^-\text{Na}^+ \text{ formed} = \frac{10}{1000} \times 0.100 = 0.001 \text{ mol}
\]

\[
\text{Amt of excess CH}_3\text{COOH added} = \frac{(20 - 10)}{1000} \times 0.100 = 0.001 \text{ mol}
\]

Amt of \(\text{CH}_3\text{COO}^-\text{Na}^+\) and \(\text{CH}_3\text{COOH}\) is the same, hence this is the point where there is maximum buffering capacity and pH = p\(K_a\).
In an experiment, 70 cm$^3$ of water at 25ºC was brought to boiling point by burning butane in excess oxygen. Given that the standard enthalpy change of combustion of butane is -2877 kJ mol$^{-1}$, calculate the volume of butane needed if this process is only 85% efficient.

Assume that the specific heat capacity of water is 4.2 J g$^{-1}$ K$^{-1}$ and that 1 mole of gas occupies 24 dm$^3$ under the given conditions.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.0721 dm$^3$</td>
<td>B</td>
<td>0.156 dm$^3$</td>
<td>C</td>
</tr>
</tbody>
</table>

Answer: D

Since $Q' = mc\Delta T = 70 \times 4.2 \times (100.0 - 25.0) = 22050$ J

Apparent amount of heat absorbed by water, $Q' = \frac{85}{100}Q$ (Actual amount of heat evolved by burning butane)

Actual amount of heat evolved, $Q = 100 \times \frac{22050}{85} = 25941$ J

$\Delta H^o_{\text{C}_4\text{H}_{10}} = \frac{25941}{n} = -2877 \times 10^3$

Amount of butane = $9.017 \times 10^{-3}$ mol

Volume of butane = $9.017 \times 10^{-3} \times 24 = 0.216$ dm$^3$

Which of the following changes does not alter the $E^o$ value measured for a Cl$_2$/Cl$^-$ half-cell that is under standard conditions?

A: Adding water into the half-cell.
B: Placing the half-cell in an ice bath.
C: Adding copper(II) ions into the half-cell.
D: Introducing an inert gas into the half-cell at a pressure of 1 atm through a separate inlet from the Cl$_2$ gas inlet.

Answer: D

A: Dilution causes the concentration of Cl$^-$ ions to be lower than 1 mol dm$^{-3}$.
B: The ice bath lowers the temperature of the half-cell to less than 298 K.
C: Cu$^{2+}$ ions will form a complex with Cl$^-$ ions and lower the concentration of Cl$^-$ ions to less than 1 mol dm$^{-3}$.
D: Introducing an inert gas through a separate inlet does not affect the pressure of Cl$_2$ gas hence doing so does not affect the $E^o$ value of the half-cell.
Which statement concerning the chlorine-containing compounds of elements in the third period, sodium to argon, is correct?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>NaCl dissolves easily in water due to favourable ion-dipole interactions and the compound with the highest electrical conductivity in molten state is AlCl₃.</td>
</tr>
<tr>
<td>B</td>
<td>PCl₃ and Cl₂O₇ are both acidic in nature due to hydration of the compounds in water.</td>
</tr>
<tr>
<td>C</td>
<td>The low boiling points of PCl₃ and Cl₂O₇ are due to the weak bond energies involved in the P-Cl bonds and the Cl-O bonds.</td>
</tr>
<tr>
<td>D</td>
<td>The different oxidation states of chlorine in NaCl and Cl₂O₇ are due to the relative electronegativities of the pairing element and chlorine.</td>
</tr>
</tbody>
</table>

Answer: **D**

A: AlCl₃ is a simple molecular structure, it does not conduct electricity.

B: PCl₃ and Cl₂O₇ are both acidic in nature due to **hydrolysis** of the compounds in water.

C: The low boiling points of PCl₃ and Cl₂O₇ are due to the weak **intermolecular** forces of attraction present and not related to bond energy.
The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.

The sketches below represent another two properties of the elements.

What are properties J and K?

<table>
<thead>
<tr>
<th></th>
<th>property J</th>
<th>property K</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>third ionisation energy</td>
<td>electronegativity</td>
</tr>
<tr>
<td>B</td>
<td>number of valence electrons</td>
<td>boiling point</td>
</tr>
<tr>
<td>C</td>
<td>ionic radius</td>
<td>nuclear charge</td>
</tr>
<tr>
<td>D</td>
<td>electrical conductivity</td>
<td>atomic radius</td>
</tr>
</tbody>
</table>

**Answer:** A
### 15. Which of the following is true about the thermal decomposition of magnesium nitrate?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>Sodium nitrate is thermally unstable as compared to magnesium nitrate.</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>Every 1 mole of magnesium nitrate burnt gives 2.5 moles of gaseous products.</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>The decomposition temperature of magnesium nitrate is higher than that of barium nitrate.</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>The solid product of the thermal decomposition of magnesium nitrate readily dissolves in water to give an alkaline solution.</td>
</tr>
</tbody>
</table>

**Answer:** **B**

**A:** Sodium nitrate is more thermally stable than magnesium nitrate due to the lower charge density, and hence lower polarising power, of Na\(^+\) as compared to Mg\(^{2+}\), leading to a smaller polarising effect on the NO\(_3^-\) electron cloud.

**B:** \[2\text{Mg(NO}_3\text{)}_2 (s) \rightarrow 2\text{MgO (s) + 4NO}_2 \text{ (g) + O}_2 \text{ (g)}\]

**C:** The decomposition temperature of magnesium nitrate is lower than that of barium nitrate due to the higher charge density, and hence greater polarising power, of Mg\(^{2+}\) as compared to Ba\(^{2+}\), leading to a greater polarising effect on the NO\(_3^-\) electron cloud.

**D:** MgO (s) dissolves very slowly, if at all, in water.

---

### 16. Which of the following gives the best description of the reactions of Group II metals and their compounds?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>All Group II metals react with steam to give hydrogen gas.</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>Barium oxide is stored in oil due to its explosive reaction with oxygen gas in air.</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>All Group II oxides undergo neutralisation with hot acids to give a salt and water.</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>Beryllium hydroxide is amphoteric due to the high charge density of the Be(^{2+}) ion.</td>
</tr>
</tbody>
</table>

**Answer:** **C**

**A:** Be (s) does not react with steam.

**B:** Ba (s), not barium oxide, is explosive in air.

**D:** The acidic nature of Be(OH)\(_2\) can be explained by its high charge density but not its basic nature.
The table below shows the results of experiments in which the halogens, $P_2$, $Q_2$ and $R_2$ were added to separate aqueous solutions containing $P^-$, $Q^-$ and $R^-$ ions.

<table>
<thead>
<tr>
<th></th>
<th>$P^-(aq)$</th>
<th>$Q^-(aq)$</th>
<th>$R^-(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2$</td>
<td>no reaction</td>
<td>no reaction</td>
<td>$R_2$ formed</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>$P_2$ formed</td>
<td>no reaction</td>
<td>$R_2$ formed</td>
</tr>
<tr>
<td>$R_2$</td>
<td>no reaction</td>
<td>no reaction</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

In which sequence is the solubility of the silver halides in aqueous ammonia arranged in increasing order?

A. $AgP < AgQ < AgR$
B. $AgQ < AgP < AgR$
C. $AgQ < AgR < AgP$
D. $AgR < AgP < AgQ$

Answer: D

From the table $R_2$ is the weakest oxidising agent while $Q_2$ is the strongest oxidising agent.

A logical deduction means $Q_2$ is chlorine, and $R_2$ is iodine.

Solubility of silver halides in NH$_3$ (aq) in increasing order is AgR, AgP and AgQ.

Aqueous sodium hydroxide was added to a pale green solution of a mixture of two metal cations. The resulting precipitate was treated with excess ammonia solution giving an intense deep blue mixture. The mixture was filtered giving a reddish–brown residue and a deep blue filtrate. The residue was washed with deionised water and treated with excess acidified ammonium thiocyanate giving a blood red solution.

Which of the following substances best explains these observations?

<table>
<thead>
<tr>
<th>reddish–brown residue</th>
<th>deep blue filtrate</th>
<th>blood–red solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Fe(OH)$_2$</td>
<td>Cu(OH)$_2$</td>
<td>[Fe(H$_2$O)$_6$]$^{2+}$</td>
</tr>
<tr>
<td>B Fe(OH)$_3$</td>
<td>[Cu(NH$_3$)$_4$]$^{2+}$</td>
<td>[Fe(H$_2$O)$_6$]$^{3+}$</td>
</tr>
<tr>
<td>C Fe(OH)$_2$</td>
<td>[Cu(H$_2$O)$_6$]$^{2+}$</td>
<td>[Fe(H$_2$O)$_5$SCN]$^{2+}$</td>
</tr>
<tr>
<td>D Fe(OH)$_3$</td>
<td>[Cu(NH$_3$)$_4$]$^{2+}$</td>
<td>[Fe(H$_2$O)$_5$SCN]$^{2+}$</td>
</tr>
</tbody>
</table>

Answer: D
### Question 19

Rhodium and its compounds are used as catalysts in many important reactions. Which of the following properties makes rhodium a suitable heterogeneous catalyst?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Rhodium has vacant d-orbitals of suitable energy.</td>
</tr>
<tr>
<td>B</td>
<td>Rhodium exhibits variable oxidation states.</td>
</tr>
<tr>
<td>C</td>
<td>Rhodium is able to form stable complexes.</td>
</tr>
<tr>
<td>D</td>
<td>Rhodium is able to form coloured compounds.</td>
</tr>
</tbody>
</table>

**Answer: A**

The only answer to explain the feature of transition elements which allow them to function as heterogeneous catalyst. Statement B is more for homogeneous catalyst.

### Question 20

Compound S was used in the following synthesis route.

\[
\text{Compound S} \xrightarrow{\text{HCN, trace KCN}} \text{Compound T} \xrightarrow{\text{Br}_2 \text{ (aq)}} \text{Compound U}
\]

What are the numbers of \( sp \), \( sp^2 \) and \( sp^3 \) hybridised carbon atoms in compound U?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0, 6, 4</td>
</tr>
<tr>
<td>B</td>
<td>0, 7, 3</td>
</tr>
<tr>
<td>C</td>
<td>1, 6, 3</td>
</tr>
<tr>
<td>D</td>
<td>1, 7, 2</td>
</tr>
</tbody>
</table>

**Answer: C**

Compound U is

![Chemical structure of Compound U]
Carvone is the main active ingredient found in spearmint and it has the following structure:

![Carvone structure]

Carvone can be reduced to compound V by heating with hydrogen gas in the presence of nickel.

How many stereoisomers do the molecules of carvone and V each have?

<table>
<thead>
<tr>
<th></th>
<th>Carvone</th>
<th>Compound V</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

Answer: D

Carvone has one chiral carbon as shown:

![Carvone chiral carbon]

hence is will have $2^1 = 2$ optical isomers

Compound V has 3 chiral carbon as shown:

![Compound V chiral carbons]

hence is will have $2^3 = 8$ optical isomers
### Problem 22
How many alcohols (including both structural and stereoisomers) can have the molecular formula C₄H₁₀O?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>6</td>
</tr>
</tbody>
</table>

**Answer:** C

- CH₃CH₂CH₂CH₂OH
- CH₃CH₂CH(OH)CH₃ (presence of chiral carbon Œ 2 isomers)
- CH₃C(CH₃)CH₂OH
- CH₃C(CH₃)(OH)CH₃

### Problem 23
A sample of ethene was added to a solution of Br₂ (aq) and NaCl (aq). Which of the following products is **not** likely to be found in the reaction mixture?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CH₂(OH)CH₂Br</td>
</tr>
<tr>
<td>B</td>
<td>CH₂BrCH₂Cl</td>
</tr>
<tr>
<td>C</td>
<td>CH₂(OH)CH₂Cl</td>
</tr>
<tr>
<td>D</td>
<td>CH₂BrCH₂Br</td>
</tr>
</tbody>
</table>

**Answer:** C

In the electrophilic substitution of ethane and Br₂(aq), the first step is:

- H₂C=CH₂ + Br⁺ → Br⁻ → slow → H⁺C⁺CH₂⁻Br⁻

Hence, the product must contain at least one Br.
Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.

Which of the following statements about hydrocortisone is true?

<table>
<thead>
<tr>
<th>Option</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>When treated with an excess of hot concentrated acidified KMnO₄, it forms a compound containing 7 carbonyl groups.</td>
</tr>
<tr>
<td>B</td>
<td>When warmed with aqueous alkaline iodine, a yellow precipitate is observed.</td>
</tr>
<tr>
<td>C</td>
<td>When treated with cold dilute KMnO₄, it forms a compound containing 2 hydroxy groups.</td>
</tr>
<tr>
<td>D</td>
<td>When treated with NaBH₄ in the presence of methanol, it forms a compound containing 5 hydroxy groups.</td>
</tr>
</tbody>
</table>

Answer: D

Ketone undergoes reduction to form:

A: C=C, primary and secondary alcohol undergo oxidation to form a compound with 4 carbonyl groups.

B: No CH₃CO- or -CH(CH₃)(OH) group observed.

C: Only alkene undergoes mild oxidation to form a diol, a compound with 5 hydroxy groups is formed.
Deuterium, D, is an isotope of hydrogen, $^2H$.

Which of the following is the product formed when the above compound reacts with hot $K_2Cr_2O_7$ in aqueous $D_2SO_4$ under controlled conditions?

A

\[
\text{O} \quad \text{CDO} \quad \text{O}
\]

B

\[
\text{OH} \quad \text{COOH}
\]

C

\[
\text{OH} \quad \text{CHO}
\]

D

\[
\text{DO} \quad \text{COOD}
\]

Answer: C

Which of the following shows the correct sequence in order of increasing ease of hydrolysis for the compounds below?

W

\[
\text{Cl}
\]

X

\[
\text{Cl}
\]

Y

\[
\text{Br}
\]

Z

\[
\text{COCl}
\]

A

\[
X < W < Y < Z
\]

B

\[
Z < X < W < Y
\]

C

\[
Z < Y < X < W
\]

D

\[
W < X < Y < Z
\]

Answer: A

Acyl chloride, Z undergoes hydrolysis readily at rtp.

Strength of C-X bond: C-Cl > C-Br

Ease of hydrolysis: R-Cl < R-Br

For X, presence of double bond strengthen C-Br bond making nucleophilic sub less readily to happen.
27 Which of the following statement about compound A is true?

![Compound A](image.png)

<table>
<thead>
<tr>
<th></th>
<th>Statement</th>
<th>Answer</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>When treated with alkaline Tollens' reagent, it forms a compound with molecular formula, C₁₅H₁₃O₅Cl.</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>When reacted with PC₁₅, 1 mole of HCl (g) are formed.</td>
<td>B</td>
</tr>
<tr>
<td>C</td>
<td>When heated with H₂ (g) in the presence of Ni catalyst, it forms a compound containing 3 hydroxy groups.</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>When treated with sodium hydroxide, hydrolysis occurred.</td>
<td></td>
</tr>
</tbody>
</table>

**Answer: B**

**A:** Compound with formula, C₁₅H₁₁O₅Cl is formed as phenol undergoes neutralisation with alkaline Tollens' reagent.

**B:** Only 1 mole of HCl(g) is formed as phenol do not react with PC₁₅.

**C:** After reduction of ketone and C=C, a compound containing 5 hydroxy groups is formed.

**D:** Neutralisation occurred not hydrolysis.
What is the ratio of sodium iodide formed when each of the three compounds reacts with alkaline aqueous iodine?

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[\text{HOH} ]</td>
<td>[\text{HOH} ]</td>
</tr>
<tr>
<td>A</td>
<td>1:1:1</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5:0:6</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>5:0:3</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1:1:2</td>
<td></td>
</tr>
</tbody>
</table>

Answer: **B**
Compound **B** can be converted to compound **C** as shown below.

\[
\begin{array}{c}
\text{CH}_2\text{CH}_2\text{OH} \\
\text{OH} \\
\text{I} \\
\text{Y} \\
\text{III} \\
\text{Compound B} \\
\text{X} \\
\text{Compound C}
\end{array}
\]

Which of the following statements is correct with regards to the given reaction scheme?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>Step <strong>I</strong> may involve the use of <strong>PCl</strong>\textsubscript{5}.</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>Step <strong>I</strong> may involve the use of hot acidified potassium manganate(VII).</td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>Step <strong>III</strong> may involve the use of aqueous sodium hydroxide.</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>Step <strong>III</strong> may involve the use of hot concentrated sulfuric acid.</td>
</tr>
</tbody>
</table>

**Answer:** **C**

**Compound B**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I</strong></td>
<td><strong>II</strong></td>
</tr>
</tbody>
</table>
| **CH}_2\text{CH}_2\text{OH} \\
\text{OH} \\
\text{OH} \\
\text{CH}_2\text{COOH} \\
\text{OH} \\
\text{CH}_2\text{COCl} \\
\text{OH} \\
\text{O} \\
\text{O} \\
\text{Compound C} |

**Step I:** hot, acidified \text{K}_2\text{Cr}_2\text{O}_7

**Step II:** \text{PCl}_5, rtp

**Step III:** \text{NaOH} (aq), rtp (to form phenoxide)
A polypeptide was partially hydrolysed using two different enzymes and the fragments were separated. Analysis of the fragments gave the following results:

Using enzyme D:
- glu-val-phe
- glu-asp-leu
- ala-ser
- val-ala

Using enzyme E:
- val-phe
- ala-glu-asp
- val
- ser-glu
- leu-ala

What is the amino acid sequence of the polypeptide?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>leu-ala-ser-glu-val-phe-val-ala-glu-asp</td>
</tr>
<tr>
<td>B</td>
<td>ala-glu-asp-leu-ala-ser-glu-val-phe-val</td>
</tr>
<tr>
<td>C</td>
<td>glu-val-phe-ala-glu-asp-leu-ala-ser-val</td>
</tr>
<tr>
<td>D</td>
<td>val-ala-glu-asp-leu-ala-ser-glu-val-phe</td>
</tr>
</tbody>
</table>

**Answer:** D
Section B

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:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
<td></td>
</tr>
</tbody>
</table>

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

31 The compound ammonium sulfate is primarily used as a fertiliser for alkaline soils. Which type(s) of bonding is/are found in the compound?

1 ionic
2 covalent
3 dative bond

Answer: A (1, 2 and 3)

32 The rate of reaction of a strip of magnesium ribbon and 45 cm$^3$ of 1.5 mol dm$^{-3}$HNO$_3$ is determined at 25°C. Which of the following cases would both conditions contribute to an increase in the rate of reaction?

1 Mg powder and 90 cm$^3$ of 1.5 mol dm$^{-3}$HNO$_3$
2 Mg powder and 45 cm$^3$ of 2.0 mol dm$^{-3}$HNO$_3$
3 45 cm$^3$ of 2.0 mol dm$^{-3}$ HNO$_3$ at 35°C

Answer: C (2 and 3 only)

1: Use of Mg powder increases rate of reaction due to increase in surface area of reaction but increase in volume does not increase rate of reaction.
2: Use of Mg powder increases rate of reaction due to increase in surface area of reaction and increase in concentration of HNO$_3$ increases rate of reaction due to increase in effective collisions.
3: Increase in concentration and temperature increases rate of reaction due to increase in effective collisions.
Which of the following statements is/are correct for the following equilibrium?

$$3\text{H}_2 (g) + \text{N}_2 (g) \rightleftharpoons 2\text{NH}_3 (g) \quad \Delta H < 0$$

<table>
<thead>
<tr>
<th>Condition</th>
<th>Position of equilibrium</th>
<th>$K_p$</th>
<th>Rate of formation of $\text{NH}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Increase in pressure</td>
<td>Right</td>
<td>No change</td>
<td>Increase</td>
</tr>
<tr>
<td>2 Decrease in temperature</td>
<td>Right</td>
<td>Increase</td>
<td>Decrease</td>
</tr>
<tr>
<td>3 Addition of catalyst</td>
<td>Left</td>
<td>No change</td>
<td>Increase</td>
</tr>
</tbody>
</table>

Answer: B (1 and 2 only)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Position of equilibrium</th>
<th>$K_p$</th>
<th>Rate of forward reaction</th>
</tr>
</thead>
</table>
| 1 Increase in pressure | Right (✓)  
Position of eqm will shift to decrease amt of gases. | No change (✗)  
$K_p$ is independent of pressure | Increase (✓)  
Increase in pressure results in increase number of effective collisions. |
| 2 Decrease in temperature | Right (✓)  
Position of eqm will shift to forward exothermic reaction. | Increase (✓)  
Forward rate constant will decrease less than backward rate constant, hence $K_p$ increases | Decrease (✗)  
Decrease in temperature leads to lower kinetic energy and decrease in number of effective collisions. |
| 3 Addition of catalyst | Left (✗)  
Catalyst does not affect eqm position | Increase (✗)  
$K_p$ is independent of catalyst | Increase (✓)  
Catalyst increases rate of reaction. |
Which of the following indicators can be used for the titration between ethylamine and hydrochloric acid?

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH transition range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Naphtholphthalein</td>
<td>7.3 – 8.7</td>
</tr>
<tr>
<td>2 Congo red</td>
<td>3.0 – 5.0</td>
</tr>
<tr>
<td>3 Azolitmin</td>
<td>4.5 – 8.3</td>
</tr>
</tbody>
</table>

Answer: C (2 and 3 only)

For the titration between ethylamine and hydrochloric acid, it is a strong acid/weak base titration. Hence, at equivalence point of titration, pH increases sharply from \( \approx 3 \) to 7.

Only Congo red and Azolitmin pH transition range) lies within the rapid pH change (\( \approx 3 \) to 7) over the equivalence point.
In which of the following pairs will compound I and compound II give the same number of cis-trans isomers after reaction with hot ethanolic potassium hydroxide?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Compound I" /></td>
<td><img src="image2.png" alt="Compound II" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image3.png" alt="Compound I" /></td>
<td><img src="image4.png" alt="Compound II" /></td>
</tr>
<tr>
<td>3</td>
<td><img src="image5.png" alt="Compound I" /></td>
<td><img src="image6.png" alt="Compound II" /></td>
</tr>
</tbody>
</table>

Answer: A (1, 2 and 3)

Pair 1 both give 2 cis-trans isomers.
Pair 2 and 3 both give 0 cis-trans isomers.

Which of the following processes lead(s) to an increase in entropy?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diffusion of CFCs into the stratosphere.</td>
</tr>
<tr>
<td>2</td>
<td>Combustion of a piece of charcoal to form CO$_2$ (g) and H$_2$O (g).</td>
</tr>
<tr>
<td>3</td>
<td>Desalination of sea water by reverse osmosis (solvent passes from a more concentrated solution to a more dilute solution).</td>
</tr>
</tbody>
</table>

Answer: B (1 and 2 only)

For option 3, there is an increase in orderliness as the solvent passes from a more concentrated solution to a more diluted solution. Hence, entropy will decrease.
The diagram shows the structure of salicylic acid:

![Salicylic Acid Structure](image)

Which compound(s) give(s) salicylic acid on acidic hydrolysis?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><a href="image">Structure</a></td>
</tr>
<tr>
<td>2</td>
<td><a href="image">Structure</a></td>
</tr>
<tr>
<td>3</td>
<td><a href="image">Structure</a></td>
</tr>
</tbody>
</table>

**Answer:** D (1 only)

2: Halogenoarenes do not undergo nucleophilic substitution.

3: will be formed instead.
In which of the following sequences does the value of $pK_b$ decrease?

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Image of structures: NH$_2$, NH$_2$, NO$_2$, CH$_3$, CH$_2$NH$_2$]</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$OHCH$_2$NH$_2$, CH$_2$CH$_2$CH$_2$NH$_2$, CH$_3$CH$_2$CH$_2$NH$_2$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>[Image of structures: COOH, COOH, OH]</td>
<td></td>
</tr>
</tbody>
</table>

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

$pK_b$ decreases means weakest base to strongest base or strongest acid to weakest acid.

- The **electron donating alkyl group** increases the **availability** of the lone pair of electrons on N atom to accept a proton via a **dative bond**. Hence, is the strongest base.

4-methylphenylamine is a **stronger** base than 4-nitrophenylamine.

- The presence of the **electron-donating methyl group** in 4-methylphenylamine **reduces** the delocalization of the lone pair of electrons on N into benzene ring.
- This **increases** the **availability** of lone pair of electrons **to accept a proton via dative bond**.
2: The electron donating alkyl group increases the availability of the lone pair of electrons on N atom to accept a proton via a dative bond. Hence, CH$_3$CH$_2$CH$_2$NH$_2$ is the strongest base.

- Proximity of withdrawing –OH substituent to NH$_2$ group:
  \[
  \text{CH}_3\text{OH} \quad \text{HCH}_2\text{NH}_2 \quad > \quad \text{CH}_2\text{CH}_2\text{NH}_2 \quad \text{OH} \quad > \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \quad \text{OH}
  \]
  Electron withdrawing effect:
  Availability of the lone pair of electrons on N atom to accept a proton via a dative bond:
  \[
  \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \quad \text{OH} \quad > \quad \text{CH}_3\text{OH} \quad \text{HCH}_2\text{NH}_2 \quad \text{OH}
  \]
  Strength of base:

3: The order of the acidity is already incorrect to begin.

39 Use of the Data Booklet is relevant to this question.

A student set up an electrolytic cell for the purpose of purifying copper metal. However, the set-up did not lead to successful purification of copper.

Which of the following could explain the failure of the set-up?

1. The electrolyte used was aqueous chromium(III) chloride.
2. The impure copper was used as the cathode and the anode was made of pure copper metal.
3. The $E^{\circ}_{\text{cell}}$ for the reaction is a negative value.

Answer: B (1 and 2 only)

1: Chromium metal would be deposited on the cathode before copper metal, hence leading to the failure of the purification of copper.

2: Impure copper should be the anode and the cathode should be pure copper metal. When the polarities are switched, the pure copper anode would be oxidised and copper metal would be deposited on the impure copper cathode, leading to the failure of the purification of copper.

3: Even if $E^{\circ}_{\text{cell}}$ is a negative value, the reaction can still occur because electricity is the source of energy for a chemical reaction to take place in an electrolytic cell.
Vanadium has the electronic structure $1s^22s^22p^63s^23p^63d^34s^2$. Which of the following vanadium compounds is/are likely to exist?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$V_2O_5$</td>
</tr>
<tr>
<td>2</td>
<td>VOC/</td>
</tr>
<tr>
<td>3</td>
<td>$K_2V_2O_7$</td>
</tr>
</tbody>
</table>

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

Oxidation of Vanadium in $V_2O_7^{2-}$ is expected to be 6 which is not possible.
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 in the space provided.
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.

<table>
<thead>
<tr>
<th>For Examiner's Use</th>
<th>For Examiner's Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1(P)</td>
</tr>
<tr>
<td></td>
<td>/40</td>
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<tr>
<td>P2</td>
<td>2</td>
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<td></td>
<td>/72</td>
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<tr>
<td>P3</td>
<td>3</td>
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<td>4</td>
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<tr>
<td>%</td>
<td>/192</td>
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<td>TOTAL</td>
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</tr>
<tr>
<td>P2</td>
<td>/72</td>
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<td>%</td>
<td></td>
</tr>
<tr>
<td>GRADE</td>
<td></td>
</tr>
</tbody>
</table>
1 (a) **Planning**

In the presence of hydrogen ions, bromate(V) ions, BrO$_3^-$, oxidise bromide ions to bromine.

\[
\text{BrO}_3^- (aq) + 5\text{Br}^- (aq) + 6\text{H}^+ (aq) \rightarrow 3\text{Br}_2 (aq) + 3\text{H}_2\text{O} (l)
\]

The reaction is relatively slow and can be followed by adding aqueous phenol and the indicator methyl orange to the reaction mixture. As bromine is formed, it reacts rapidly with the phenol present until the latter is used up. The free bromine in solution now bleaches the methyl orange indicator.

The initial rate of the reaction can be investigated by measuring the time taken for the methyl orange indicator to be bleached.

You are to plan a series of experiments to determine the order of reaction with respect to the bromide ion.

In addition to the standard apparatus present in a laboratory, you are provided with the following:

**FA 1** 0.01 mol dm$^{-3}$ aqueous KBr.
**FA 2** 1.0 mol dm$^{-3}$ potassium bromate(V), KBrO$_3$.
**FA 3** 1.0 mol dm$^{-3}$ sulfuric acid, H$_2$SO$_4$.
Aqueous phenol containing methyl orange indicator
Distilled water

(i) Complete the table below and outline, by means of a series of numbered steps,

- the apparatus to be used
- the experimental procedure
- the measurements to be taken to collect the required data.

<table>
<thead>
<tr>
<th>Expt .</th>
<th>Volume of phenol/methyl orange indicator solution / cm$^3$</th>
<th>Volume of FA1 / cm$^3$</th>
<th>Volume of FA2 / cm$^3$</th>
<th>Volume of FA3 / cm$^3$</th>
<th>Volume of distilled water / cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.0</td>
<td>50.0</td>
<td>50.0</td>
<td>20.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>20.0</td>
<td>40.0</td>
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<tr>
<td>3</td>
<td>20.0</td>
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<td>4</td>
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<td>20.0</td>
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<tr>
<td>5</td>
<td>20.0</td>
<td></td>
<td></td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>
Outline of experiment:

(ii) In order to find the order of reaction with respect to bromide, a graph of \( \log_{10}(\frac{1}{t}) \) against \( \log_{10}(\text{volume of KBr (aq))} \) can be plotted. Use the general rate equation to derive a relationship between \( \log_{10}(\frac{1}{t}) \) and \( \log_{10}(\text{volume of KBr (aq))} \). Hence, explain how the order of reaction with respect to bromide can be found from the plotted graph.

(iii) The concentration of phenol used in the experiment is very low. Suggest why this is so.
An experiment was carried out to measure the enthalpy change for the reaction of zinc with aqueous copper(II) sulfate.

The equation for the reaction is:

\[ \text{Zn (s) + CuSO}_4 \text{ (aq)} \rightleftharpoons \text{ZnSO}_4 \text{ (aq) + Cu (s)} \]

- A measuring cylinder was used to transfer separate 50 cm\(^3\) samples of 1.25 mol dm\(^{-3}\) copper(II) sulfate solution into polystyrene cups.
- Different weighed amounts of zinc powder were added to each sample of copper(II) sulfate.
- Each mixture was stirred thoroughly and the temperature rise noted.

The results of the experiment is summarised on the graph below.

(i) Explain the shape of the graph.

(ii) Using the data from the graph, calculate the \(\Delta H_{\text{reaction}}\).

(iii) Suggest a simple practical change to the method that will make the experiment more accurate.
2 (a) Pyruvic acid is an important component in living cells as it is involved in the aerobic process of supplying energy. The flow chart shows a series of reactions starting with compound A, which has an empirical formula of CH₂.

(i) Draw the structures of compounds A, B and C in the boxes above.

(ii) State the reagents and conditions for steps I and II.

Step I: ..............................................................

Step II: ..............................................................
(b) Element D can form two different chlorides. The two chlorides of element D is commonly used in Organic Chemistry qualitative analysis to test for a specific functional group. When dissolved in a solution containing methyl orange, chlorides of element D turn the solution red.

10 cm³ of liquid organic compound E, CₙH₂ₙ₊₂O, is vaporised and burnt in excess oxygen. After the reaction is cooled to 25°C, a contraction of 20 cm³ in the gas volume was observed. When the resultant gases from the combustion were passed through aqueous sodium hydroxide, the gas volume decreased a further 20 cm³. The vapour of E is also observed to react with the same reagents and conditions of step II mentioned in (a).

(i) State the identities of element D and organic compound E.

D: ........................................

E: ........................................

(ii) Hence write an equation, if any, between one of the chlorides of element D and organic compound E.

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

[3]

Total 8 marks
3 (a) (i) Both strontium and manganese are silvery metals. Complete the electronic configurations of manganese and strontium below.

Mn: [Ar] ....................
Sr: [Kr] .....................

(ii) Manganese and strontium both contribute two electrons into the sea of delocalised electrons.

Explain if strontium or manganese has a higher melting point.

(iii) Manganese is particularly important in the manufacturing of stainless steel. A reaction scheme involving manganese-containing compounds is shown below. F undergoes a reaction to form G and H.

Using the information provided, state the oxidation number of manganese in F and K. (Manganese and its compounds have different oxidation states).

(iv) Suggest a chemical formula for the purple solution J.
(v) Suggest the type of reaction that takes place when F forms G and H. Write a balanced chemical equation, including state symbols, for this reaction.

(b) Strontium compounds such as SrF₂ and SrSO₄ are sparingly soluble in water. Their solubility products at 298 K are given in the table below:

<table>
<thead>
<tr>
<th>Strontium compound</th>
<th>Numerical value of K_{sp}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF₂</td>
<td>2.5 x 10⁻⁹</td>
</tr>
<tr>
<td>SrSO₄</td>
<td>3.2 x 10⁻⁷</td>
</tr>
</tbody>
</table>

(i) Suggest, using quantitative calculations, which of the two compounds is less soluble in water at 298 K.

(ii) A sample of strontium(II) fluoride is dissolved in a solution of sodium fluoride. Predict qualitatively the effect, if any, on the solubility and solubility product of strontium(II) fluoride.
(c) Propose chemical test(s) to differentiate between the following organic compounds. You are to state clearly in your answer the reagents and conditions used and observations made. Write chemical equation(s) for any reactions that occur.

\[
\begin{array}{c}
\text{H}_2\text{N} & \text{O} & \text{O} \\
\text{O} & \text{O} & \text{N} \\
\text{H} & \text{O}
\end{array}
\]

and

[4]

Total 18 marks
4(a) Amino acids serve as the building blocks of proteins. They can be linked together in varying sequences to form a vast variety of proteins. An example of a segment of a protein is shown below.

![Amino acid structure](image)

(i) In the space provided below, draw the structural formulae of the amino acids formed from the hydrolysis of the above protein with aqueous sodium hydroxide.

(ii) Amino acids can be separated using electrophoresis. With reference to the isoelectric point of the amino acids provided, indicate the positions of the amino acids on the gel at a pH of 5.96.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Structure</th>
<th>Isoelectric point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspartic acid</td>
<td><img src="image" alt="Aspartic acid structure" /></td>
<td>2.77</td>
</tr>
<tr>
<td>Proline</td>
<td><img src="image" alt="Proline structure" /></td>
<td>6.30</td>
</tr>
<tr>
<td>Valine</td>
<td><img src="image" alt="Valine structure" /></td>
<td>5.96</td>
</tr>
</tbody>
</table>
(iii) A common secondary structure of proteins is the alpha helix. With the aid of a diagram and your knowledge in chemical bonding, describe the alpha helix structure.

(b) (i) Methamphetamine, $C_{10}H_{15}N$, is a psychostimulant. It has high potential for abuse and addiction. In high doses, it can induce euphoria and anxiety. Under the Misuse of Drugs Act in Singapore, a person who carries 500 grams of methamphetamine will be sentenced to the Mandatory Death Penalty. Its structure is as shown:

![Methamphetamine structure]

A 25.0 cm$^3$ sample of 0.500 mol dm$^{-3}$ methamphetamine was titrated with aqueous hydrochloric acid of the same concentration.

Would you expect the pH at equivalence point to be above or below 7? Explain your answer.

(ii) State the formula of the organic product formed when methamphetamine was reacted with sulfuric acid instead of hydrochloric acid.
Elements \( L \) to \( S \) are consecutive Period 3 elements with proton number less than 20. The following graph shows the third ionisation energies of these elements. [\( L \) to \( S \) are not specific elements from the Periodic Table].

(a) Identify the group that element \( P \) belongs to.

(b) Sketch a graph to show the successive ionisation energies of element \( P \) when the first eight electrons are removed from it.
(c) Explain the drop in the third ionisation energy from N to P.

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[2]

(d) Write down the equations for the reactions of the oxide of M with aqueous hydrochloric acid and aqueous sodium hydroxides separately.

............................................................................................................................................................................................
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[2]

(e) Describe the reactions, if any, of the chlorides of M and P with water, suggesting the pH of the resulting solutions and writing equations where appropriate.

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[6]

Total 12 marks
6 (a) Nitrogen monoxide in the air can be converted to nitric acid, which results in acid rain. Both nitrogen monoxide and nitrogen dioxide participate in ozone layer depletion. One way of forming nitrogen monoxide is through the dissociation of nitrogen dioxide.

\[ \text{2NO}_2 (g) \rightleftharpoons \text{2NO (g)} \, \text{+ O}_2 (g) \]

At 494 °C, the value of \( K_p \) for the above reaction is 36.9 kPa.

When a certain partial pressure of nitrogen dioxide is put into an empty vessel at 494 °C, equilibrium is reached when 45% of the original nitrogen dioxide has decomposed.

(i) Write an expression for the equilibrium constant, \( K_p \), for the reaction.

(ii) Calculate the original partial pressure of nitrogen dioxide before any dissociation occurred.
(b) Draw the structural formula of the organic products formed when compound T reacts with the following reagents.

(i) Alkaline aqueous KMnO₄, heat

(ii) Br₂ in CCl₄, absence of UV light
(c) Compound U has the molecular formula C₉H₁₂O.

It reacts with chlorine gas in the presence of light to form compound V, C₉H₁₁OCI, which is optically active.

On addition of bromine water at room temperature, U forms a white precipitate W, C₉H₁₀OBr₂.

When treated with acidified potassium manganate(VII) under reflux, U forms compound X, C₈H₆O₅. 1 mol of X reacts with 2 mol of thionyl chloride.

Draw the structures for compounds U to X.
Planning

In the presence of hydrogen ions, H⁺, bromate(V) ions, BrO₃⁻, oxidise bromide ions, Br⁻, to bromine, Br₂.

\[ \text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(aq) + 3\text{H}_2\text{O}(l) \]

The reaction is relatively slow and can be followed by adding aqueous phenol and the indicator methyl orange to the reaction mixture. As bromine is formed, it reacts rapidly with the phenol present until the latter is used up. The free bromine now in solution bleaches the methyl orange indicator.

The initial rate of the reaction can be investigated by measuring the time taken to bleach the methyl orange indicator.

You are to plan a series of experiments, to determine the order of reaction with respect to the bromide ion.

In addition to the standard apparatus present in a laboratory, you are provided with the following:

- **FA 1**: 0.01 mol dm⁻³ aqueous KBr.
- **FA 2**: 1.0 mol dm⁻³ potassium bromate(V), KBrO₃.
- **FA 3**: 1.0 mol dm⁻³ sulfuric acid, H₂SO₄.
- Aqueous phenol containing methyl orange indicator
- Distilled water

(i) Complete the table below and outline, by means of a series of numbered steps,

- the apparatus to be used
- the experimental procedure
- the measurements to be taken, to collect the required data.
<table>
<thead>
<tr>
<th>Expt</th>
<th>Volume of phenol/methyl orange indicator solution / cm³</th>
<th>Volume of FA1 / cm³</th>
<th>Volume of FA2 / cm³</th>
<th>Volume of FA3 / cm³</th>
<th>Volume of distilled water / cm³</th>
</tr>
</thead>
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<tr>
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<td>3</td>
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<td>50.0</td>
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<td>20.0</td>
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<tr>
<td>4</td>
<td>20.0</td>
<td>20.0</td>
<td>50.0</td>
<td>20.0</td>
<td>30.0</td>
</tr>
<tr>
<td>5</td>
<td>20.0</td>
<td>10.0</td>
<td>50.0</td>
<td>20.0</td>
<td>40.0</td>
</tr>
</tbody>
</table>

1. Using a measuring cylinder, add 20.0 cm³ of the phenol/indicator solution into a clean, dry conical flask.

2. Using different measuring cylinders, place 50.0 cm³ of FA 1 and 20.0 cm³ of FA 3 into the conical flask.

3. Place the conical flask on a white tile.

4. From another measuring cylinder, measure 50.0 cm³ of FA 2.

5. Add FA 2 into the conical flask, simultaneously starting the stopwatch.

   Swirl the conical flask carefully.

6. Stop the stopwatch when the colour of the indicator just disappears to leave a colourless solution. Record the time taken.

7. Repeat procedure 1 to 6 for experiments 2 to 5.
(ii) In order to find the order of reaction with respect to bromide, a graph of \( \log_{10} \left( \frac{1}{t} \right) \) against \( \log_{10}(\text{volume of KBr(aq)}) \) can be plotted.

Use the rate equation to derive a relationship between \( \log_{10} \left( \frac{1}{t} \right) \) and \( \log_{10}(\text{volume of KBr(aq)}) \).

Hence, explain how the order of reaction with respect to bromide can be found from the plotted graph.

In these experiments, the total volume has been kept constant and only the concentration of FA 1 in the reaction mixture has been changed. The rate equation, where \( n \) is the rate order with respect to FA 1, can be simplified to

\[
\text{rate} = k' [\text{Br}^-]^n \quad (\text{where } k' = k[\text{BrO}_3^-]^m[H^+]^n)
\]

- taking logarithms of the factors in this equation gives

\[
\lg(\text{rate}) = n \times \lg ([\text{Br}^-]) + \lg (k)
\]

Hence, by finding the gradient of the plotted graph, order of reaction wrt Br\(^-\) can be found.

(iii) The concentration of the phenol used in the experiment is very low. Suggest why this is so.

If too much phenol was present, it is possible that the reaction could have taken longer OR if a large amount of phenol was added the mixture may not have decolourised at all as all the bromine formed would have reacted with the phenol present.
An experiment was carried out to measure the enthalpy change for the reaction of zinc with aqueous copper (II) sulfate. The equation for the reaction is:

\[
\text{Zn (s) + CuSO}_4 \text{ (aq) } \xrightarrow{\text{)} } \text{ZnSO}_4 \text{ (aq) + Cu (s)}
\]

- A measuring cylinder was used to transfer separate 50 cm\(^3\) samples of 1.25 mol dm\(^{-3}\) copper (II) sulfate solution into polystyrene cups.
- Different weighed amounts of zinc powder were added to each sample of copper (II) sulfate.
- Each mixture was stirred thoroughly and the temperature rise noted.

The results of the experiments are summarised on the graph below.

(i) Explain why the graph shows an initial rise in temperature and then levels off.

Initially \textbf{CuSO}_4 \textit{in excess so amount of reaction depends on amount of Zn}

Or \textbf{more CuSO}_4 \textit{reacts (as more Zn added)}

Graph levels off because \textbf{all CuSO}_4 \textit{used up}

(reject just ‘\textit{Reaction is complete}’)

(ii) Using the data from the graph, calculate the \(\Delta H\)\(_{\text{reaction}}\).

\[
Q = 50 \times 63.5 \times 4.18 = 13271.5 \text{ J}
\]

Amount of \textbf{CuSO}_4 = \(50 \times \frac{1.25}{1000} = 0.0625 \text{ mol}\)

\[
\Delta H = - \frac{13271.5}{0.0625} = -212 \times 10^3 \text{ J mol}^{-1}
\]

(iii) Suggest a simple practical change to the method that will make the experiment more accurate.

\textbf{Use a lid on the cup (to reduce heat loss), extra insulation for cup, weigh CuSO}_4 \textit{solution, use burette/pipette to measure volumes}

(Reject \textit{Repeat experiments} OR use more accurate balance OR \textit{Smaller mass intervals})

\textbf{Total 12 marks}
Pyruvic acid is an important component in living cells as it is involved in the aerobic process of supplying energy. The flow chart shows a series of reactions starting with compound A, which has an empirical formula of CH₂.

Draw the structures of compounds A, B and C in the boxes above.

<table>
<thead>
<tr>
<th>Step I</th>
<th>Step II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ( \xrightarrow{\text{H}_2\text{O}/\text{H}^+} ) B ( \xrightarrow{\text{Cr}_2\text{O}_7^{2-}/\text{H}^+} ) distillation Ethanal ( \xrightarrow{\text{HCN, NaCN, cold}} ) B ( \xrightarrow{\text{H}^+, \text{heat}} ) C ( \xrightarrow{\text{HCN, NaCN, cold}} ) Ethanedioic acid</td>
<td></td>
</tr>
</tbody>
</table>

(i) State the reagents and conditions for Steps I and II.

(ii) [5]

Step I: *methanolic NaBH₄* or *H₂ nickel catalyst, heat or H₂ platinum, rtp*

Step II: *I₂ (aq), NaOH (aq), warm, followed by H⁺(aq)*
Element D can form two different chlorides. The two chlorides of element D is commonly used in Organic Chemistry qualitative analysis to test for a specific functional group. When dissolved in a solution containing methyl orange, chlorides of element D turn the solution red.

10 cm³ of liquid organic compound E, CₙH₂ₙ₊₂O, is vaporised and burnt in excess oxygen. After the reaction is cooled to 25 °C, a contraction of 20 cm³ in the gas volume was observed. When the resultant gases from the combustion was passed through aqueous sodium hydroxide, the gas volume decreased a further 20 cm³. The vapour of E is also observed to react with the same reagents and conditions of step II mentioned in (a).

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(b)</td>
<td>Element D can form two different chlorides. The two chlorides of element D is commonly used in Organic Chemistry qualitative analysis to test for a specific functional group. When dissolved in a solution containing methyl orange, chlorides of element D turn the solution red.</td>
</tr>
<tr>
<td></td>
<td>10 cm³ of liquid organic compound E, CₙH₂ₙ₊₂O, is vaporised and burnt in excess oxygen. After the reaction is cooled to 25 °C, a contraction of 20 cm³ in the gas volume was observed. When the resultant gases from the combustion was passed through aqueous sodium hydroxide, the gas volume decreased a further 20 cm³. The vapour of E is also observed to react with the same reagents and conditions of step II mentioned in (a).</td>
</tr>
</tbody>
</table>

(i) State the identities of element D and organic compound E.

- D is phosphorus.
- E is ethanol.

(Since 10 cm³ of vapour E combusted to give 20 cm³ of CO₂, by Avogadro’s and volume ratio, n =2 E C₂H₅O)

(ii) Hence, write an equation, if any, between one of the chlorides of element D and organic compound E.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₃CH₂OH + PCl₅ → CH₃CH₂C/ + POCl₃ + HC</td>
</tr>
<tr>
<td></td>
<td>or 3CH₃CH₂OH + PCl₃ → 3CH₃CH₂C/ + H₃PO₃</td>
</tr>
</tbody>
</table>

Total 8 marks
Both strontium and manganese are silvery metals. Write the electronic configurations of manganese and strontium.

Mn: \([Ar]3d^54s^2\)
Sr: \([Kr]5s^2\)

Manganese and strontium both contribute two electrons into the sea of delocalised electrons.

Suggest if strontium or manganese has a higher melting point.

**Cationic radius of manganese is smaller as compared to strontium ions.**

Electrostatic forces of attraction b/w the cations and sea of delocalised electrons (metallic bonding) is stronger in Mn than in Sr. Thus more energy is required to overcome these forces of attraction. **Mn has a higher melting point than Sr.**

(For your information m.p. of strontium is 777°C and manganese is 1246°C)

Manganese is particularly important in the manufacturing of stainless steel. Below shows a reaction schematic of manganese containing compounds. F undergoes a reaction to form G and H.

Using the information provided, state the oxidation number of manganese in F and K. (All Mn and its compounds have different oxidation state).

**F: +3**  
**K: +6**

Suggest the formula of purple solution J.

\[ \text{NaMnO}_4 \]
(v) Suggest the type of reaction when $F$ forms $G$ and $H$. Write a balanced chemical equation, including state symbols, for this reaction.

**Disproportionation reaction**

Reduction: $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$

Oxidation: $2\text{H}_2\text{O} + \text{Mn}^{3+} \rightarrow \text{MnO}_2 + 4\text{H}^+ + e^-$

Overall: $\text{Mn}^{3+} (\text{aq}) + 2\text{H}_2\text{O} (\ell) \rightarrow \text{Mn}^{2+} (\text{aq}) + \text{MnO}_2 (\text{s}) + 4\text{H}^+ (\text{aq})$

(b) Strontium compounds such as SrF$_2$ and SrSO$_4$ are sparingly soluble in water. Their solubility products at 298 K are given in the table below:

<table>
<thead>
<tr>
<th>Strontium compound</th>
<th>Numerical value of $K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrF$_2$</td>
<td>$2.5 \times 10^{-9}$</td>
</tr>
<tr>
<td>SrSO$_4$</td>
<td>$3.2 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

(i) Suggest, using quantitative calculations, which of the two compounds is less soluble in water at 298 K.

SrF$_2$ (s) $\rightarrow$ Sr$^{2+}$ (aq) + 2F$^-$ (aq)

$K_{sp}(\text{SrF}_2) = [\text{Sr}^{2+}][\text{F}^-]^2$

$2.5 \times 10^{-9} = (s)(2s)^2$

$s = 8.55 \times 10^{-4} \text{ mol dm}^{-3}$

SrSO$_4$ (s) $\rightarrow$ Sr$^{2+}$ (aq) + SO$_4^{2-}$ (aq)

$K_{sp}(\text{SrSO}_4) = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$

$3.2 \times 10^{-7} = (s)^2$

$s = 5.66 \times 10^{-4} \text{ mol dm}^{-3}$

Based on the calculated solubilities, **SrSO$_4$ is less soluble** than SrF$_2$.
A sample of strontium(II) fluoride is dissolved in a solution of sodium fluoride. Predict qualitatively the effect (if any) on the solubility and solubility product of strontium(II) fluoride.

\[
\text{SrF}_2 (s) \rightarrow \text{Sr}^{2+} (aq) + 2\text{F}^- (aq)
\]
\[
\text{NaF} (s) \rightarrow \text{Na}^+ (aq) + \text{F}^- (aq)
\]

There will be **common ion effect** due to the increase in \([\text{F}^-]\). By Le Chatelier’s Principle, position of equilibrium will shift to the **left** to decrease \([\text{F}^-]\). The solubility of \text{SrF}_2 is **reduced**.

The solubility product of \text{SrF}_2 is **not affected** as it is only dependent on temperature.

Propose chemical test(s) to differentiate the following organic compounds. You are to state clearly in your answer the reagents and conditions used and observations made. Write chemical equation(s) for any reactions that have occurred.

**Test:** Add NaOH (aq), heat

**Observation:**

\[
\begin{align*}
\text{H}_2\text{N} & : \text{effervescence} \\
\text{H} & : \text{No effervescence}
\end{align*}
\]

**Equation:**

\[
\begin{align*}
\text{H}_2\text{N} \quad + \quad 2\text{NaOH} \quad &\rightarrow \quad \text{Na}^+\text{O}^-\text{O}\text{Na}^+ \quad + \quad \text{NH}_3 \\
\text{H} \quad + \quad 2\text{NaOH} \quad &\rightarrow \quad \text{Na}^+\text{O}^-\text{O}\text{Na}^+ \quad + \quad \text{NH}_3
\end{align*}
\]

(Test for \(\text{NH}_3\): Moist red litmus paper turns blue)

Total 18 marks
Amino acids serve as the building blocks of proteins. They can be linked together in varying sequences to form a vast variety of proteins. An example of a segment of a protein is shown below.

\[
\begin{align*}
\text{C} & : \text{C} - \text{N} - \\
\text{CH}_2 & : \text{O} - \text{H} - \text{O} - \\
\text{OH} & : \text{N} - \text{H} - \text{C} - \text{O} - \text{H} - \text{(CH}_2)_2 \text{COOH} \\
\end{align*}
\]

(i) In the space provided below, draw the structural formulae of the amino acids formed from the hydrolysis of the above protein with aqueous sodium hydroxide.

\[
\begin{align*}
\text{O} & : \text{H} - \text{H} - \text{N} - \\
\text{CH}_2 & : \text{O} - \text{C} - \text{N} - \\
\text{OH} & : \text{C} - \text{O} - \text{H} - \text{(CH}_2)_2 \text{COO}^- \\
\end{align*}
\]

(ii) Amino acids from can be separated using electrophoresis. With reference to the isoelectric point of the amino acids provided, indicate the positions of the amino acid on the gel at a pH of 5.96.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Structure</th>
<th>Isoelectric point</th>
</tr>
</thead>
</table>
| Aspartic acid | \[
\begin{align*}
\text{HO} & : \text{C} - \text{C} - \text{H} - \text{NH}_2 \\
\text{H} & : \text{C} - \text{COOH} \\
\end{align*}
\] | 2.77 |
| Proline     | \[
\begin{align*}
\text{HO} & : \text{O} - \text{C} - \text{N} - \text{H} \\
\text{H} & : \text{C} - \text{O} - \text{H} - \text{(CH}_2)_2 \text{COO}^- \\
\end{align*}
\] | 6.30 |
| Valine      | \[
\begin{align*}
\text{H}_2\text{N} & : \text{C} - \text{O} - \text{H} - \text{C} - \text{H} - \text{C} - \text{H} - \text{CH}_3 \\
\end{align*}
\] | 5.96 |

Analysis: Species at 5.96 for respective amino acids:

- For aspartic acid: \[
\begin{align*}
\text{HO} & : \text{C} - \text{C} - \text{H} - \text{NH}_2 \\
\text{H} & : \text{C} - \text{COOH} \\
\end{align*}
\] \( \overrightarrow{\text{E}} \) shift towards anode

- For proline: \[
\begin{align*}
\text{HO} & : \text{O} - \text{C} - \text{N} - \text{H} \\
\text{H} & : \text{C} - \text{O} - \text{H} - \text{(CH}_2)_2 \text{COO}^- \\
\end{align*}
\] \( \overrightarrow{\text{E}} \) shift towards cathode

- For valine: \[
\begin{align*}
\text{H}_2\text{N} & : \text{C} - \text{O} - \text{H} - \text{C} - \text{H} - \text{C} - \text{H} - \text{CH}_3 \\
\end{align*}
\] \( \overrightarrow{\text{E}} \) remains in the middle
A common secondary structure of proteins is the alpha helix. With the aid of a diagram and your knowledge in chemical bonding, describe the alpha helix structure.

On diagram:
1) 2 lone pair of electrons on O atom
2) dipoles (δ+ and δ-) and
3) hydrogen bond (IIIIIII) must be shown

Hydrogen bonds formed between O atom of (-C=Oδ-) group for C₁ and the H atom of (-N-Hδ+) group of the fourth peptide bond for C₄ down the same protein chain which stabilises the structure.
**Methamphetamine**, \( \text{C}_10\text{H}_{15}\text{N} \), is a psychostimulant. It has high potential for abuse and addiction. In high doses, it can induce euphoria and anxiety. Under the Misuse of Drugs Act in Singapore, a person who carries 500 grams of methamphetamine will be sentenced to the Mandatory Death Penalty. Its structure is as shown:

![Methamphetamine structure](image)

A 25.0 cm\(^3\) sample of 0.500 mol dm\(^{-3}\) methamphetamine was titrated with aqueous hydrochloric acid of the same concentration.

Would you expect the equivalence point to be above 7 or below 7? Explain your answer.

Due to salt hydrolysis, pH of equivalence point should be below 7.

(ii) State the formula of the organic product formed when methamphetamine was reacted with sulfuric acid instead of hydrochloric acid.

![Organic product formula](image)

[3]

Total 10 marks
Elements L to S are consecutive Period 3 elements with proton number less than 20. The following graph shows the third ionisation energies of these elements. [L to S are not specific elements from the Periodic Table].

(a) Identify the group that element P belongs to.  
[1]

Group V

(b) Sketch a graph to show the successive ionisation energies of element P when the first eight electrons are removed from it.  
[1]
(c) Explain the drop in the third ionisation energy from element N to P.

\[ \text{N}^{2+}: 1s^22s^22p^63s^2 \]
\[ \text{P}^{2+}: 1s^22s^22p^63s^23p^1 \]

The 3p electron to be removed from P\(^{2+}\) is **further away** from the nucleus than the 3s electron to be removed from N\(^{2+}\).

The 3p electron experiences **weaker electrostatic forces of attraction** than the 3s electron and requires less energy to remove. Thus there is a drop in third ionisation energy from element N to P.

(d) Write down the equations for the reaction of the oxide of M with aqueous hydrochloric acid and aqueous sodium hydroxide.

\[ \text{M}_2\text{O}_3(s) + 6 \text{HCl (aq)} \rightarrow 2 \text{MCl}_3(aq) + 3 \text{H}_2\text{O (l)} \]
\[ \text{M}_2\text{O}_3(s) + 2 \text{NaOH(aq)} + 3 \text{H}_2\text{O(l)} \rightarrow 2 \text{Na}[\text{M(OH)}_4] \text{(aq)} \]

(e) Describe the reactions, if any, of the chlorides of element M and P with water, suggesting the pH of the resulting solutions and writing equations, where appropriate.

\[ \text{M} \text{Cl}_3 \text{(s)} + 6 \text{H}_2\text{O (l)} \rightarrow \text{[M(H}_2\text{O)}_6]^{3+} \text{(aq)} + 3 \text{Cl}^- \text{(aq)} \]
\[ \text{[M(H}_2\text{O)}_6]^{3+}(aq) \rightarrow \text{[M(H}_2\text{O)}_5(OH)]^{2+} \text{(aq)} + \text{H}^+ \text{(aq)} \]

pH of solution = 3

\[ \text{PCl}_3 \text{(l)} + 3 \text{H}_2\text{O (l)} \rightarrow \text{H}_3\text{PO}_3 \text{(aq)} + 3 \text{HCl (aq)} \]
Or \[ \text{PCl}_3 \text{(l)} + 4 \text{H}_2\text{O (l)} \rightarrow \text{H}_3\text{PO}_4 \text{(aq)} + 5 \text{HCl (aq)} \]

pH of solution = 2

[L to S are not specific elements from the Periodic Table]

**Total 12 marks**
Nitrogen monoxide in the air can be converted to nitric acid, which results in acid rain. Both nitrogen monoxide and nitrogen dioxide participate in ozone layer depletion. One way of forming nitrogen monoxide is through the dissociation of nitrogen dioxide.

\[
2\text{NO}_2 (g) \rightleftharpoons 2\text{NO} (g) + \text{O}_2 (g)
\]

At 494 °C, the value of \( K_p \) for the above reaction is 36.9 kPa.

When a certain partial pressure of nitrogen dioxide is put into an empty vessel at 494 °C, equilibrium is reached when 45% of the original nitrogen dioxide has decomposed.

(i) Write an expression for the equilibrium constant, \( K_p \), for the reaction.

\[
K_p = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2}
\]

(ii) What is the original partial pressure of nitrogen dioxide before any dissociation occurred?

Let the initial pressure of NO2 be \( x \) mol.

\[
\begin{align*}
2 \text{ NO}_2 (g) & \rightleftharpoons 2 \text{ NO} (g) + \text{ O}_2 (g) \\
\text{Initial pressure (kPa)} & \quad x \quad 0 \quad 0 \\
\text{Change in Pressure} & \quad -0.45x \quad +0.45x \quad +0.225x \\
\text{Equilibrium pressure (kPa)} & \quad 0.55x \quad 0.45x \quad 0.225x
\end{align*}
\]

\[
K_p = \frac{(0.225x)(0.45x)^2}{(0.55x)^2} = 36.9
\]

\[
x = 244 \text{ kPa}
\]

Hence, initial pressure of NO2 = 244 kPa
(b) Draw the structural formula of the organic products formed when compound T reacts with the following reagents.

<table>
<thead>
<tr>
<th></th>
<th>Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>Alkaline aqueous KMnO₄, heat</td>
</tr>
</tbody>
</table>
|    | ![Alkaline aqueous KMnO₄](image)
| (ii)| Br₂ in CCl₄, absence of UV light  |
|    | ![Br₂ in CCl₄](image) |
Compound U has the molecular formula C₉H₁₂O. It reacts with chlorine gas in the presence of light to form compound V, C₉H₁₁OCl, which is optically active.

On addition of bromine water at room temperature, U forms a white precipitate W, C₉H₁₀OBr₂.

When treated with acidified potassium manganate(VII) under reflux, U forms compound X, C₈H₆O₅. 1 mole of X reacts with 2 mole of thionyl chloride.

Draw the structures for compounds U to X.

Total 12 marks
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 any four questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in 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 13 printed pages and 1 blank page
Answer any **four** questions

1  (a) Aqueous sodium hydroxide is an important reagent in many organic reactions where the hydroxide ion can act as both a base and a nucleophile.

In the Reimer-Tiemann reaction, phenol is heated with chloroform in the presence of aqueous sodium hydroxide to give 2-hydroxybenzaldehyde, compound B. The reaction involves the formation of a reactive intermediate, CC\textsubscript{1}\textsubscript{2}, through an acid-base reaction.

\[
\text{CHCl}_3 + \text{OH}^- \rightarrow \text{CCl}_2 + \text{H}_2\text{O} + \text{Cl}^-
\]

chloroform

\[\text{I}\hspace{1cm} \text{II}\]

(i) State the type of reaction that occurred in reaction I.

(ii) Suggest a chemical test to differentiate compounds B and A under room conditions.

(iii) Compound B can undergo further reaction to form the product below.

![Diagram of the reaction](image)

Name and describe the mechanism involved, using curly arrows to show the movement of electrons and indicating all charges.

(iv) Comment on the relative acidity of phenol and compound B. [9]
(b) Besides its extensive use in organic chemistry, aqueous sodium hydroxide is also used in photographic development.

The black-and-white photography process involves four steps:

Step 1 Photo-taking: Interaction of light with silver halides (AgX) on film.

Step 2 Developing: Redox reactions to develop the actual image.

Step 3 Fixing: Changing the solubility of chemical compounds with different conditions to preserve the image on the film.

Step 4 Printing: Shining light through the film onto photosensitive paper, producing the final photograph using the same chemistry as step 1 to 3.

When light is shone on the film during the phototaking process, a very small number of X\(^-\) ions in AgX are oxidised.

(i) A small amount of silver is produced as a result of the oxidation reaction of \(X^-\). The silver produced catalyses the reduction of the surrounding AgX to black silver metal in the presence of a reducing agent, D, during the developing process.

\[2AgX + D + 2OH^- \rightarrow 2Ag + E + 2H_2O + 2X^-\]

State and explain why the rate of reaction changes as the developing process proceeds.

(ii) Under appropriate conditions, chloride can be oxidised to chlorine gas. With the aid of an equation, suggest how Cl\(_2\) will react with hydroxide ions under room conditions.

(iii) \(E\), formed from the oxidation of \(D\), has the molecular formula C\(_6\)H\(_4\)O\(_2\).

\(E\) forms an orange precipitate when warmed with 2,4-dinitrophenylhydrazine. One mole of \(E\) decolourises two mole of bromine dissolved in tetrachloromethane. Heating \(E\) with acidified potassium manganate(VII) produces only one product.

\(D\) has the molecular formula C\(_6\)H\(_6\)O\(_2\). It is insoluble in water but can dissolve in aqueous sodium hydroxide. Addition of sodium carbonate to \(D\) does not result in effervescence but addition of sodium metal to \(D\) gives mild effervescence.

Suggest the structures of \(D\) and \(E\), explaining your reasoning.
(You are not required to explain the oxidation process of \(E\) from \(D\))

Total 20 marks
2 Halogens are highly reactive and they are the only group in the Periodic Table which contains elements in all three familiar states of matter at 25 °C and 1 atm.

The halogens form hydrogen halides with hydrogen, all of which are strong acids with the exception of HF.

(a) Discuss the thermal stability trend of the hydrogen halides, HCl, HBr and HI and variation in volatility of the halogens from fluorine to iodine. [5]

(b) Concentrated sulfuric acid will react with solid sodium halides NaX. (X = Cl⁻, Br⁻ or I⁻).

Using relevant data from the Data Booklet, describe and explain why hydrogen chloride can be prepared by the reaction between sodium chloride and concentrated sulfuric acid while hydrogen iodide cannot be synthesised using a similar method with sodium iodide and concentrated sulfuric acid. You are to include relevant chemical equation(s) in your discussion. [5]

(c) Halogens form many compounds with metals. These compounds range from ionic compounds such as lithium chloride, monomeric covalent compounds such as uranium hexafluoride, and polymeric covalent compounds like palladium chloride.

The Corey-Posner, Whitesides-House reaction is an organic reaction that involves the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane, an organocopper compound and a lithium halide.

The formation of propane from a halogeno compound using the Corey-Posner, Whitesides-House reaction is as shown.

\[ (\text{CH}_3)\text{CuLi} + \text{CH}_3\text{CH}_2\text{X} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_3\text{Cu} + \text{LiX} \]

(\(X = \text{Cl}^-, \text{Br}^-\text{ or } \text{I}^-\))

(i) Draw the structural formulae of the three alkanes produced when \((\text{C}_3\text{H}_7)_2\text{CuLi}\) and \(\text{C}_3\text{H}_7\text{Br}\) undergo the Corey–Posner, Whitesides–House reaction.

(ii) Suggest with reasoning which of the alkanes in (c)(i) has the lowest boiling point. [6]
(d) Chlorine and fluorine react exothermically to form an interhalogen compound, C/\text{F}_3.

(i) With the help of a Lewis structure, state the shape of the C/\text{F}_3 molecule.

(ii) The interhalogen compounds are very strong oxidising agents.

When gaseous C/\text{F}_3 is added to water, a vigorous reaction occurs, giving three gases as the only products. The gaseous product mixture appears as white fumes which forms a weak acid. The gaseous mixture not only turns moist blue litmus paper red but also bleaches it. In addition, it relights a glowing splint.

State the three gases in the gaseous mixture. Hence, construct a balanced equation, including state symbols, for the reaction.

[4]

Total 20 marks
3 (a) Nitrous acid, \( \text{HNO}_2 \), is an unstable, weakly acidic compound. It can easily be prepared by acidifying a solution of a nitrite.

Barium nitrite, \( \text{Ba(NO}_2\text{)}_2 \) is often used since the insoluble barium sulfate can be easily filtered off.

\[
\text{Ba(NO}_2\text{)}_2 \text{ (aq)} + \text{H}_2\text{SO}_4 \text{ (aq)} \xrightarrow{\text{\dagger}} 2\text{HNO}_2 \text{ (aq)} + \text{BaSO}_4 \text{ (s)}
\]

Nitrite ions can be oxidised by potassium manganate(VII) to form nitrate ions:

\[
5\text{NO}_2^{-} \text{ (aq)} + 2\text{MnO}_4^{-} \text{ (aq)} + 6\text{H}^{+} \text{ (aq)} \rightarrow 5\text{NO}_3^{-} \text{ (aq)} + 2\text{Mn}^{2+} \text{ (aq)} + 3\text{H}_2\text{O} \text{ (l)}
\]

The following are some thermochemistry data.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H^\circ ) / kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>enthalpy change of atomisation of barium</td>
<td>+175</td>
</tr>
<tr>
<td>enthalpy change of Ba (s) ( \rightarrow ) Ba(^{2+}) (aq) +2e</td>
<td>+286</td>
</tr>
<tr>
<td>enthalpy change of hydration of NO(_3^{-})</td>
<td>-325</td>
</tr>
<tr>
<td>lattice energy of barium nitrate</td>
<td>-1395</td>
</tr>
</tbody>
</table>

(i) Using the data above, and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of hydration of the barium ion.

(ii) The \( \Delta S^\circ_{\text{hydration}} \) of barium ion is -188 J mol\(^{-1}\) K\(^{-1}\). Explain why the sign of \( \Delta S^\circ_{\text{hydration}} \) is negative.

(iii) Hence, calculate \( \Delta G^\circ_{\text{hydration}} \) of barium ion at 298K.

(iv) Predict the effect of high temperature on the spontaneity of the above reaction.

(v) Using your answer in (a)(i), and relevant data from the table, calculate the enthalpy change of solution of barium nitrate.

(b) (i) When barium nitrate is heated, it decomposes. Write an equation to represent the thermal decomposition of barium nitrate.

(ii) Group II iodates decomposed according to the following equation.

\[
2\text{Mg(}\text{IO}_3\text{)}_2 \text{ (s)} \xrightarrow{\text{\dagger}} 2\text{MgO} \text{ (s)} + 2\text{I}_2 \text{ (g)} + 5\text{O}_2 \text{ (g)}
\]

Describe and explain how the thermal stabilities of Group II iodates vary down the group.

[10]
(c) Nitrous acid is useful in converting amines into diazonium compounds:

*Reaction 1*

\[
\text{NH}_2 \quad \text{HNO}_2 \quad \text{H}_2\text{SO}_4 \quad \text{->} \quad \text{Nitrobenzene} \quad \text{diazonium salt} \quad \text{HSO}_4^- \quad 2\text{H}_2\text{O}
\]

In a process named the Sandmeyer reaction, the \( {\text{N}}\equiv{\text{N}} \) is replaced by \(-{\text{Cl}}\) or \(-{\text{Br}}\) using the corresponding cuprous halide, \( \text{CuX} \), together with concentrated \( \text{HCl} \).

*Reaction 2*

\[
\text{Nitrobenzene} \quad \text{diazonium salt} \quad \text{CuX} \quad \text{conc HCl} \quad \text{1,3-dichlorobenzene}
\]

Outline how you could convert nitrobenzene into 1,3-dichlorobenzene in a **four steps synthesis**, using both reactions 1 and 2 in your synthesis. In your answer, you are to clearly state the reagents and conditions used and the intermediates formed.

[5]
(d) The diazonium salt can undergo a coupling reaction with activated aromatic rings to obtain brightly coloured azo compounds which can be used as dyes.

The dye, Disperse Yellow, is formed as follows:

\[
\text{NHCOCH}_3\quad \text{OH} \quad \text{CH}_3
\]

\[
\text{NHCOCH}_3\quad \text{N} \quad \text{N} \quad \text{OH} \quad \text{CH}_3
\]

\[
\text{NH}_2 \quad \text{N} \quad \text{CH}_3
\]

\[
\text{NH}_2 \quad \text{N} \quad \text{CH}_3
\]

\[
\text{NHCOCH}_3
\]

Disperse Yellow

(i) Identify a reagent which might be used for step I.

(ii) Propose a chemical test to differentiate \( \text{NH}_2 \quad \text{N} \quad \text{CH}_3 \) and \( \text{CH}_3 \quad \text{HO} \quad \text{CH}_3 \).

In your answer, state clearly the reagents and conditions required and any observations made.

(iii) Another azo dye, \( \text{H} \), can be obtained from an amine and a phenol under suitable conditions.

\[
\text{H}_3\text{N} \quad \text{N} \quad \text{CH}_3 \quad \text{N} \quad \text{CH}_3 \quad \text{OH} \quad \text{CH}_3 \quad \text{CH}_3
\]

azo dye, \( \text{H} \)

Draw the structural formulae of the amine and of the phenol used to make \( \text{H} \).  

[5]

Total 20 marks
The pickling of steel is the process of removing rust, or iron(III) oxide, from steel by using excess concentrated hydrochloric acid to react with layers of the oxide and iron metal. The reaction produces a solution of iron(II) chloride.

A chemist used the set-up shown below to investigate if the resulting solution which consists of concentrated hydrochloric acid and iron(II) chloride, from the pickling of steel, can be used to produce iron metal via electrolysis.

(a) An organic fuel cell, the direct ethanol fuel cell, is used to drive the electrolysis. The reaction that takes place at one of the electrodes involves the reduction of oxygen gas as follows:

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]

(i) Construct the overall equation for the fuel cell reaction, given that carbon dioxide is produced at the anode.

(ii) Write the cell diagram for the direct ethanol fuel cell, stating the polarity of the respective electrodes.

(b) (i) Construct a balanced equation for the reaction that takes place during the pickling of steel, indicating the state symbols clearly.

(ii) Write half-equations for the reactions taking place at the cathode and anode of the electrolytic cell and state all observations made within the cell.

(iii) Suggest the observation made at the anode when nitric acid is used in the pickling of steel instead of hydrochloric acid.
(c) Upon addition of cyanide ions, the colour of the electrolyte changes from pale green to “Prussian blue”.

Explain why iron complexes are coloured. \[3\]

(d) Another chloride of iron, FeCl₃, has similar characteristics as aluminium chloride. Both form dimers at low temperatures, produce acidic solutions when dissolved in water and are used in the electrophilic substitution reactions of benzene rings.

(i) Using suitable data from the Data Booklet, explain the acidic nature of FeCl₃ in water.

(ii) State what role does iron(III) chloride play in the electrophilic substitution reaction of benzene ring with chlorine. \[4\]

(e) (i) Haemoglobin, which contains iron(II) ions is a protein found in the red blood cells that carries oxygen. Describe the protein components of haemoglobin.

(ii) In World War II, the use of cyanide pills were frequently recorded. Pilots of B-29 Superfortress bombers sent to drop atomic bombs on Japan were issued with the lethal pills. Fortunately, all aircraft returned safely and none of the pills were used. These pills contain a concentrated solution of potassium cyanide and the release of the fast-acting poison causes brain death within minutes.

Suggest why brain death occurs within minutes after the poison is administered. \[4\]

Total 20 marks
(a) The Kastle-Meyer test is often used to test for the presence of blood at a crime scene. It relies on the peroxidase-like activity of haemoglobin in blood to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base.

Phenolphthalein has the following structure:

![Structure of Phenolphthalein]

Phenolphthalein is a weak acid which dissociates in water according to the following equation:

\[
\text{colourless (acid)} \quad \text{HO} \quad \text{O} \quad \text{O} \quad \text{OH} \quad + \quad \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{pink (conjugate base)} \quad \text{HO} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad + \quad \text{H}_3\text{O}^+ 
\]

The pKₐ of phenolphthalein is 9.7.

(i) Draw the structure of the compound formed when phenolphthalein is heated with aqueous sodium hydroxide.

(ii) Using Le Chatelier's principle, explain why phenolphthalein appears colourless in an acidic solution.

(iii) Calculate the ratio of the concentration of the conjugate base to the concentration of the acid at pH 10. Using this ratio, predict and explain the colour of phenolphthalein at pH 10.

(b) Cinnamic acid, commonly found in cinnamon, has a molecular formula of C₉H₈O₂.

It is known that cinnamic acid can react with liquid bromine in the dark. It also undergoes oxidation to form benzoic acid and in the process, carbon dioxide gas was released.

An isomer of cinnamic acid also reacts with liquid bromine in the dark. Upon oxidation with potassium manganate(VII), 1 mole of this isomer reacts with 1 mole of sodium carbonate.

Suggest the displayed formulae of cinnamic acid and its isomer and state the type of isomerism exhibited by cinnamic acid.
(c) Phenolphthalein is usually used as an indicator in a strong base and weak acid titration.

Aqueous magnesium chloride can act as a weak monobasic acid. In an experiment, 50.0 cm$^3$ of aqueous magnesium chloride was titrated with 1.00 mol dm$^{-3}$ sodium hydroxide. The variation of pH of the solution is as shown in the diagram.
(i) Explain what is meant by the term weak acid.

(ii) Write an equation showing hydrated magnesium ion acting as an acid.

(iii) Using the graph above, calculate the initial concentration of magnesium ions.

(iv) Calculate the $K_a$ value for aqueous magnesium chloride.

(v) At the point where 10.0 cm$^3$ of sodium hydroxide has been added to the solution, a saturated solution of a sparingly soluble salt, magnesium hydroxide, Mg(OH)$_2$, is formed.

Calculate the solubility product, $K_{sp}$ of Mg(OH)$_2$. 

(d) Iodine reacts with propanone in acid solution as follows.

$$I_2 + CH_3COCH_3 + H^+ \rightarrow CH_3COCH_2I + HI$$

Kinetics studies have shown that the reaction is second order overall, and it has been suggested that the mechanism involves the following three steps.

$$CH_3COCH_3 + H^+ \rightleftharpoons CH_3C(OH)CH_3 \quad \text{(fast)}$$

$$CH_3C(OH)CH_3 \rightleftharpoons H_2C\equiv C(OH)CH_3 + H^+ \quad \text{(slow)}$$

$$H_2C\equiv C(OH)CH_3 + I_2 \rightarrow CH_3COCH_2I + HI \quad \text{(fast)}$$

(i) Explain the meaning of order of reaction.

(ii) Construct the rate equation for this reaction.

(iii) An experiment was carried out at 60 °C using reagents of the following concentrations.

<table>
<thead>
<tr>
<th>Initial concentration / mol dm$^{-3}$</th>
<th>$[I_2]$</th>
<th>$[CH_3COCH_3]$</th>
<th>$[H^+]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.050</td>
<td>0.050</td>
<td></td>
</tr>
</tbody>
</table>

The initial rate of reaction was found to be $1.25 \times 10^{-6}$ mol dm$^{-3}$ s$^{-1}$ under these conditions. Calculate the rate constant for this reaction, stating its units.

Total 20 marks

END
Aqueous sodium hydroxide is an important reagent in many organic reactions where the hydroxide ion can act as both a base and a nucleophile.

In the Reimer-Tiemann reaction, phenol is heated with chloroform in the presence of aqueous sodium hydroxide to give 2-hydroxybenzaldehyde, compound B. The reaction involves the formation of a reactive intermediate, CCl₂, through an acid-base reaction.

\[
\text{CHCl}_3 + \text{OH}^- \rightarrow \text{CCl}_2 + \text{H}_2\text{O} + \text{Cl}^- \\
\text{chloroform}
\]

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 (a)</strong></td>
<td>Aqueous sodium hydroxide is an important reagent in many organic reactions where the hydroxide ion can act as both a base and a nucleophile. In the Reimer-Tiemann reaction, phenol is heated with chloroform in the presence of aqueous sodium hydroxide to give 2-hydroxybenzaldehyde, compound B. The reaction involves the formation of a reactive intermediate, CCl₂, through an acid-base reaction.</td>
</tr>
</tbody>
</table>
|   | \[
\text{CHCl}_3 + \text{OH}^- \rightarrow \text{CCl}_2 + \text{H}_2\text{O} + \text{Cl}^- \\
\text{chloroform}
\]
|   |   |
|   | **(i)** State the type of reaction that occurred in reaction I. |
|   | Electrophilic substitution |
|   | **(ii)** Suggest a chemical test to differentiate compounds B and A under room conditions. |
|   | Add **2,4-DNPH** to B and A separately.  
B: **Orange precipitate** formed  
A: **No orange precipitate** formed  
Note: Tollens’ reagent and aqueous NaOH tests are not allowed, as both require heating, which is not “room conditions” |
(iii) Compound B can undergo further reaction to form the product below.

\[
\begin{array}{c}
\text{OH} \quad \text{CHO} \\
\text{B} \\
\text{OH} \quad \text{CHO} \quad \text{CN}
\end{array}
\]

Name and describe the mechanism involved, using curly arrows to show the movement of electrons and indicating all charges.

**Mechanism: Nucleophilic addition**

\[
\begin{array}{c}
\text{OH} \quad \text{C} \quad \text{H} \\
\text{OH} \quad \text{C} \quad \text{OH} \quad \text{CN} \\
\end{array}
\]

(iv) Comment on the relative acidity of phenol and compound B.

Presence of electron withdrawing –CHO attached on the benzene ring.

**Negative charge of the phenoxide ion of compound B will be further dispersed.** Phenoxide ion of compound B is more stabilised.

**Compound B is a stronger acid as compared to phenol.**

(b) Besides its extensive use in organic chemistry, aqueous sodium hydroxide is also used in photographic development.

The black-and-white (B/W) photography process involves four steps:

- **Step 1** Photo-taking: Interaction of light with silver halides (AgX) on film.
- **Step 2** Developing: Redox reactions to develop the actual image.
- **Step 3** Fixing: Changing the solubility of chemical compounds with different conditions to preserve the image on the film.
- **Step 4** Printing: Shining light through the film onto photosensitive paper, producing the final photograph using the same chemistry as step 1 to 3.

When light is shone on the film during the phototaking process, a very small number of X⁻ ions in AgX are oxidised.
A small amount of silver is produced as a result of the oxidation reaction of X⁻. The silver produced catalyses the reduction of the surrounding AgX to black silver metal in the presence of a reducing agent, D, during the developing process.

\[ 2\text{AgX} + \text{D} + 2\text{OH}^- \rightarrow 2\text{Ag} + \text{E} + 2\text{H}_2\text{O} + 2\text{X}^- \]

State and explain why the rate of reaction changes as the developing process proceeds.

The reaction is autocatalytic. (Ag produced catalyses the reaction.)

The rate of reaction decreases at first due to the formation of the Ag catalyst, then decreases as the reactants are used up.

Under appropriate conditions, chloride can be oxidised to chlorine gas. With an aid of an equation, suggest how Cl₂ will react with hydroxide ions under room conditions.

\[ 2\text{OH}^- (\text{aq}) + \text{Cl}_2 (\text{aq}) \rightarrow \text{Cl}^- (\text{aq}) + \text{ClO}^- (\text{aq}) + \text{H}_2\text{O (l)} \]

E, formed from the oxidation of D, has the molecular formula C₆H₄O₂.

E forms an orange precipitate when warmed with 2,4-dinitrophenylhydrazine. One mole of E decolourises two mole of bromine dissolved in tetrachloromethane. Heating E with acidified potassium manganate(VII) produces only one product.

D has the molecular formula C₆H₆O₂. It is insoluble in water but can dissolve in aqueous sodium hydroxide. Addition of sodium carbonate to D does not result in effervescence but addition of sodium metal to D gives mild effervescence.

Suggest the structures of D and E, explaining your reasoning. (You are not required to explain the oxidation process of E from D)

E undergoes condensation with 2,4-DNPH
⇒ E is a carbonyl compound

1 mol of E undergoes electrophilic addition with 2 mol of Br₂
⇒ E contains two alkene functional groups

E undergoes oxidation with hot acidified KMnO₄ (aq) to give two identical compounds ⇒ E is a symmetrical alkene

D is insoluble in water due to large hydrophobic benzene ring but can undergo neutralisation with NaOH (aq)
⇒ D contains phenol or carboxylic acid group

D does not undergo neutralisation with Na₂CO₃ but undergoes redox reaction with Na
⇒ D is not a carboxylic acid, so D contains phenol group

D: OHHO
E: O═O

Total 20 marks
Halogen Are Highly Reactive And They Are The Only Group In The Periodic Table Which Contains Elements In All Three Familiar States Of Matter At 25°C And 1 atm.

The Halogens Form Binary Compounds With Hydrogen And These Compounds Are Known As Hydrogen Halides, All Of Which Are Strong Acids With The Exception Of HF.

(a) Discuss The Thermal Stability Trend Of The Hydrogen Halides, HCl, HBr And HI And Variation In Volatility Of The Halogens From Fluorine To Iodine.

Order Of Thermal Stability: HCl > HBr > HI
Down The Group,
- Covalent Bond Length Of H-X Increases
- Covalent Bond Strength Decreases
- Bond Dissociation Energy Decreases

The Number Electrons In The Halogen Molecules Increase, Thus, Intermolecular Van Der Waals’ Forces Of Attraction Become More Extensive.
This Leads To Increase In Their Boiling Point.
Volatility Of Halogens Decreases Down The Group

(b) Concentrated Sulfuric Acid Will React With Solid Sodium Halides NaX. (X = Cl⁻, Br⁻ or I⁻).

Using Relevant Data From The Data Booklet, Describe And Explain Why Hydrogen Chloride Can Be Prepared By The Reaction Between Sodium Chloride And Concentrated Sulfuric Acid While Hydrogen Iodide Cannot Be Synthesised Using A Similar Method With Sodium Iodide And Concentrated Sulfuric Acid. You Are To Include Relevant Chemical Equation(s) In Your Discussion.

The Reducing Power Of The Halides Increases Down The Group As Shown By The Stated E° Values.

\[ \text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^- + 1.36 \text{ V} \]
\[ \text{Br}_2 + 2e^- \rightleftharpoons 2\text{Br}^- + 1.07 \text{ V} \]
\[ \text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^- + 0.54 \text{ V} \]

\[ \text{NaCl} (s) + \text{H}_2\text{SO}_4 (l) \rightleftharpoons \text{HCl} (g) + \text{NaHSO}_4 \]
HC\(\text{l}\) Is Produced As Cl⁻ Is A Weaker Reducing Agent.

\[ \text{NaI} (s) + \text{H}_2\text{SO}_4 (l) \rightarrow \text{NaHSO}_4 (s) + \text{HI} (g) \]

2 HI (g) + H₂SO₄ (l) → I₂ (g) + 2H₂O (l) + SO₂ (g) or

6HI (g) + H₂SO₄ (l) → 3I₂ (g) + 4H₂O (l) + S (s) or

8HI (g) + H₂SO₄ (l) → 4I₂ (g) + H₂S (g) + 4H₂O

HI Is Not Produced As Iodide Is A Stronger Reducing Agent And It Will Reduce The Sulphur To A Lower Oxidation State.
Halogen form many compounds with metals. These compounds range from ionic compounds such as lithium chloride, monomeric covalent compounds such as uranium hexafluoride, and polymeric covalent compounds like palladium chloride.

The Corey-Posner, Whitesides-House reaction is an organic reaction that involves the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane, an organocopper compound and a lithium halide.

The formation of propane from a halogeno compound using the Corey-Posner, Whitesides-House reaction is as shown.

\[(\text{CH}_3)_2\text{CuLi} + \text{CH}_3\text{CH}_2\text{X} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_3\text{Cu} + \text{LiX}\]

\((X = \text{Cl}^-, \text{Br}^- \text{or} \text{I}^-)\)

(i) Draw the structural formulae of the three alkanes produced when \((\text{C}_3\text{H}_7)_2\text{CuLi}\) and \(\text{C}_3\text{H}_7\text{Br}\) undergo the Corey–Posner, Whitesides–House reaction.

(ii) Suggest with reasoning which of the alkanes in (c)(i) has the lowest boiling point.

Alkanes has simple molecule structure \(\text{CH}_3\text{C}–\text{C}\text{H}_2\text{C}–\text{C}\text{H}_3\) has the lowest boiling point as the extensiveness of VDW is reduced due to the branched structure.

(d) Chlorine and fluorine react exothermically to form an interhalogen compound, \(\text{ClF}_3\).

(i) With the help of a Lewis structure, state the shape of the \(\text{ClF}_3\) molecule.

\[
\text{F} \\
\text{C}–\text{F} \\
\text{F}
\]

\(\therefore\) T-shape molecule
The interhalogen compounds are very strong oxidising agents.

When gaseous ClF$_3$ is added to water, a vigorous reaction occurs, giving three gases as the only products. The gaseous product mixture appears as white fumes which forms a weak acid. The gaseous mixture not only turns moist blue litmus paper red but also bleaches it. In addition, it relights a glowing splint.

State the three gases in the gaseous mixture.
Hence, construct a balanced equation, including state symbols, for the reaction.

<table>
<thead>
<tr>
<th>O$_2$, Cl$_2$ and HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H$_2$O(l) + 4ClF$_3$(g) → 3O$_2$(g) + 2Cl$_2$(g) + 12HF(g)</td>
</tr>
</tbody>
</table>

Total 20 marks
Nitrous acid is an unstable, weakly acidic compound. It can easily be prepared by acidifying a solution of a nitrite. Barium nitrite, Ba(NO$_2$)$_2$ is often used since the insoluble barium sulfate can be easily filtered off.

$$\text{Ba(NO}_2\text{)}_2 \text{(aq)} + \text{H}_2\text{SO}_4 \text{(aq)} \rightarrow 2\text{HNO}_2 \text{(aq)} + \text{BaSO}_4 \text{(s)}$$

Nitrite ion can be oxidised by KMnO$_4$ to form nitrate ion:

$$5\text{NO}_2^- \text{(aq)} + 2\text{MnO}_4^- \text{(aq)} + 6\text{H}^+ \text{(aq)} \rightarrow 5\text{NO}_3^- \text{(aq)} + 2\text{Mn}^{2+} \text{(aq)} + 3\text{H}_2\text{O} (l)$$

The following are some thermochemistry data pertaining to the experiment.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta H^\circ / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy change of atomisation of barium</td>
<td>+175</td>
</tr>
<tr>
<td>Enthalpy change of Ba(s) $\rightarrow$ Ba$^{2+}$ (aq) $+2e$</td>
<td>+286</td>
</tr>
<tr>
<td>Enthalpy change of hydration of NO$_3^-$</td>
<td>-325</td>
</tr>
<tr>
<td>Lattice energy of barium nitrate</td>
<td>-1395</td>
</tr>
</tbody>
</table>

(i) Using the above data, and relevant data from the *Data Booklet*, construct an energy cycle to calculate the enthalpy change of hydration of the barium ion.

$$\Delta H_{\text{rxn}} = +286 \text{ kJ mol}^{-1}$$

$\text{Ba}(s) \rightarrow \text{Ba}^{2+}(aq) + 2e$

$\Delta H_a(Ba) = +175 \text{ kJ mol}^{-1}$

$\Delta H_{\text{hyd}}$

$1^\text{st} \text{IE} + 2^\text{nd} \text{IE} = +502 + 966 = 1468 \text{ kJ mol}^{-1}$

$\text{Ba}(g) \rightarrow \text{Ba}^{2+}(g) + 2e$

$\Delta H_{\text{hyd}}(\text{Ba}^{2+}) = -1468 - 175 + 286$

$= -1360 \text{ kJ mol}^{-1}$

(ii) The $\Delta S^\circ_{\text{hydration}}$ of barium ion is -188 J mol$^{-1}$ K$^{-1}$. Explain why the sign of $\Delta S^\circ_{\text{hydration}}$ is negative.

When Ba$^{2+}$ is hydrated, the ions are surrounded by water molecules. There is an increase in orderliness of the water molecules. Hence, $\Delta S_{\text{hydration}}$ is negative.

(iii) Hence, calculate $\Delta G^\circ_{\text{hydration}}$ of barium ion at 298K.

$$\Delta G^\circ_{\text{hydration}} = \Delta H_{\text{hydration}} - T\Delta S_{\text{hydration}}$$

$$= -1360 - (298)(-188 \times 10^{-3})$$

$$= -1300 \text{ kJ mol}^{-1}$$
<table>
<thead>
<tr>
<th>(iv)</th>
<th>Predict the effect of high temperature on the spontaneity of the above reaction.</th>
</tr>
</thead>
</table>
| ΔH = -ve  
ΔS = -ve  
Since ΔG°_hydration = ΔH°_hydration - TΔS°_hydration  
ΔG°_hydration = -ve - (-ve)  
= -ve + TΔS  
As temperature increases, ΔG°_hydration will become more positive; reaction will become less spontaneous, at high temperature. |

<table>
<thead>
<tr>
<th>(v)</th>
<th>Using your answer in (a)(i), and relevant data from the table, calculate the enthalpy change of solution of barium nitrate.</th>
</tr>
</thead>
</table>
| ![Chemical Equation](image)  
\[ \Delta H_{\text{solution}} = \Delta H_{\text{hyd}}(\text{Ba}^{2+}) + 2\Delta H_{\text{hyd}}(\text{NO}_3^-) - \text{LE} \]  
\[ = -1360 + 2(-325) - (-1395) \]  
\[ = -615 \text{ kJ mol}^{-1} \] |

<table>
<thead>
<tr>
<th>(b) (i)</th>
<th>Write an equation to represent the thermal decomposition of barium nitrate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\text{Ba(NO}_3\text{)}_2 (s) \rightarrow 2\text{BaO (s) + 4NO}_2 (g) + \text{O}_2 (g) ) or ( \text{Ba(NO}_3\text{)}_2 (s) \rightarrow \text{BaO (s) + 2NO}_2 (g) + \frac{1}{2}\text{O}_2 (g) )</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(ii)</th>
<th>Group II iodates decomposed according to the following equation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2\text{Mg(}\text{IO}_3\text{)}_2 (s) \rightarrow 2\text{MgO (s) + 2I}_2 (g) + 5\text{O}_2 (g) )</td>
<td></td>
</tr>
</tbody>
</table>

Describe and explain how the thermal stabilities of Group II iodates vary down the group. 

For Group II cations when going down the group, 
- **Cationic radius of M\(^{2+}\) increases.** 
- **Charge remains constant.** 
- **Polarising power of cation decreases** and M\(^{2+}\) is less able to distort the electron cloud of anion 
- **Polarising effect on anion decreases** 
- **Higher temperature** (more energy) is required to decompose the compound. 
- Hence, **stability of nitrates increases.**
Nitrous acid is useful in converting amines into diazonium compounds:

**Reaction 1**

\[
\text{NH}_2 + \text{HNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{diazonium salt} + \text{HSO}_4^- + 2\text{H}_2\text{O}
\]

In a process named the Sandmeyer reaction, the \( ^{\dagger}\text{NΞN} \) is replaced by \( ^{\dagger}\text{Cl} \) or \( ^{\dagger}\text{Br} \) using the corresponding cuprous halide, \( \text{CuX} \), together with concentrated \( \text{HCl} \).

**Reaction 2**

\[
\text{CuX} \quad \text{conc HCl} \quad \rightarrow \quad \text{diazonium salt} \quad \rightarrow \quad \text{X}
\]

Outline how you could convert nitrobenzene into 1,3-dichlorobenzene in a **four steps synthesis**, using both reactions 1 and 2 in your synthesis. In your answer, you are to clearly state the reagents and conditions used and the intermediates formed.

\[
\begin{align*}
\text{NO}_2 & \rightarrow \text{conc HNO}_3 \\
\text{NO}_2 & \rightarrow \text{conc H}_2\text{SO}_4 \\
\text{NO}_2 & \rightarrow \text{Sn, conc HCl} \\
\text{NO}_2 & \rightarrow \text{heat} \\
\text{NH}_2 & \rightarrow \text{HNO}_2, \text{H}_2\text{SO}_4 \\
\text{X} & \rightarrow \text{CuCl, conc HCl}
\end{align*}
\]
The diazonium salt can undergo a coupling reaction with activated aromatic rings to obtain brightly coloured azo compounds which can be used as dyes.

The dye, Disperse Yellow, is formed as follows:

\[
\begin{align*}
\text{Disperse Yellow} & \\
\text{diazonium salt} & \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]

(i) Identify a reagent which might be used for step I.

CH₃COCl

(ii) Propose a chemical test to differentiate \( \text{NH}_2\text{H}_2\text{N} \) and \( \text{CH}_3\text{HO} \).

In your answer, state clearly the reagents and conditions required and any observations made.

Test: Add neutral \( \text{FeCl}_3 \) or \( \text{KMnO}_4 \) in \( \text{H}_2\text{SO}_4 \), heat

Observations:

\[
\begin{align*}
\text{NH}_2\text{H}_2\text{N} & : \text{No violet complex observed} & (\text{Purple solution remains}) \\
\text{CH}_3\text{HO} & : \text{Violet complex observed} & (\text{Purple solution decolourised})
\end{align*}
\]

(iii) Another azo dye, H, can be obtained from an amine and a phenol under suitable conditions.

\[
\begin{align*}
\text{azo dye, H}
\end{align*}
\]

Draw the structural formulae of the amine and of the phenol used to make H.

[5] Total 20 marks
The pickling of steel is the process of removing rust, or iron(III) oxide, from steel by using excess concentrated hydrochloric acid to react with layers of the oxide and iron metal. The reaction produces a solution of iron(II) chloride.

A chemist used the set-up shown below to investigate if the resulting solution which consists of concentrated hydrochloric acid and iron(II) chloride, from the pickling of steel, can be used to produce iron metal via electrolysis.

<table>
<thead>
<tr>
<th>(a)</th>
<th>An organic fuel cell, the direct ethanol fuel cell, is used to drive the electrolysis. The reaction that takes place at one of the electrodes involves the reduction of oxygen gas as follows:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{CH}_3\text{CH}_2\text{OH (l)} \quad \text{H}^+ (\text{aq}) )</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
|   | Fe (s) 
|   | Pt (s) |
|   | concentrated hydrochloric acid and iron(II) chloride |
|   |  
| (i) | Construct the overall equation for the fuel cell reaction, given that carbon dioxide is produced at the anode. |
|   | \( \text{CH}_3\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \) |
(ii) Write the cell diagram for the direct ethanol fuel cell, stating the polarity of the respective electrodes.

Pt (s) | CH₃CH₂OH (l) | CO₂ (g) || O₂ (g) | H₂O (l) | Pt (s)
Negative Positive

(b) (i) Construct a balanced equation for the reaction that takes place during the pickling of steel, indicating the state symbols clearly.

Fe₂O₃ (s) + Fe (s) + 6HCl (aq) → 3FeCl₂ (aq) + 3H₂O (l)

(ii) Write half-equations for the reactions taking place at the cathode and anode of the electrolytic cell and state all observations made within the cell.

Fe (s) cathode: Fe²⁺ + 2e⁻ → Fe
Observation: Fe (s) cathode increases in mass or pale green solutions fade off
Anode: 2Cl⁻ → Cℓ₂ + 2e⁻ (high concentration of Cℓ⁻ ions from conc. HCl)
Observation: Effervescence observed.

(iii) Suggest the observation made at the anode when nitric acid is used in the pickling of steel instead of hydrochloric acid.

Effervescence observed. Oxygen is evolved instead of chlorine gas.

(c) Upon addition of cyanide ions, the colour of the electrolyte changes from pale green to “Prussian blue”.

Explain why iron complexes are coloured.

The d orbitals are split into two groups due to the ability of the ligands to split them into two energy levels.

The d electron undergoes d-d transition and is promoted to a higher energy d orbital.

The d electron absorbs a certain wavelength of light energy from the visible region of the electromagnetic spectrum and transmits the remaining wavelength, which appear as the colour observed.

(d) Another chloride of iron, FeCℓ₃, has similar characteristics as aluminium chloride. Both form dimers at low temperatures, produce acidic solutions when dissolved in water and are used in the electrophilic substitution reactions of benzene rings.

(i) Using suitable data from the Data Booklet, explain the acidic nature of FeCℓ₃ in water.

From the Data Booklet, Fe³⁺ has a small cationic radius of 0.064 nm and high charge of +3. Thus, Fe³⁺ ion has high charge density and high polarising power. Hydrolysis of water molecules occurs, thus releasing H⁺ ions in aqueous
(i) \[ \text{or} \quad [\text{Fe}(\text{H}_2\text{O})_6]^{3+} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}^+ \]

(ii) State what role does iron(III) chloride play in the electrophilic substitution reaction of benzene ring with chlorine.

FeCl$_3$ acts as a catalyst or halogen carrier or Lewis acid or form the electrophile CCl$_3^-$ catalysing the reaction.

(e) (i) Haemoglobin, which contains iron(II) ions is a protein found in the red blood cells that carries oxygen. Describe the protein components of haemoglobin.

Haemoglobin consists of 4 polypeptide chain: 2 α-sub-units and 2 β-sub-units, with each sub-unit being non-covalently bonded to a haem (iron) group.

Each heme group consists of a central Fe$^{2+}$ ion that can bond to one O$_2$ oxygen. Each haemoglobin is able to carry a maximum of four O$_2$ oxygen. **All four components** (4 sub-units and 4 haem groups) **must be present** to form haemoglobin.

(ii) In World War II, the use of cyanide pills were frequently recorded. Pilots of B-29 Superfortress bombers sent to drop atomic bombs on Japan were issued with the lethal pills. Fortunately, all aircraft returned safely and none of the pills were used. These pills contain a concentrated solution of potassium cyanide and the release of the fast-acting poison causes brain death within minutes.

Suggest why brain death occurs within minutes after the poison is administered.

In the presence of cyanide, the CN$^-$ bonds irreversibly with haemoglobin to form a stable complex.

This prevents haemoglobin from transporting oxygen and cells die of oxygen starvation

| Total 20 marks |
The Kastle-Meyer test is often used to test for the presence of blood at a crime scene. It relies on the peroxidase-like activity of haemoglobin in blood to catalyse the oxidation of colourless phenolphthalein into its bright pink conjugate base.

Phenolphthalein has the following structure:

![Phenolphthalein Structure](image)

Phenolphthalein is a *weak acid* which dissociates in water according to the following equation:

\[
\text{HO}_\text{O}_\text{O}_\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{HO}_\text{O}_\text{O}_\text{O}^- + \text{H}_3\text{O}^+
\]

- colourless (acid)
- pink (conjugate base)

The pK\text{a} of phenolphthalein is 9.7.

(i) Draw the structure of the compound formed when phenolphthalein is heated with aqueous sodium hydroxide.

(ii) Using Le Chatelier's principle, explain why phenolphthalein appears colourless in an acidic solution.

In acidic solution, the concentration of \( \text{H}_3\text{O}^+ \) is high, hence the above equilibrium position is shifted to the left and the concentration of the conjugate base is too low for the pink colour to be observed.
### (iii)
Calculate the ratio of the concentration of the conjugate base to the concentration of the acid at pH 10. Using this ratio, predict and explain the colour of phenolphthalein at pH 10.

\[
[H_2O^+] = 10^{-10} \text{ mol dm}^{-3}
\]

\[
K_a = \frac{[H_2O^+][\text{conjugate base}]}{[\text{acid}]}
\]

\[
= \frac{[10^{-10}][\text{conjugate base}]}{[\text{acid}]} = 10^{-9.7}
\]

\[
\frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{10^{-9.7}}{10^{-10}} = 1.995 \approx 2.00
\]

Since the concentration of the conjugate base is much more than the acid (2 times), the solution will appear pink (the colour of the conjugate base).

### (b)
Cinnamic acid, commonly found in cinnamon, has a molecular formula of \(\text{C}_9\text{H}_8\text{O}_2\).

It is known that cinnamic acid can react with liquid bromine in the dark. It also undergoes oxidation to form benzoic acid and in the process, carbon dioxide gas was released.

An isomer of cinnamic acid also reacts with liquid bromine in the dark. Upon oxidation with potassium manganate(VII), 1 mol of this isomer reacts with 1 mol of sodium carbonate.

Suggest the displayed formulae of cinnamic acid and its isomer. State the type of isomerism exhibited by cinnamic acid.

![Cinnamic acid and isomer of cinnamic acid](image)

Both undergo electrophilic addition with liquid bromine.

1 mol of this isomer reacts with 1 mol of sodium carbonate. Indicates there are 2 carboxylic acid group \(\text{C} = \text{C}\) and 2 side chains.

Cinnamic acid exhibits **geometric isomerism (cis-trans isomerism)**.
**Phenolphthalein** is usually used as an indicator in a strong base and weak acid titration.

Aqueous magnesium chloride can act as a weak monobasic acid. In an experiment, 50.0 cm$^3$ of aqueous magnesium chloride was titrated with 1.00 mol dm$^{-3}$ sodium hydroxide. The variation of pH of the solution is as shown in the diagram.

<table>
<thead>
<tr>
<th>(i) Explain what is meant by the term weak acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A <strong>weak acid</strong> is one which <strong>dissociates partially</strong> in solution to give <strong>protons</strong> (H$^+$).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(ii) Write an equation showing hydrated magnesium ion acting as an acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mg(H}_2\text{O)}_6]^{2+} \quad \xrightarrow{\text{H}^+} \quad [\text{Mg(H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}^+$</td>
</tr>
</tbody>
</table>
### (iii) Using the graph above, calculate the initial concentration of magnesium ions.

\[ V_{\text{NaOH for equivalence}} = 20.00 \text{ cm}^3 \]
\[ \therefore [\text{Mg}^{2+}]_{\text{initial}} = \frac{20.00 \times 1000}{50.00} = 0.4 \text{ mol dm}^{-3} \]

### (iv) Calculate the $K_a$ value for aqueous magnesium chloride.

Initial pH = 6 $\Rightarrow [H^+] = 1 \times 10^{-6}$

\[ K_a = \frac{[\text{Mg(H}_2\text{O)}_6\text{OH}]^+ [H^+]}{[\text{Mg}^{2+}]} \]
\[ = \frac{(10^{-6})^2}{0.4} \]
\[ = 2.5 \times 10^{-12} \text{ mol dm}^{-3} \]

### (v) At the point where 10.0 cm$^3$ of sodium hydroxide has been added to the solution, a saturated solution of a sparingly soluble salt, magnesium hydroxide, Mg(OH)$_2$, is formed.

Calculate the solubility product, $K_{sp}$ of Mg(OH)$_2$.

At 10 cm$^3$, pH = 9

\[ \text{pOH} = 5 \Rightarrow [\text{OH}^-] = 1 \times 10^{-5} \]
\[ [\text{Mg}^{2+}] = \frac{10.00 \times 1}{60.00} = 0.167 \]
\[ K_{sp} = [\text{Mg}^{2+}] [\text{OH}^-]^2 = (0.167) (1 \times 10^{-5})^2 = 1.67 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} \]

### (d) Iodine reacts with propanone in acid solution as follows.

\[ \text{I}_2 + \text{CH}_3\text{COCH}_3 \xrightarrow{\text{H}^+} \text{CH}_3\text{COCH}_2\text{I} + \text{HI} \]

Kinetics studies have shown that the reaction is second order overall, and it has been suggested that the mechanism involves the following three steps.

\[ \text{CH}_3\text{COCH}_3 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{C(OH)}\text{CH}_3 \quad \text{(fast)} \]
\[ \text{CH}_3\text{C(OH)}\text{CH}_3 \rightleftharpoons \text{H}_2\text{C}==\text{C(OH)}\text{CH}_3 + \text{H}^+ \quad \text{(slow)} \]
\[ \text{H}_2\text{C}==\text{C(OH)}\text{CH}_3 + \text{I}_2 \rightleftharpoons \text{CH}_3\text{COCH}_2\text{I} + \text{HI} \quad \text{(fast)} \]

### (i) Explain the meaning of order of reaction.

Order of reaction with respect to a reactant is the power to which its concentration is raised in the rate equation.
(ii) Construct the rate equation for this reaction.

\[
\text{Rate} = k \ [\text{CH}_3\text{COCH}_3] \ [\text{H}^+]\n\]

(iii) An experiment was carried out at 60 °C using the reagents of the following concentrations.

<table>
<thead>
<tr>
<th>Initial concentration / mol dm(^{-3})</th>
<th>([\text{I}_2])</th>
<th>([\text{CH}_3\text{COCH}_3])</th>
<th>([\text{H}^+])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.050</td>
<td>0.050</td>
<td></td>
</tr>
</tbody>
</table>

The initial rate of reaction was found to be \(1.25 \times 10^{-6}\) mol dm\(^{-3}\) s\(^{-1}\) under these conditions. Calculate the rate constant for this reaction, stating its units.

\[
\begin{align*}
\text{k} &= \frac{\text{Rate}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]} \\
&= \frac{1.25 \times 10^{-6}}{0.05 \times 0.05} \\
&= 5.00 \times 10^{-4}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}
\end{align*}
\]

Total 20 marks
READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

Write your name, Civics Group and index number on the Answer Sheet in the spaces provided unless this has been done for you.

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

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet.
Section A

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

1. If a mixture of 0.4 g hydrogen and 9.6 g oxygen is exploded, what will be the volume of the remaining gas at room temperature and pressure?
   - A 0.60 dm³
   - B 1.20 dm³
   - C 2.40 dm³
   - D 4.80 dm³

2. Which of the following contains two isoelectronic species?
   - A NH₄⁺ and BH₃
   - B NH₄⁺ and CH₄
   - C BF₃ and NH₃
   - D PF₅ and BF₄⁻

3. For a given mass of an ideal gas, which of the following graphs display a different shape from the rest?
   - A PV against V (at constant T)
   - B V/T against T (at constant P)
   - C 1/density against T (at constant P)
   - D PV against P (at constant T)

4. 25.0 cm³ of 0.0200 mol dm⁻³ of yellow FA₁ solution reacts with x g of zinc and the latter is oxidised to Zn²⁺. The resulting solution required 15.0 cm³ of 0.0200 mol dm⁻³ of acidified KMnO₄ to restore its original colour. Find x.
   - A 0.0196 g
   - B 0.0218 g
   - C 0.0327 g
   - D 0.0491 g
An aqueous sample containing the following anions is analysed.

\[ \text{Cl}^- \quad \text{CO}_3^{2-} \quad \text{SO}_4^{2-} \]

In which order should the reagents be added to determine the amount of chloride in the sample?

[If a precipitate is formed, filtration process is carried out before the addition of the next reagent to the filtrate.]

<table>
<thead>
<tr>
<th>Reagent 1</th>
<th>Reagent 2</th>
<th>Reagent 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>AgNO_3</td>
<td>HNO_3</td>
</tr>
<tr>
<td>B</td>
<td>HNO_3</td>
<td>Pb(NO_3)_2</td>
</tr>
<tr>
<td>C</td>
<td>HNO_3</td>
<td>Ba(NO_3)_2</td>
</tr>
<tr>
<td>D</td>
<td>Ba(NO_3)_2</td>
<td>NH_3</td>
</tr>
</tbody>
</table>

The successive ionisation energies (IE) of two elements \( X \) and \( Y \), are given below:

<table>
<thead>
<tr>
<th>IE/ kJ mol(^{-1})</th>
<th>1(^{st})</th>
<th>2(^{nd})</th>
<th>3(^{rd})</th>
<th>4(^{th})</th>
<th>5(^{th})</th>
<th>6(^{th})</th>
<th>7(^{th})</th>
<th>8(^{th})</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>786</td>
<td>1580</td>
<td>3230</td>
<td>4360</td>
<td>16000</td>
<td>20000</td>
<td>23600</td>
<td>29100</td>
</tr>
<tr>
<td>Y</td>
<td>1251</td>
<td>2298</td>
<td>3822</td>
<td>5158</td>
<td>6542</td>
<td>9330</td>
<td>11000</td>
<td>33604</td>
</tr>
</tbody>
</table>

The compound formed when \( X \) and \( Y \) combine is most likely to be

\[ \begin{align*}
\text{A} & \quad \text{ionic, with formula } X_2Y \\
\text{B} & \quad \text{ionic, with formula } XY_2 \\
\text{C} & \quad \text{covalent, with formula } XY_4 \\
\text{D} & \quad \text{covalent, with formula } X_2Y_5
\end{align*} \]
The reaction between phosphorus and hydrogen can result in the formation of phosphine as shown:

\[ \text{P}_4(\text{s}) + 6\text{H}_2(\text{g}) \rightarrow 4\text{PH}_3(\text{g}) \]

The graph shows the change in concentration of hydrogen for this reaction in which the system was disturbed after four hours.

Which of the following could explain the change in the hydrogen concentration at time, \( t = 4 \) hours?

A. The volume of the reaction vessel was decreased.
B. A catalyst was added.
C. The pressure on the reaction mixture was decreased.
D. More phosphorus was added.
If compound $A$ is heated, it decomposes according to the equation:

$$2A(g) \rightleftharpoons B(g) + C(g)$$

The following diagram shows the progress of the reaction.

![Diagram showing concentration over time](image)

What is the equilibrium constant for the reaction?

A. 0.8  
B. 2.0  
C. 4.0  
D. 10.0

In a blast furnace, carbon or carbon monoxide can be used to reduce iron(III) oxide.

$$Fe_2O_3(s) + \frac{3}{2}C(s) \rightarrow 2Fe(s) + \frac{3}{2}CO_2(g) \quad \Delta H = +234 \text{ kJ mol}^{-1}$$

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \quad \Delta H = -24.8 \text{ kJ mol}^{-1}$$

Carbon monoxide can be formed by the following reaction.

$$C(s) + CO_2(g) \rightarrow 2CO(g) \quad \Delta H_1$$

What is the value of $\Delta H_1$?

A. +86.3 kJ mol$^{-1}$  
B. +139.5 kJ mol$^{-1}$  
C. +172.5 kJ mol$^{-1}$  
D. +258.8 kJ mol$^{-1}$

Which of the following reactions shows a positive change in entropy? [Assume that all measurements are taken at 298 K and 1 atm pressure.]

A. $N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$  
B. $Fe(s) + S(s) \rightleftharpoons FeS(s)$  
C. $Ca(s) + \frac{1}{2}O_2(g) \rightleftharpoons CaO(s)$  
D. $C_3H_6(g) + H_2(g) \rightleftharpoons C_3H_8(g)$
11 Car manufacturers are developing engines that use H₂ as a fuel. Approximately 5% of industrial hydrogen is produced by electrolysis of water. How many coulombs are needed to produce 1.02 × 10⁶ mol of H₂ gas?

A 1.02 × 10⁶ C  
B 9.84 × 10¹⁰ C  
C 1.97 × 10¹¹ C  
D 1.97 × 10¹⁴ C

12 Ethyl ethanoate undergoes a slow acid-catalysed hydrolysis in water where the concentration of acid in the solution remains constant.

\[
\text{H}^+ + \text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
\]

The rate equation is found to be

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

When 0.1 mol dm⁻³ of HCl is reacted with 0.2 mol dm⁻³ of ethyl ethanoate, the half-life was found to be 62 min.

Another reaction was carried out with 0.2 mol dm⁻³ of HCl and 0.2 mol dm⁻³ of ethyl ethanoate. How long does it take for the concentration of ethyl ethanoate to fall to 0.025 mol dm⁻³?

A 31 min  
B 62 min  
C 93 min  
D 124 min

13 25 cm³ of 0.1 mol dm⁻³ monobasic acid X is titrated with 25 cm³ of 0.2 mol dm⁻³ NaOH. The end point cannot be detected using screened methyl orange.

Which of the following is not correct?

A The solution acts as a buffer when 12.50 cm³ of NaOH has been added.  
B Initial pH of the solution is more than 1.00.  
C pH of the equivalence point is more than 7.  
D Acid X is a weak acid.
14 A 100 cm$^3$ solution consists of 0.20 mol dm$^{-3}$ MgC$_2$ and 0.10 mol dm$^{-3}$ CuC$_2$. A solution of sodium hydroxide is added to the mixture. Mg(OH)$_2$ starts precipitating when 40 cm$^3$ of sodium hydroxide has been added.

The solubility product values of Mg(OH)$_2$ and Cu(OH)$_2$ are $6.3 \times 10^{-10}$ and $2.2 \times 10^{-20}$ respectively.

What is the concentration, in mol dm$^{-3}$, of Cu$^{2+}$ in the solution when Mg(OH)$_2$ just precipitates?

A $4.99 \times 10^{-12}$

B $6.98 \times 10^{-12}$

C $6.60 \times 10^{-5}$

D $7.14 \times 10^{-2}$

15 Which of the following graphs shows the correct trend in the physical property of the period 3 elements?

A ionic radii

B electronegativity

C melting point

D electrical conductivity
16 When a white solid \( W \) reacts with concentrated \( \text{H}_2\text{SO}_4 \), the products include pungent-smelling gases and a dark brown solution containing a yellow precipitate. When aqueous sodium thiosulfate is added, the yellow precipitate remains but the dark brown colour disappears.

What is \( W \)?

A  \( \text{NaNO}_2 \)
B  \( \text{KI} \)
C  \( \text{MgCl}_2 \)
D  \( \text{Ag}_2\text{CO}_3 \)

17 Which statement is true about the first row transition metals or their compounds?

A  \([\text{Ni(C}_2\text{O}_4)_2(\text{CN})_2]^{4-}\) has a coordination number of 4.
B  Yellow \( \text{CrO}_4^{2-} \) is oxidised to orange \( \text{Cr}_2\text{O}_7^{2-} \) in an acidic medium.
C  \( \text{Fe}^{3+} \) is more stable in acidic than in alkaline medium.
D  \( \text{Fe}_2(\text{CO}_3)_3 \) cannot be prepared by reacting \( \text{FeCl}_3(\text{aq}) \) with \( \text{Na}_2\text{CO}_3(\text{aq}) \).

18 Transition metals like nickel are used in the manufacture of margarine. Which of the following statements best explains the role of transition metals in this use?

A  Transition metals have very high melting points because both 3d and 4s electrons are involved in forming strong metallic bond.
B  Transition metals have partially filled 3d orbitals for adsorption of reactant molecules.
C  Transition metals can exhibit variable oxidation states in their compounds as 3d and 4s electrons have similar energies.
D  Transition metals form coloured ions due to absorption of energy in the visible light region to promote an electron from a lower to a higher energy 3d orbital.

19 Which row in the table below has the correct number and type of bonds in

\[
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{H}_2\text{C} = \text{C} - \text{C} \equiv \text{CH}
\end{array}
\]

<table>
<thead>
<tr>
<th>Number of ( \sigma ) - bonds</th>
<th>Number of ( \pi ) - bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 4</td>
<td>3</td>
</tr>
<tr>
<td>B 8</td>
<td>5</td>
</tr>
<tr>
<td>C 10</td>
<td>2</td>
</tr>
<tr>
<td>D 10</td>
<td>3</td>
</tr>
</tbody>
</table>
20 Pentane was reacted with limited bromine in the presence of \( uv \) light. Assuming that only monobromination took place and the reaction occurred at the same rate at all carbon atoms, the ratio of the 3 possible products, 1-bromopentane : 2-bromopentane : 3-bromopentane is

A 3 : 2 : 1  
B 1 : 2 : 3  
C 1 : 3 : 2  
D 3 : 1 : 2

21 Phenylethene undergoes the following reactions to form compound A.

\[ \text{Phenylethene} \xrightarrow{\text{HCl}} \xrightarrow{\text{BrC/FeCl}_3} A \]

What is the structural formula of A?

A  
B  
C  
D
The demand for 'natural' shampoos and detergents has led to the development of more biodegradable detergents such as sorbitan monolaurate, which is made from plants. Its structure is shown below.

Which statement is correct?

A. There will be no colour change on heating the compound with acidified potassium dichromate(VI) solution.
B. It is optically inactive.
C. It can react with concentrated sulfuric acid on heating.
D. It is a cyclic ester.

In which pair of molecules is the $pK_a$ of molecule I bigger than that of molecule II?

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>COCH$_3$-CO$_2$H</td>
<td>CH$_2$CH$_3$-CO$_2$H</td>
</tr>
<tr>
<td>B</td>
<td>$^+$NH$_3$</td>
<td>$^+$NH$_3$</td>
</tr>
<tr>
<td>C</td>
<td>OH</td>
<td>O$_2$N-</td>
</tr>
<tr>
<td>D</td>
<td>CH$_3$CH$_2$CHCH$_2$OH</td>
<td>C/CH$_2$CH$_2$CH$_2$CH$_2$OH</td>
</tr>
</tbody>
</table>
24. The C–H bond lengths of four hydrocarbons are given in the table below.

<table>
<thead>
<tr>
<th>compound</th>
<th>structural formula</th>
<th>C–H bond length /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>CH₄</td>
<td>0.110</td>
</tr>
<tr>
<td>ethane</td>
<td>CH₃CH₃</td>
<td>0.110</td>
</tr>
<tr>
<td>ethene</td>
<td>CH₂=CH₂</td>
<td>0.108</td>
</tr>
<tr>
<td>ethyne</td>
<td>CH≡CH</td>
<td>0.106</td>
</tr>
</tbody>
</table>

Which of the following helps to explain the shortest C–H bond length observed in ethyne?

A. Ethyne is a linear molecule.
B. The carbon orbital used in formation of the C–H bond in ethyne has the greatest s orbital character.
C. An sp-sp overlap is observed between the two carbon atoms in ethyne.
D. The carbon-carbon triple bond in ethyne is the strongest.

25. A drug containing a carboxyl group can bind to an amino group on a receptor site in three different ways.

Hydrogen-bond acceptor       Hydrogen-bond donor       Ionic interaction

![Diagram showing different binding sites]

The drug with the following structure could bind to the same site

A. only by ionic interaction
B. only as a hydrogen-bond donor
C. only as a hydrogen-bond acceptor
D. both as a hydrogen-bond donor and acceptor
26 The reduction of a nitrile Q produced a compound of the formula CH₃CH₂NH₂. The same nitrile Q was also hydrolysed separately in acidic medium.

What would be formed if the products from the two reactions are mixed together?

A (CH₃CH₂NH₃)(CH₃CO₂⁻)
B (CH₃CH₂NH₃)(CH₃CH₂CO₂⁻)
C CH₃CH₂CONHCH₂CH₃
D CH₃CONHCH₂CH₃

27 The reaction conditions for four different transformations are given.

Which transformation has the correct conditions?

A \[ \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{Alcoholic CH}_3\text{CH}_2\text{O}^-\text{Na}^+} \text{Reflux} \rightarrow \text{CH}_2=\text{CH}_2 \]

B \[ \text{CH}_3\text{C}^\text{=O} \xrightarrow{\text{NaBH}_4, \text{alcohol as solvent}} \text{Room temperature} \rightarrow \text{CH}_3\text{CH}_2\text{OH} \]

C \[ \text{C}^\text{=C} \xrightarrow{\text{Anhydrous A/Cl}_3, \text{Cl}_2(aq)} \text{Room temperature} \rightarrow \text{C}^\text{=C} \text{Cl} \]

D \[ \text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/H^+} \text{Heat} \rightarrow \text{CH}_3\text{C}^\text{=O} \text{OH} + \text{CO}_2 \]
28 Compound X has the following structure.

Which of the following statements is true for compound X?

A It will give white fumes with SOCl₂.
B It is insoluble in both aqueous acids and alkalis.
C The nitrogen containing group in the ring has a higher pKₐ than the nitrogen containing group in the side chain.
D It contains a total of six sp² hybridised carbon atoms.

29 Compound Y is used to treat hypertension.

Which of the following statements about compound Y is true?

A One mole of compound Y reacts with 3 moles of CH₃COCl.
B One mole of compound Y reacts with 3 moles of NaOH on heating.
C One mole of compound Y liberates 1 mole of hydrogen gas with Na metal.
D Compound Y gives an orange precipitate with 2,4-dinitrophenylhydrazine.

30 Which statement about ammonia, methylamine and phenylamine is not correct?

A Basic strength in aqueous solution increases from phenylamine to ammonia to methylamine.
B All of them can act as nucleophiles using the lone pair on the nitrogen atom.
C All are trigonal pyramidal in shape with respect to the nitrogen atom.
D Only methylamine and phenylamine form white precipitate with aqueous bromine.
Section B

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

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

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

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

31 Chromate and dichromate ions form an equilibrium according to the following equation.

\[ 2\text{CrO}_4^{2-}(aq) + 2\text{H}^+(aq) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(aq) + \text{H}_2\text{O}(l) \]

Which solution would increase the concentration of the chromate ion, \( \text{CrO}_4^{2-} \), when added to the equilibrium mixture?

1 Sodium ethanoate
2 Ammonium chloride
3 Sodium nitrate

32 When metal A is placed in a solution of a salt of metal B, the surface of metal A changes colour. When metal B is placed in an acidic solution, gas bubbles form on the surface of the metal. When metal A is placed in a solution of a salt of metal C, no change is observed.

Which of the following statements are correct?

1 When metal B is placed in a solution of silver nitrate, silver deposits can be formed.
2 The order of decreasing reducing strength is C > A > B > H₂.
3 H⁺ is being oxidised to H₂ when metal B is placed in acidic solution.
The responses A to D should be selected on the basis of

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
</tr>
</tbody>
</table>

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

33 The table below shows the experimental results obtained for the following reaction.

\[ 2YO + O_2 \rightarrow 2YO_2 \]

<table>
<thead>
<tr>
<th>partial pressure of YO (in arbitrary units)</th>
<th>100</th>
<th>100</th>
<th>50</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>partial pressure of O(_2) (in arbitrary units)</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>D</td>
</tr>
<tr>
<td>relative rate</td>
<td>1.00</td>
<td>0.50</td>
<td>0.25</td>
<td>1.00</td>
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Which of the following statements are correct?
1 The value of D is 400.
2 The reaction is first order with respect to YO.
3 Keeping partial pressure of YO constant, increasing partial pressure of O\(_2\) does not change the relative rate.

34 Which combination of solutions would give a buffer solution?
1 10 cm\(^3\) of 0.1 mol dm\(^{-3}\) CH\(_3\)CO\(_2\)H and 10 cm\(^3\) of 0.1 mol dm\(^{-3}\) CH\(_3\)CO\(_2\)Na.
2 10 cm\(^3\) of 0.1 mol dm\(^{-3}\) HC\(_2\) and 20 cm\(^3\) of 0.1 mol dm\(^{-3}\) CH\(_3\)CO\(_2\)Na.
3 20 cm\(^3\) of 0.1 mol dm\(^{-3}\) HC\(_2\) and 10 cm\(^3\) of 0.1 mol dm\(^{-3}\) Mg(CH\(_2\)CO\(_2\))^\(_2\)\.)

35 The enthalpy changes involved in the formation of KCl(aq) from K(s) and Cl\(_2\)(g) are as follows:

\[ \begin{align*}
\text{K(s)} & \quad \Delta H_1 & \quad \text{K(g)} & \quad \Delta H_2 & \quad \text{K}^+(g) & \quad \Delta H_3 & \quad \text{KCl(s)} & \quad \Delta H_4 & \quad \text{K}^+(aq) \\
\frac{1}{2} \text{Cl}_2(g) & \quad + & \quad \text{Cl}(g) & \quad + & \quad \text{Cl}^-(g) & \quad \quad & \quad + & \quad \text{Cl}^-(aq)
\end{align*} \]

Which statements are true?
1 The enthalpy change of solution of potassium chloride is \( \Delta H_5 + \Delta H_4 \).
2 The enthalpy change of formation of solid potassium chloride is \( \Delta H_1 + \Delta H_2 + \Delta H_3 \).
3 The lattice energy of potassium chloride is \( \Delta H_3 \).
The responses A to D should be selected on the basis of

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<td>1, 2 and 3 are correct</td>
<td>1 and 2 only are correct</td>
<td>2 and 3 only are correct</td>
<td>1 only is correct</td>
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No other combination of statements is used as a correct response.

36 Beryllium resembles aluminium in its chemical properties. Which property of beryllium compounds is not correct?

- 1 Beryllium chloride is an ionic compound.
- 2 Beryllium chloride can form the dimer $\text{Be}_2\text{Cl}_4$.
- 3 Beryllium chloride dissolves in water to give an acidic solution.

37 Barium is an element in Group II. Which of the following statements are correct?

- 1 Barium burns with apple green flame.
- 2 $\text{Ba(OH)}_2$ has a higher solubility in water than $\text{Mg(OH)}_2$.
- 3 Barium metal rapidly changes from silvery-white to dark grey colour in presence of air.

38 Chemists in the late 1800s knew that cyclic molecules existed, but the limitations on the ring sizes were unclear. Rings of all sizes from three to thirty and beyond can now be prepared easily.

Cyclopropane is known to be less stable than cyclohexane.

Cyclopropane

Cyclohexane

Which reasons explain the difference in stability?

- 1 The sp²-sp² overlap strengthens the carbon–carbon bonds in cyclohexane.
- 2 The C-C-C bond angle of cyclopropane experiences a larger deviation from the ideal value of 109.5°.
- 3 The carbon atoms of cyclohexane are not in the same plane, allowing bond angles to be near the ideal value.
The responses A to D should be selected on the basis of

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

39 Polyethene is made by polymerization of ethene molecules via a free radical mechanism under high temperature and pressure, in the presence of an organic peroxide.

*Chain initiation*

\[ \text{organic peroxide} \]

\[
R - C - O - O - C - R \rightarrow 2 R - C - O - \cdot \rightarrow 2\text{CO}_2 + 2R \cdot 
\]

\[ R \cdot + \text{CH}_2=\text{CH}_2 \rightarrow R\text{CH}_2\text{CH}_2 \cdot \]

*Chain propagation*

\[
\text{RCH}_2\text{CH}_2 \cdot + n\text{CH}_2=\text{CH}_2 \rightarrow \text{R(CH}_2\text{CH}_2)_n\text{CH}_2\text{CH}_2 \cdot 
\]

The chain process is eventually ended by combination of two radicals in the termination step.

Which of the following can be formed in the free radical mechanism?

1. \([\text{R(CH}_2\text{CH}_2)_n\text{CH}_2\text{CH}_2]_2\)
2. \(\text{R} - \text{C} - \text{OCH}_2\text{CH}_2 \cdot \)
3. \(\text{R(CH}_2\text{CH}_2)_2\text{R}\)

40 An amino acid has the structural formula \(\text{HOCH}_2\text{CH(NH}_2\text{)CO}_2\text{H}\). Which of the following statements apply to this amino acid?

1. In a buffer solution of pH 9, this amino acid is attracted towards the anode when a potential difference is applied.
2. It is an \(\alpha\)-amino acid which is optically active.
3. In a polypeptide, the hydroxyl group of this amino acid maintains the secondary structure by forming ionic bonds with polar R groups of other amino acid residues.
### 2012 TJC H2 Chemistry Preliminary Exam Paper 1 Solutions

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