

Catholic Junior College
JC 2 Preliminary Examinations
Higher 2

CANDIDATE NAME

CLASS

CHEMISTRY
 Paper 1 Multiple Choice **9729/01**
15 September 2022
 1 hour

Additional Materials: Multiple Choice Answer Sheet
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
 Do not use staples, paper clips, glue or correction fluid.
 Write your name, class and NRIC/FIN number on the Answer Sheet in the spaces provided.
 There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers A, B, C and D.
 Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
 Any rough working should be done in this booklet.
 The use of an approved scientific calculator is expected, where appropriate.

WORKED SOLUTIONS

This document consists of 31 printed pages.

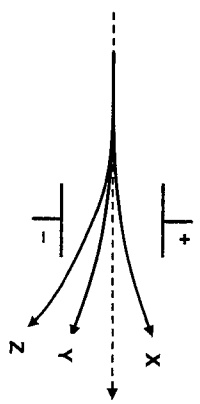
- 1 Which statement about 27 g of Al is always correct?
- A It contains the same number of atoms as $\frac{1}{12}$ g of ^{12}C .
 - B It contains the same number of atoms as 24 dm^3 of krypton gas at room temperature and pressure.
 - C It contains the same number of hydrogen ions as 1 dm^3 of 1 mol dm^{-3} aqueous sulfuric acid.
 - D It contains the same number of atoms as 28 g of nitrogen gas.

Topic: Mole Concept

- No of Al atoms in 27 g = $\frac{27}{27.0} \times 6.02 \times 10^{23} = 6.02 \times 10^{23}$
- A No of C atoms in $\frac{1}{12.0} \text{ g}$ of $^{12}\text{C} = \frac{1}{12.0} \times 6.02 \times 10^{23} = 4.18 \times 10^{21}$
- B No of Kr atoms in 24 dm^3 of Kr = $\frac{24}{24.0} \times 6.02 \times 10^{23} = 6.02 \times 10^{23}$
- C $\text{H}_2\text{SO}_4 \equiv 2\text{H}^+$
 No of H^+ ions in 1 dm^3 of aq $\text{H}_2\text{SO}_4 = 1 \times 1 \times 2 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}$
- D $\text{N}_2 \equiv 2\text{N}$
 No of N atoms in 28 g of $\text{N}_2 = \frac{28}{28.0} \times 2 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}$

Answer: B

- 2 The following are flight paths of charged particles as they pass through an electric field at the same speed.



Which of the following correctly identifies X, Y and Z?

- | | | |
|---------------------|----------------------|-----------------------|
| X | Y | Z |
| A $^{14}\text{N}^-$ | $^{16}\text{O}^{2+}$ | $^{28}\text{Si}^{2+}$ |
| B $^{14}\text{N}^+$ | $^{14}\text{C}^+$ | $^{28}\text{Si}^{4+}$ |
| C $^{15}\text{O}^+$ | $^{14}\text{C}^+$ | $^{14}\text{N}^+$ |
| D $^{15}\text{O}^-$ | $^{14}\text{C}^+$ | $^{28}\text{Si}^{4+}$ |

Concept: Angle of deflection

particles	$^{14}\text{N}^-$	$^{14}\text{C}^+$	$^{28}\text{Si}^{4+}$
m/z	1/14	1/14	4/28 = 1/7

angle of deflection $\propto \frac{\text{charge of particle}}{\text{mass}}$

$^{14}\text{N}^-$ is negatively charged, so it is attracted to anode while $^{14}\text{C}^+$ and $^{28}\text{Si}^{4+}$ are attracted to cathode. Since angle of deflection is charge/mass ratio, $^{14}\text{N}^-$ and $^{14}\text{C}^+$ have roughly the same angle of deflection (paths X and Y), while $^{28}\text{Si}^{4+}$ has almost double the angle of deflection (path Z).

Answer: B

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

Species containing one or more unpaired electrons can be attracted by an external magnetic field and are said to be paramagnetic.

Which of the following species is paramagnetic?

- 1 Cr^{3+}
- 2 Cu^+
- 3 Ni^{2+}

- A 3
B 1 and 2
C 1 and 3
D 1, 2 and 3

Concept: Electronic Configuration

Cr^{3+} : $[\text{Ar}]3d^3$

Cu^+ : $[\text{Ar}]3d^{10}$ (Does not have any unpaired electrons)

Ni^{2+} : $[\text{Ar}]3d^8$

Answer: C

4 In which of the following sequences are the species quoted in order of decreasing boiling points?

- A RbCl , KCl
 B K , Ca
 C K , Ca
 D CO , CO_2

Concept: Boiling points

Option A: Both of them have giant ionic lattice structure with strong electrostatic forces of attractions between cations and anions. The strength of ionic bonding $\propto \frac{q_+ \cdot q_-}{r_+ + r_-}$

Rb^+ has larger cationic size than K^+ , hence RbCl has weaker ionic bonding than KCl .

Option B: HF has a higher boiling point than HCl as it has stronger intermolecular hydrogen bonding while HCl has weaker permanent dipole-permanent dipole between its molecules.

Option C: Both K and Ca have giant metallic lattice structure with strong electrostatic forces of attractions between cations and sea of delocalised electrons. The strength of metallic bonding \propto the number of valence electrons involved in the delocalisation.

K : $4s^1$

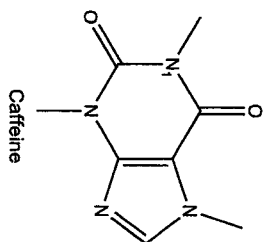
Ca : $4s^2$

Ca has higher boiling point than K because it has more valence electrons than K involved in the delocalisation.

Option D: Both of them have simple molecular structure. CO_2 has larger electron cloud size compared to CO . CO_2 has higher boiling point as it has stronger intermolecular instantaneous dipole-induced dipole attractions between its molecules compared to the weaker intermolecular permanent dipole-permanent dipole between CO molecules.

Answer: B

- 5 People drink beverages containing caffeine to relieve or prevent drowsiness and to improve cognitive performance.



Which statement about caffeine is true?

- A Caffeine molecule has a planar structure.
 B The π bond in $C=C$ is formed by sideways overlap of $2p$ orbitals.
 C The nitrogen atom in caffeine, N_1 is basic.
 D There are 16 sigma bonds in a caffeine molecule.

Concept: Chemical Bonding

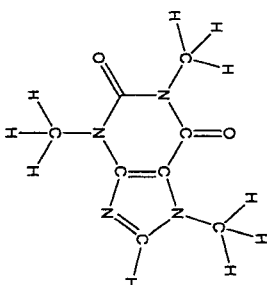
Option A is wrong. There are sp^3 carbon atoms which have tetrahedral geometry.

Option B is correct. The pi bond is formed by sideways overlap of parallel unhybridised p orbitals.

Option C is wrong. The lone pair of electrons in the unhybridised p orbital of N_1 has overlapped sideways with the adjacent π electron cloud of $C=O$ bond resulting in the delocalisation of lone pair of electrons. Hence, lone pair of electrons is unavailable for protonation.

Option D is wrong. There are 25 σ bonds in a caffeine molecule. There is one σ bond and one π bond in a double bond.

Answer: D



- 6 Which of the following substances conduct electricity due to delocalised electrons?

- 1 Graphite
- 2 Solid magnesium
- 3 Molten sodium chloride

- A 1 only
 B 1 and 2 only
 C 2 and 3 only
 D 1, 2 and 3

Concept: Physical properties of compounds

Answer: B

Molten sodium chloride conducts electricity due to the presence of free mobile ions.

7

Which of the following statements is incorrect?

- A When methane gas is subjected to low pressure, it liquefies.
 B Tyre pressure readings are higher on a hot day.
 C The boiling point of water is lower than 100°C at a higher altitude.
 D The density of an ideal gas at constant pressure is inversely proportional to the temperature.

Concept: Gaseous State

A: Gas should be subjected to high pressure for it to be liquified.

B: $P \propto T$, when tyre is hot, T increases hence pressure is higher.

C: At a higher altitude than sea level, the atmospheric pressure is lower than atmospheric pressure at sea level, thus boiling point will be lowered as $P \propto T$.

D: $\rho = \frac{PM}{RT}$ density is inversely proportional to temperature.

Answer: A

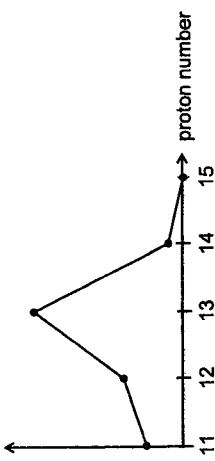
8 For the oxides of Period 3 elements (Na to P), which property decreases from Na₂O to P₄O₁₀?

- A melting point
- B covalent character
- C pH when mixed with water
- D solubility in aqueous alkali

Concept: Properties of oxides of Period 3
Answer: C

Oxide formula	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ and P ₄ O ₁₀
Structure	Giant ionic				Simple covalent (molecular)
Melting Point / °C	1280	2900	2040	1610	24 580
Acid/base behaviour	Basic: Na ₂ O + 2H ⁺ → 2Na ⁺ + H ₂ O	Basic: MgO + 2H ⁺ → Mg ²⁺ + H ₂ O	Amphoteric: Al ₂ O ₃ + 6H ⁺ → 2Al ³⁺ + 3H ₂ O Al ₂ O ₃ + 2OH ⁻ + 3H ₂ O → 2Al(OH) ₄ ⁻	Acidic: forms SiO ₃ ²⁻ with base SiO ₂ + 2NaOH → Na ₂ SiO ₃ + H ₂ O SiO ₂ + CaO → CaSiO ₃	Acidic: P ₄ O ₆ + 8NaOH → 4Na ₂ HPO ₃ + 2H ₂ O P ₄ O ₁₀ + 12NaOH → 4Na ₃ PO ₄ + 6H ₂ O
Rxn w/H ₂ O	Eqn	Na ₂ O + H ₂ O → 2NaOH	MgO + H ₂ O ⇌ Mg(OH) ₂ (slightly alkaline as only mildly soluble)	Giant ionic with high lattice energy. Will not dissolve in water.	P ₄ O ₆ + 6H ₂ O → 4H ₃ PO ₃ P ₄ O ₁₀ + 6H ₂ O → 4H ₃ PO ₄
	pH	13	9	7 (the pH of water)	2

9 The following graph shows how a property of the elements in Period 3, from Na to P, or their compounds, varies with proton number.



What property is shown by the graph?

- A ionisation energies of elements
- B melting point of element
- C pH of aqueous chloride
- D electrical conductivity of element

Concept: Trends of different physical properties of Period 3 elements.

Electrical conductivity increases from Na to Al due to the increase in number of mobile delocalised electrons. Electrical conductivity then decrease to Si as Si is a semi-conductor and has poor conductivity under normal conditions. P does not conduct electricity as it neither have delocalised electrons nor mobile charge carriers.

Answer: D

10 Use of Data Booklet is relevant to this question.

The $\Delta G^\circ_{\text{solution}}$ and $\Delta S^\circ_{\text{solution}}$ for silver chloride, AgCl, are +55.6 kJ mol⁻¹ and +33.2 J mol⁻¹ K⁻¹ respectively.

What is the standard enthalpy change (ΔH°) when 287 g of AgCl is precipitated under the same conditions?

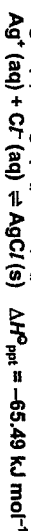
- A +65.5 kJ
- B -65.5 kJ
- C +131 kJ
- D -131 kJ

Concept: Gibbs' Free Energy

$$\text{Amount of AgCl precipitated} = \frac{287}{107.9+35.5} = 2.00 \text{ mol}$$

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

$$55.6 = \Delta H^\circ_{\text{solution}} - (298)(0.0332)$$



For 2 mol of AgCl precipitated, standard enthalpy change is -131 kJ.

Answer: D

11

The rate equation for a reaction between A and B is given by: rate = $k[A]$
Which of the following statements about the reaction is true?

- A is involved in the rate-determining step in the reaction mechanism.
- The rate constant, k , increases with increasing concentration of A.
- A graph of rate against $[A]$ gives a straight line that passes through the origin.

A 1, 2 and 3 B 1 and 3 only C 2 only D 1 only

Concept: Reaction mechanism

- True statement. From the rate equation, 1 molecule of A is involved in the rate determining step of the reaction.
- False. Rate constant, k , is only affected by temperature and catalyst.
- True statement. From the rate equation, rate is directly proportional to $[A]$ hence is reflected as a straight line passing through the origin.

Answer: B

12

What is the pH of the final solution when $V \text{ cm}^3$ of dilute nitric acid of pH 2.0 is mixed with $V \text{ cm}^3$ of dilute nitric acid of pH 4.0 followed by the addition of $2V \text{ cm}^3$ of water?

A 2.3 B 2.6 C 3.0 D 3.6

Topic: Chemistry of aqueous solutions

Concept: Calculation of pH of acidic solutions

$$\text{Total volume of final solution} = V + V + 2V = 4V \text{ cm}^3$$

$$\text{Total amount of H}^+ \text{ ions in final solution} = (10^{-2} \times \frac{V}{1000}) + (10^{-4} \times \frac{V}{1000}) \text{ mol}$$

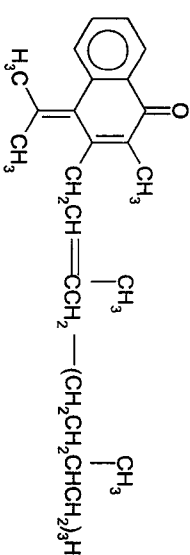
$$[\text{H}^+] \text{ in final solution} = \frac{(10^{-2} \times \frac{V}{1000}) + (10^{-4} \times \frac{V}{1000})}{\frac{4V}{1000}} = 0.002525 \text{ mol dm}^{-3}$$

$$\text{pH of final solution} = -\log(0.002525) = 2.6$$

Answer: B

13

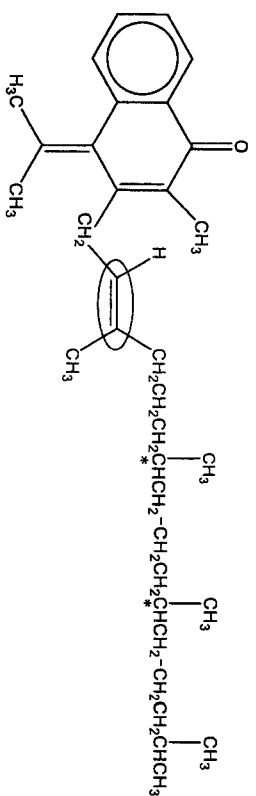
Compound K is a yellow viscous oil found in plants. It has the following structure.



What is the total number of stereoisomers for compound K?

A 4 B 8 C 16 D 32

Topic: Stereoisomerism



There are 2 chiral carbons and 1 carbon-carbon double bond that can display cis-trans isomerism. Therefore $n = 3$
No. of stereoisomers = 2^n
= 8

Answer: B

14 In the free radical substitution reaction of methane, CH_4 , one of the side-products formed is ethane, CH_3CH_3 , which is formed when two $\bullet\text{CH}_3$ radicals combine. Upon careful heating, a sample of butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, reacted with chlorine gas in a free radical substitution reaction to give only mono-substituted products.

How many possible organic side-products would be obtained in this reaction when the radicals produced combine with each other?

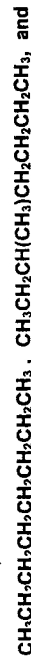
- A 2 B 3 C 4 D 5

Topic: Free Radical substitution

Only 2 organic radicals are produced in the mono-substitution of

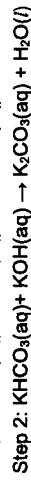


Therefore, there can be 3 different products:



Answer: B

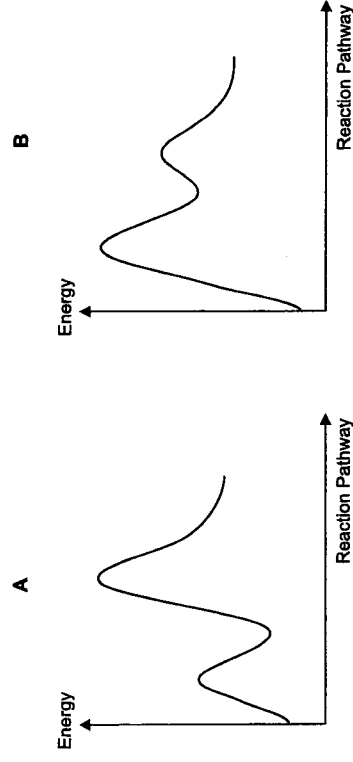
15 The reaction between carbon dioxide and potassium hydroxide is exothermic. The proposed two-step mechanism of the reaction is shown below:



Experiments were carried out to study the rate of the reaction above.

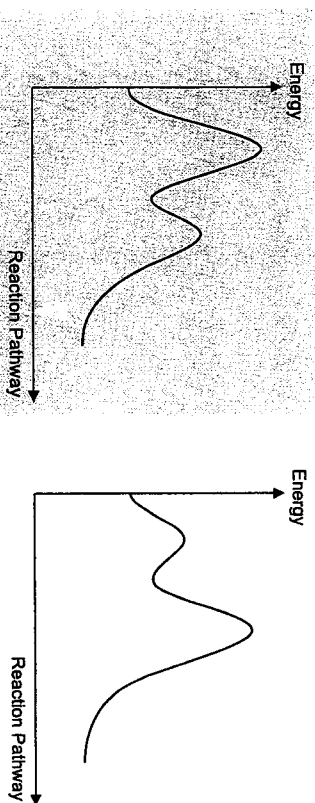
Experiment Number	Initial concentration of CO_2 / mol dm^{-3}	Initial concentration of KOH / mol dm^{-3}	Initial reaction rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.2	0.2	0.0034
2	0.4	0.2	0.0068
3	0.2	0.1	0.0017

Which of the following graphs most likely describes the energy profile of the reaction above?



A

B



Concept: Kinetics (Reaction mechanism and order of reactions)

Answer: C

Comparing Expts 1 and 2, using the inspection method, by keeping concentrations of KOH constant, while doubling the concentration of CO_2 , the rate doubles. Hence, the rate of reaction is directly proportional to $[\text{CO}_2]$. Therefore the reaction is first order wrt CO_2 .

Comparing Expts 1 and 3, using the inspection method, by keeping concentrations of CO_2 constant, while halving the concentration of KOH, the rate is halved. Hence, the rate of reaction is directly proportional to $[\text{KOH}]$. Therefore the reaction is first order wrt KOH.

$$\text{Rate} = k[\text{CO}_2][\text{KOH}]$$

Based on the rate equation, it can be inferred that 1 molecule of CO_2 reacts with 1 molecule of KOH in the rate determining step, i.e. slow step which corresponds to step 1 of the reaction mechanism proposed.

Since the slow step has a high activation energy and is an overall exothermic reaction, therefore the graph reflected corresponds to option C.

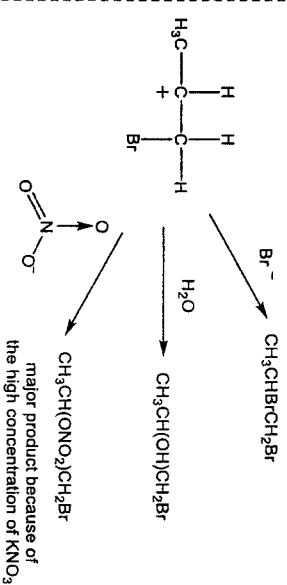
- 16 Aqueous bromine can react with propene in the presence of concentrated potassium nitrate solution.

Which of the following is the major product formed in the reaction?

- A $\text{CH}_3\text{CHBrCH}_2\text{ONO}_2$
 B $\text{CH}_3\text{CHBrCH}_2\text{Br}$
 C $\text{CH}_3\text{CHBrCH}_2\text{OH}$
 D $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{Br}$

Topic: Alkenes

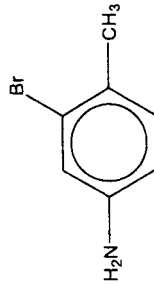
Concept: Electrophilic addition, Markovnikov's rule



In the second step of the reaction, the nitrate ion is preferred relative to water owing to its negative charge.

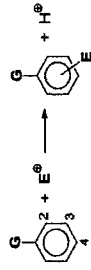
Answer: D

17 Which synthetic route is most likely to lead to the most successful synthesis of the following product from benzene?



- A nitration, bromination, alkylation, reduction
- B nitration, bromination, reduction, alkylation**
- C nitration, alkylation, reduction, bromination
- D alkylation, bromination, nitration, reduction

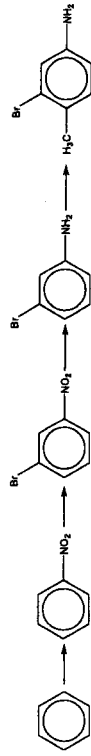
Topic: Arenes
 Concept: Orientating effect of groups in aromatic substitution reactions



G	-alkyl -OR -NH ₂ -NHR or -NR ₂ -NHCO ₂ R	-Cl, -Br, -I	-CHO, -COR -CO ₂ H, -CO ₂ R -NO ₂ -NO ₂ , -CN
Reactivity of ring (compared to benzene)	Activated	Deactivated	Deactivated
Position of E (relative to position of G)	2- and/or 4-	2- and/or 4-	3-

Option A results in a contest between the -NO₂ and -Br groups to determine the position of the -CH₃ group

Option B will result in the best yield because the -NH₂ and -Br groups are both -2,4-directing and will reinforce each other's activating effects on the incoming -CH₃.



Option C results in a contest between the -NO₂ and -CH₃ groups to determine the position of the Br group.

Option D results in a contest between the -Br and -CH₃ groups to determine the position of the NO₂ group.

Answer: B

18

A few drops of 1-chlorobutane, 1-bromobutane, 1-iodobutane were placed separately into three test-tubes each, containing 1.0 cm³ of aqueous silver nitrate at 60 °C.

A hydrolysis reaction occurred. (X is the halogen atom)



Which of the following would be the best explanation for the rate of the reaction?

~~A The bond polarity of C-X bond decreases from C-Cl to C-I.~~

B The bond polarity of C-X bond decreases from C-Cl to C-I.

C The electron deficiency of the carbon atom bonded to X decreases from C-Cl to C-I.

D The solubility of AgX decreases from AgCl to AgI.

Topic: Halogen Derivatives
Concept: Hydrolysis in RX

Answer: A

Bond energy of C-X (kJ mol⁻¹): C-Cl (340) > C-Br (280) > C-I (240).
 The rate of hydrolysis increases from CH₃CH₂CH₂CH₂Cl to CH₃CH₂CH₂CH₂I. The rate of hydrolysis is determined by the bond energy of C-X bond.
 The bond energy of C-X bond decreases from C-Cl to C-I.
 Ease to break the C-X bond increases from C-Cl to C-I.

- 19 Concentrated ammonia was heated in a sealed tube with excess bromoethane. Which of the following product will not be formed?

- A. C₄H₁₀N
 B. C₄H₁₁N
 C. C₆H₁₅N
 D. C₈H₂₀NBr

Topic: Halogen derivatives

Concept: Alkylation of nitrogen compounds



Answer: A

- 20 An alcohol **A** with molecular formula C₄H₁₀O is oxidised by acidified potassium dichromate(VI) under certain conditions to give **B**. The following shows some properties of **B**:
- B** does not produce a yellow precipitate with aqueous alkaline iodine.
 - B** gives a brick-red precipitate when reacted with Fehling's solution.

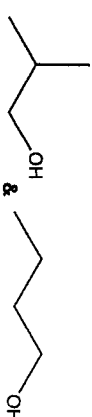
How many isomers of alcohol **A** could result in the observations for **B**?

- A. 1 B. 2 C. 3 D. 4

Concept: Reactions of alcohols

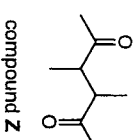
Answer: B

Since product **B** does not produce a yellow precipitate, it can be concluded that **B** does not contain a secondary alcohol with a methyl group.
 Since product **B** gives a brick-red precipitate when reacted with Fehling's solution, an aliphatic aldehyde functional group is present.
 Since aldehydes are formed from controlled oxidation of primary alcohol, the possible structures of primary alcohol from C₄H₁₀O are:



Therefore, there are 2 isomers.

- 21 Compound **Z** shown below is an intermediate used to generate pyrroles which are essential to the production of many different chemicals in the pharmaceutical industry.



Which sentence is correct for compound **Z**?

- A It produces a silver mirror with Tollens' reagent.
 B It decolourises acidified potassium manganate(VII).
 C It produces a yellow precipitate with aqueous alkaline iodine.
 D It does not produce an orange precipitate with 2,4-dinitrophenylhydrazine.

Concept: reactions and distinguishing tests relating to carbonyl compounds

Compound Z is a diketone.

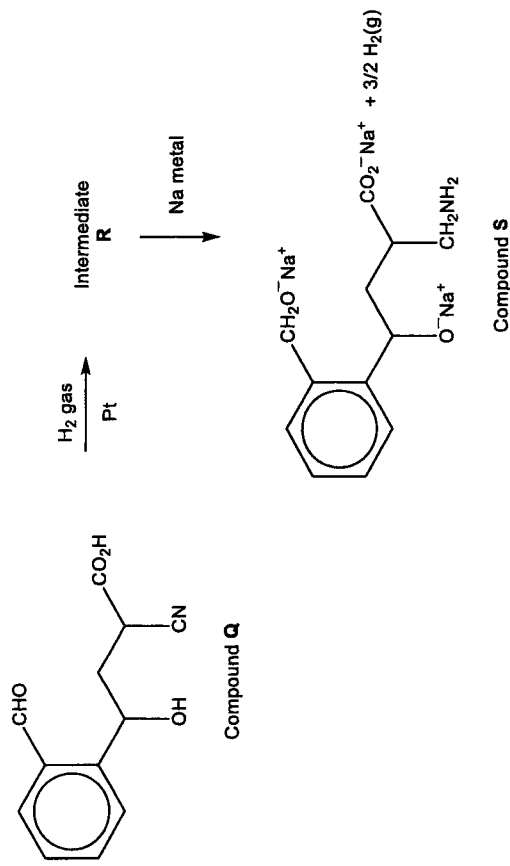
Option A: Incorrect since there is no aldehyde functional group in compound Z and thus cannot give a silver mirror with Tollens' reagent.

Option B: Incorrect since ketone cannot undergo further oxidation.

Option C: Correct since it has $\text{C}=\text{O}$ group and thus able to give a yellow precipitate with alkaline aqueous iodine.

Option D: Incorrect as ketone can undergo condensation with 2,4-DNPH to give an orange precipitate.

Answer: C

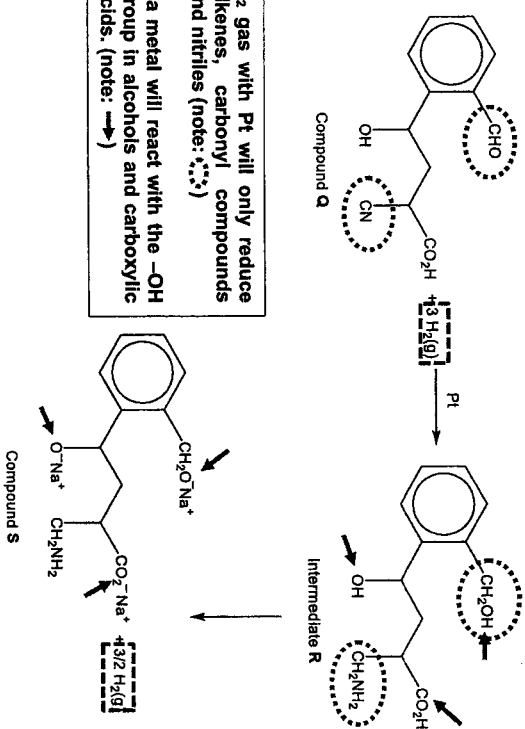


If 96 dm³ of hydrogen gas was reacted with one mole of compound Q, followed by the addition of sodium metal at room temperature and pressure, what is the final gas volume when the reaction was completed? (Given $V_m = 24 \text{ dm}^3 \text{ mol}^{-1}$ at r.t.p.)

- A Gas volume decreases by 36 dm³.
 B Gas volume decreases by 60 dm³.
 C Gas volume increases by 36 dm³.
 D No change in gas volume.

22 Compound S can be obtained via the following 2-step synthesis from compound Q.

Topic: Carbonyl Compounds, Alcohols and Carboxylic Acids
Concept: Reduction of carbonyl compounds and nitriles, redox reaction of -OH group



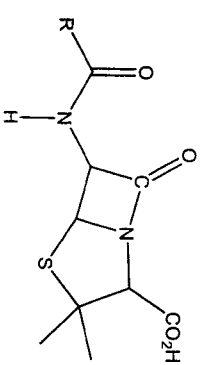
H₂ gas with Pt will only reduce alkenes, carbonyl compounds and nitriles (note: $\text{C}=\text{O}$)

Na metal will react with the -OH group in alcohols and carboxylic acids. (note: $\text{O}-\text{H}$)

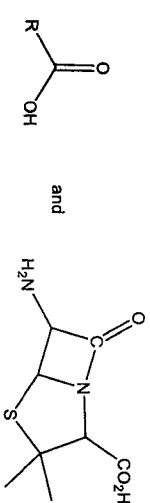
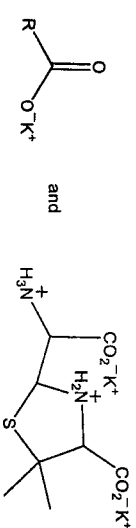
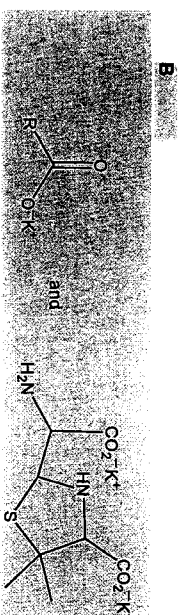
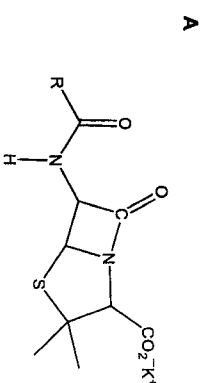
3 mol of H₂ gas was used up for reduction while 1.5 mol of H₂ gas was produced from the redox reaction, hence more H₂ gas was consumed and there will be a decrease in gas volume.
 Change in gas volume = $1.5 \times 24 = 36 \text{ dm}^3$

Answer: A

23 Penicillin is an antibiotic commonly used to treat a number of bacterial infections. The general structure of a penicillin molecule is given below.



What are the products formed when penicillin is boiled with excess aqueous potassium hydroxide?



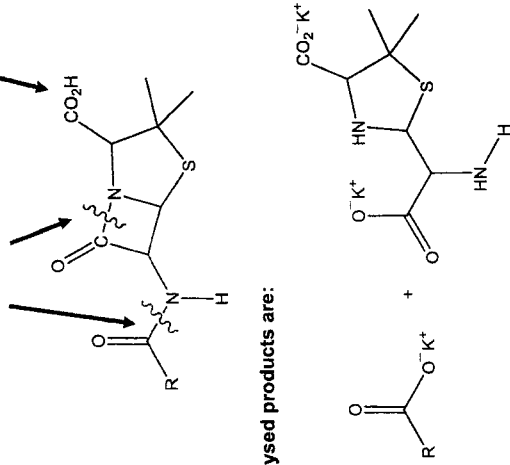
23

Topic: Nitrogen Compounds

Concept: Alkaline hydrolysis of amides

amide bond will undergo hydrolysis

Carboxylic acid will undergo acid-base reaction with alkali

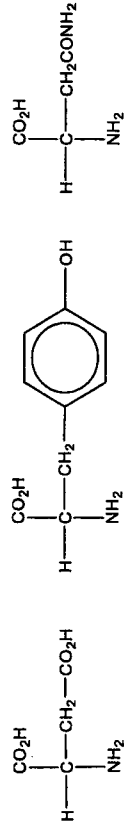


Hence, the hydrolysed products are:

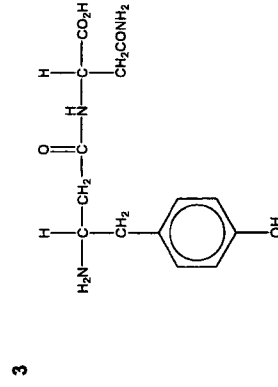
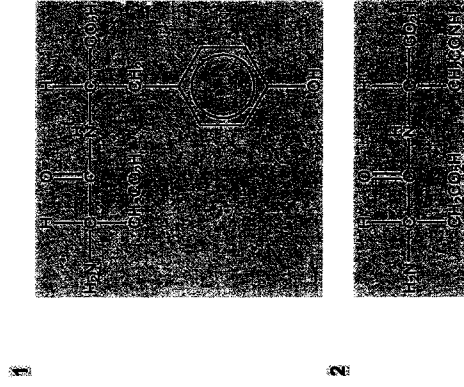
Answer: B

24

24 The following shows the structures of three amino acids.



Which of the following represent the dipeptides formed from these amino acids?



- A 1, 2 and 3
- ~~B 1 and 2~~
- C 1 and 3
- D 2 only

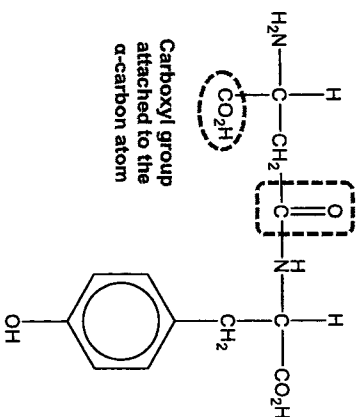
Topic: Nitrogen Compounds

Concept: Formation of peptide bonds

Peptide bonds are formed between the carboxyl group ($-\text{CO}_2\text{H}$) of one amino acid with the amino ($-\text{NH}_2$) group of another amino acid. Both the carboxyl and amino groups are attached to the α -carbon atoms in the amino acids.

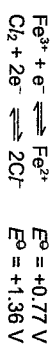
Option 3 is wrong because the carboxyl group in the first amino acid is not attached to the α -carbon atom.

Carboxyl group that is one carbon away from the α -carbon



Answer: B

25 Two electrode potentials are given.



Which species is the strongest reducing agent?

- A Fe^{3+} B Fe^{2+} C Cl_2 D Cl^-

Topic: Electrochemistry

Concept: Using E^{\ominus} to determine strength of oxidising power.

A reducing agent reduces others and it gets oxidised (donates electrons).

The only 2 species undergoing oxidation are Fe^{2+} and Cl^- .

For the species ions to donate electrons, it must be more readily oxidised, i.e. less positive E^{\ominus} value in the data booklet. Thus the only possible answer is B.

Answer: B

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

An electrochemical cell is set up using a $\text{Fe}^{2+}(\text{aq})|\text{Fe}(\text{s})$ half-cell and a $\text{VO}_2^+(\text{aq})|\text{VO}^{2+}(\text{aq})|\text{Pt}(\text{s})$ half-cell.

Which of the following gives a correct effect on the E_{cell} and a correct explanation for the effect when each of the changes is made to the cell separately?

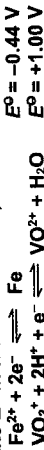
- | | change | effect on E_{cell} | explanation |
|---|---|-----------------------------|--|
| 1 | add $\text{KCN}(\text{aq})$ to the $\text{Fe}^{2+}(\text{aq}) \text{Fe}(\text{s})$ half-cell | increases | concentration of $\text{Fe}^{2+}(\text{aq})$ decreases |
| 2 | add water to the $\text{VO}_2^+(\text{aq}) \text{VO}^{2+}(\text{aq}) \text{Pt}(\text{s})$ half-cell | decreases | concentration of water increases |
| 3 | increase temperature of the $\text{Fe}^{2+}(\text{aq}) \text{Fe}(\text{s})$ half-cell | no change | temperature change does not affect E_{cell} |

- A 1, 2 and 3 B 1 and 2 C 2 and 3 D 1 only

Topic: Electrochemistry

Concept: Finding value of E_{cell} under non standard conditions

From the E° in the Data Booklet,



Fe^{2+}/Fe is the anode (-0.44V) while $\text{VO}_2^+/\text{VO}^{2+}$ is the cathode ($+1.00\text{V}$).

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{red}}^\circ - E_{\text{oxid}}^\circ \\ &= (+1.00) - (-0.44) \\ &= +1.44 \text{ V} \end{aligned}$$

1: Adding KCN to Fe^{2+}/Fe half-cell will result in formation of $[\text{Fe}(\text{CN})_6]^{4-}$ and hence cause $[\text{Fe}^{2+}]$ to decrease. $E_{\text{Fe}^{2+}/\text{Fe}}$ will become more negative as its p.o.e. in equation 1 shifts to the left, hence E_{cell} will become more positive (increases).



2: Adding water to $\text{VO}_2^+/\text{VO}^{2+}$ half-cell will decrease both $[\text{VO}_2^+]$ and $[\text{VO}^{2+}]$. Its p.o.e. shifts to the left as there are more ions on the left. $E_{\text{VO}_2^+/\text{VO}^{2+}}$ becomes less positive, hence E_{cell} will become less positive (decreases).



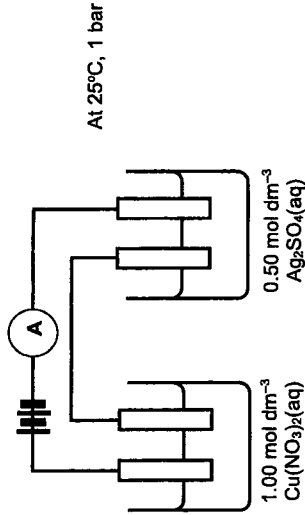
OR concentration of water remains unchanged.

3: E_{cell} changes with temperature unless ΔH of half-cell = 0

Answer: D

27 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.



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 ~~0.85~~

Topic: Electrochemistry

Concept: Electrolysis

Relevant mole ratio: $\text{Cu} \equiv 2e$ (from Cu^{2+}) and $\text{Ag} \equiv e$ (from Ag^+)

Since same current pass through in t minutes, same amount of electrons passed (notice this is INDEPENDENT of the initial concentrations of the solutions) to find mole ratio between Cu and Ag formed,
 $\text{Cu} \equiv 2e$ and $2\text{Ag} \equiv 2e$ so $\text{Cu} \equiv 2\text{Ag}$

Ratio of mass of Ag to mass of Cu = $2 \times 107.9 : 63.5 = 3.40$

Answer: D

- 28 A current of 10 A is passed for 150 minutes through molten aluminium oxide using inert electrodes.

What will be the approximate volume of gas liberated, measured at s.t.p.?

- A 0.089 dm³ B 5.3 dm³ C 5.6 dm³ D 11.2 dm³

Topic: Electrochemistry

Concept: Electrolysis

Using $Q = It$,

$$Q = 10 \times 150 \times 60 \\ = 90\,000\text{ C}$$

$$\text{No. of Faradays} = \frac{90\,000}{9.65 \times 10^4} = 0.9326\text{ F}$$

In molten aluminium oxide, no water is present, so the oxygen gas liberated is from Al_2O_3 . The oxide ion in Al_2O_3 is O^{2-} .



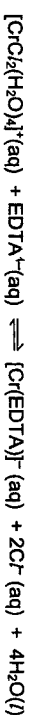
Since $\text{O}_2 \equiv 4\text{e}$,

4 F liberates 1 mol of O_2 gas
0.9326 F liberates 0.2332 mol of O_2 gas

$$\text{Vol of } \text{O}_2 \text{ gas} = 0.2332 \times 22.7 \text{ dm}^3 = 5.29 \text{ dm}^3$$

Answer: B

- 29 EDTA⁴⁻(aq) solution is added dropwise until in excess to a solution of $[\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_4]^{2-}$. The equilibrium constant for this reaction is greater than 1 and the equation for the reaction is as shown below.



Which one of the following statements about the above reaction is correct?

- A There is no change in colour of the solution after addition of EDTA⁴⁻.
B $[\text{Cr}(\text{EDTA})]^{2-}$ is a less stable complex ion than $[\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_4]^{2-}$.
C Both $[\text{Cr}(\text{EDTA})]^{2-}$ and $[\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_4]^{2-}$ are octahedral complexes.
D The above is a redox reaction.

Topic: Transition Metals

Option A is incorrect:

The colour of a transition metal complex depends on the energy gap, ΔE . The energy gap, ΔE , in turn depends on the nature of the ligands.

Different ligands split the energy level of d orbitals to different extent.

⇒ Amount of energy, ΔE , absorbed by d electron in d-d transition differ.

⇒ Colour of transition metal complex solution would change with different ligands used.

⇒ There would be color of the solution will lighten after adding EDTA⁴⁻.

Option B is incorrect:

It is given that the equilibrium constant for the above reaction is more than 1,

⇒ Concentration of $[\text{Cr}(\text{EDTA})]^{2-}$ > concentration of $[\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_4]^{2-}$

⇒ $[\text{Cr}(\text{EDTA})]^{2-}$ is more stable than $[\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_4]^{2-}$.

Option C is correct:

For $[\text{Cr}(\text{C}_2\text{H}_2\text{O}_4)_4]^{2-}$, the central Cr^{3+} ion has 6 bond pairs. Hence, it is an octahedral complex.

EDTA⁴⁻ is a hexadentate ligand that forms only six dative bonds with the central metal cation. Hence, the central Cr^{3+} ion in $[\text{Cr}(\text{EDTA})]^{2-}$ has 6 bond pairs. It is an octahedral complex.

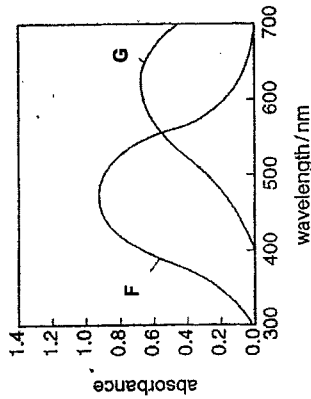
Option D is incorrect:

The above reaction does not involve any change in the oxidation no of the elements involved. Hence, it is not a redox reaction. Instead, it is a ligand exchange reaction.

Answer: C

30 The absorbance of a solution at a particular wavelength is proportional to the concentration of ion responsible for the absorption.

The visible spectra of solutions of two transition metal complexes **F** and **G** are shown in the diagram below. Both complexes contain the same transition metal ion.



Given that energy is inversely proportional to wavelength and the visible region of the electromagnetic spectrum is as follows:

violet	blue	green	yellow	orange	red
400	500	600	700		

Which of following statements can be deduced from the spectra?

- Complex **F** is likely to be red while complex **G** is likely to be blue.
 - The energy gap in complex **F** is greater than that in complex **G**.
 - The K_c value for the formation of complex **F** is higher than the K_c value for formation of complex **G**.
- A** 1, 2 and 3 are correct
B 1 and 2 only are correct
C 2 and 3 only are correct
D 1 only is correct

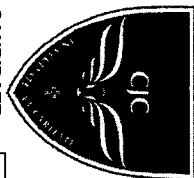
Topic: Transition Metals

Option 1 is correct as Complex **F** absorbed light of lower wavelength (green) and the complementary colour (red) is observed. Complex **G** absorbed light of higher wavelength (orange) and the complementary colour (blue) is observed.

Option 2 is correct as Complex **F** absorbed light of lower wavelength and thus ΔE is larger (since $\Delta E \propto 1/\lambda$) than that of Complex **G**. This means that the ligand in **F** is a stronger field ligand than that in complex **G**.

Option 3 is wrong as we cannot determine K_c value base on individual absorption curve. We can determine the magnitude of K_c value only if we are looking at a mixture absorption curve whereby there is equal amount of both ligands.

Ans: B



Catholic Junior College
JC2 Preliminary Examination
Higher 2

CANDIDATE
NAME

CLASS

ZT

CHEMISTRY

Paper 2 Structured Questions

26 August 2022

9729/02

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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

**MARK SCHEME WITH
EXAMINER'S
COMMENTS**

For Examiner's Use	
Paper 1	30
Q1	/13
Q2	/11
Q3	/15
Q4	/12
Q5	/11
Q6	/13
Paper 2	75
Paper 3	80
Paper 4	55
OVERALL (100%)	
GRADE	

This document consists of 20 printed pages.

Turn over

- 1 (a) Fehling's solution is used in Qualitative Analysis of organic compounds.
It is prepared fresh by mixing a solution of CuSO_4 (Fehling's A solution) with a mixture of tartrate ions and NaOH (Fehling's B solution). When the two solutions are mixed, the tartrate ions act as ligands to form a complex ion with the Cu^{2+} ions.

(i) Another reagent with similar action to Fehling's solution is Benedict's solution, which is also an alkaline solution of Cu^{2+} , but the ligand forming the complex ion is citrate ion instead of tartrate ion.
Suggest why the presence of the ligand is necessary in Fehling's (and Benedict's) solution.

Without the ligand to form the complex ion, Cu^{2+} ions would precipitate out as $\text{Cu}(\text{OH})_2$ due to the NaOH present.

EXAMINER'S COMMENTS

Qualitative Analysis – Precipitation of insoluble metal hydroxides in $\text{NaOH}(\text{aq})$

In this question, students were expected to note that Cu^{2+} ions were being mixed with a solution of NaOH (and tartrate or citrate ions), and use their QA knowledge to predict that a blue precipitate of $\text{Cu}(\text{OH})_2$ would result – which does not occur, and this must be due to the formation of the copper(II) complex with tartrate or citrate, which brings the Cu^{2+} down such that ionic product of $\text{Cu}(\text{OH})_2$ does not exceed its K_{sp} .

The question was poorly answered. Most students instead resorted to a template explanation of the origin of colour in transition metal complexes or stated that the ligand is necessary for the observation of colour in the distinguishing test (which does not make sense as Cu^{2+} itself is a coloured ion – due to the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex which already exists in $\text{CuSO}_4(\text{aq})$, i.e., without the need for tartrate or citrate ligands!

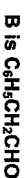
Fehling's solution was used to distinguish between three unknown compounds, A, B and C:

Compound	Observation with Fehling's solution
A	blue solution
B	red ppt
C	blue solution

It is known that compounds A, B, and C are the following (not necessarily in order):



(ii) Based on the above observations, state the identity of compound B.



[1]

EXAMINER'S COMMENTS

Fehling's Solution – test for aliphatic aldehydes

As Fehling's solution gives a red ppt only for aliphatic aldehydes, only $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ will give a positive result. The aromatic aldehyde $\text{C}_6\text{H}_5\text{CHO}$ will not give a red ppt, neither will the ketone $\text{C}_6\text{H}_5\text{COCH}_3$. The observation is blue solution for these two compounds, since Fehling's solution is blue in colour.

A handful of students responded with Cu_2O , which showed poor comprehension ability.

- (iii) Give a simple chemical test to distinguish compounds A and C. In your answer, the observations for each compound must be stated.
- To a sample of each compound (A and C) in separate test tubes, add Tollens' reagent and heat.
- C_6H_5CHO would give a silver mirror while there would be no silver mirror.
- for $C_6H_5COCH_3$.

EXAMINER'S COMMENTS

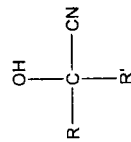
A significant number of students had the incorrect idea that the compounds were presented in order of A, B, C, in spite of the question stating that the compounds were not necessarily in this order. These students referred to the observations for each compound as "A would give [observation] while C would give [observation]". A number of students even referred to compound B instead of C for this question!

Students who gave the ketone in (ii) would not be able to distinguish the remaining aldehydes (since the only reagent that can do so, Fehling's solution, was already used in the question).

Some students missed out the "heat" condition (or gave "heat under reflux" when reflux is not suitable for distinguishing test) or did not specify the acid used with $K_2Cr_2O_7$. Others, in spite of clear instructions (which need not be stated), did not properly give the observation for the compound with the negative test.

Students are to note that " $KMnO_4(aq)/H_2SO_4(aq)$, heat" was generally not accepted because the ketone given in this question, phenylethanone, is a special ketone that can be oxidized by $KMnO_4$ (see Carbonyl Compounds lecture notes, pg 15-18).

- 1 (a) Compounds A, B and C are all able to form hydroxynitriles when subject to the same reagents and conditions.



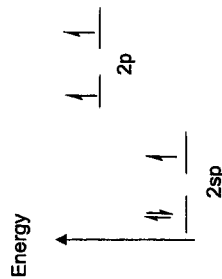
- (iv) State the reagents and conditions required for the above transformation.
- HCN, trace NaOH (or trace NaCN), 10-20 °C

EXAMINER'S COMMENTS

Carbonyl Compounds – Nucleophilic Addition

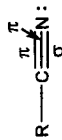
This was a basic question with a very generic compound, testing on whether students were able to correctly recall the reagents and conditions for nucleophilic addition of HCN to carbonyl compounds (aldehydes & ketones). Finer details that were missed out include the use of trace amounts of either NaOH or NaCN to generate the CN⁻ nucleophile (only small amounts needed as it is regenerated – a catalyst), and the temperature conditions (a handful failed to mention which temperature scale – Celsius or Fahrenheit?, while others wrote "heat").

- (v) The N atom of the nitrile group is sp hybridised. Complete the energy level diagram to show how the electrons are arranged in the second quantum shell of the N atom so that the bonding in the nitrile can occur.



EXAMINER'S COMMENTS

Chemical Bonding – hybridization, overlap of atomic orbitals in bonding



The N atom in the nitrile forms 1 σ bond and 2 π bonds with C atom. The two unhybridized p orbitals are used to form these π bonds, and one of the sp hybrid orbitals is used to form the σ bond. Since the formation of these three bonds involves contribution of one electron each from N and C atoms, there should be one electron (i.e., from N atom) in each of these orbitals in the diagram. The remaining two electrons of N atom's five valence electrons will go into the remaining orbital, which is an sp hybrid orbital, to form the lone pair of electrons.

- (vi) Hence, suggest why nitriles are weaker bases than amines, given that N atom in amine is sp^3 hybridised.

The lone pair of electrons on N of the nitrile is less available to accept H^+ because it is located in an sp hybrid orbital, which is held closer to the nucleus than the corresponding lone pair of electrons on N of the amine, which is located in an sp^3 hybrid orbital (or accept p orbital).

EXAMINER'S COMMENTS

Basicity – availability of lone pair of electrons on N atom

Note that for base dissociation, the OH^- comes from the water molecule of the solvent, as the base acts as proton (H^+) acceptor by using its lone pair of electrons to form a dative bond:



This question was poorly answered. In the first place, many students failed to even focus their explanation on the availability of the lone pair of electrons on N atom as the indication of basic strength. Common errors included comparing strength or number of covalent bonds to be broken to release OH^- (covalent bonds in the amine/nitrile are NOT broken), confusing basicity with acidity explanation by referring the dispersal of negative charge, vague references to electron density without reason nor direct reference to the lone pair of electrons on N, etc. The clue was given to students to use info from (v) (sp hybridisation of nitrile N) and (vi) (sp³ hybridisation of amine N) consider how hybridization affects the availability of the lone pair of electrons. Students had to make use of the % s or % p character to make their deduction. (The lower energy level of sp orbital due to its greater s character was also accepted reasoning.)

(b) Most of the world's copper comes from the mining of copper-containing minerals. Copper ions exist as either one of the two oxidation states, +1 or +2. Two examples of such minerals are bornite and chalcopyrite.

(i) Bornite has the chemical formula Cu_3FeS_4 . Given that the oxidation state of S is -2 in bornite, write down the oxidation states of Cu and Fe in bornite.

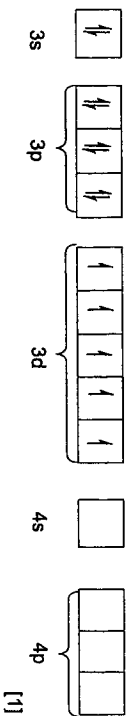
Oxidation state of Cu:+1

Oxidation state of Fe:+3

EXAMINER'S COMMENTS
Redox – Oxidation states in compound

This question was well done.

1 (b) (ii) Complete the diagram to show the arrangement of electrons in the third and fourth principal quantum shells of the ion of Fe in bornite.



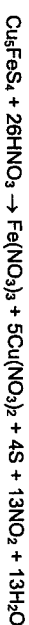
EXAMINER'S COMMENTS
Electronic configuration of Fe^{3+}

This question was not so well done. Many of the incorrect responses did not follow the correct order of removing electrons from Fe atom to form Fe^{3+} ion, and thus ended up with electrons still in the 4s orbital. Some responses paired up the 3d electrons as if there was a low spin state, when no such information was given in the question – there is no need to consider low/high spin! Some incorrect responses did not even have the correct number of electrons, with some filling up even the 4p subshell.

Chalcopyrite is also composed of the elements Cu, Fe and S. Let the chemical formula of chalcopyrite be $\text{Cu}_x\text{Fe}_y\text{S}_z$.

Both bornite and chalcopyrite react with HNO_3 to give sulfur precipitate and NO_2 gas.

(iii) The balanced equation for the reactions of bornite and chalcopyrite with HNO_3 are as follows:



$\text{Cu}_x\text{Fe}_y\text{S}_z + (6 + 4x)\text{HNO}_3 \rightarrow \text{Fe}(\text{NO}_3)_3 + x\text{Cu}(\text{NO}_3)_2 + y\text{S} + (3 + 2x)\text{NO}_2 + (3 + 2x)\text{H}_2\text{O}$
When 1 mole each of bornite and chalcopyrite were fully reacted with HNO_3 , bornite produced 64.2 g more sulfur precipitate and $1.92 \times 10^6 \text{ cm}^3$ more nitrogen dioxide than chalcopyrite, at room temperature and pressure.

Determine the values of x and y.

Sulfur precipitate:

$$4 - y = \frac{64.2}{32.1}$$

$$\therefore y = 2$$

NO_2 gas:

$$13 - (3 + 2x) = \frac{1.92 \times 10^6}{24000}$$

$$10 - 2x = 8$$

$$\therefore x = 1$$

[3]

EXAMINER'S COMMENTS

Mole Concept & Stoichiometry – mole ratio, mass \rightarrow mol conversion and volume \rightarrow mol conversion.

Students experienced varying degrees of success in attempting this question. Firstly, there were quite a number of students who did not identify bornite (Cu_3FeS_4 – first mentioned in (b)(i)) and chalcopyrite ($\text{Cu}_x\text{Fe}_y\text{S}_z$ – first mentioned just above (c)) correctly. Secondly, the fact that bornite produced more sulfur ppt and NO_2 gas than chalcopyrite! These were crucial to obtaining the correct relationships to solve for x and y. Conversion-wise, students found it tougher to handle the NO_2 volume which was in cm^3 than the S ppt mass in g.

[Total: 13]

2 A sodium-vapor lamp is a gas-discharge lamp that uses sodium in an excited state to produce light at a characteristic wavelength near $5.89 \times 10^{-7} \text{ m}$. Low-pressure sodium lamps are highly efficient electrical light sources but due to their yellow light, they are widely used as street lamps. The yellow light is produced by an excited electron in a sodium atom falling from a 3p orbital to the 3s orbital. The wavelength for this transition is $5.898 \times 10^{-7} \text{ m}$.

The energy, E (in joules), corresponding to the light of wavelength, λ (in metre), is given by the following equation:

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant = $6.63 \times 10^{-34} \text{ J s}$

c is the speed of light = $3.00 \times 10^8 \text{ m s}^{-1}$

(a) State the electronic configuration of a sodium atom in the ground state.

Na: $1s^2 2s^2 2p^6 3s^1$

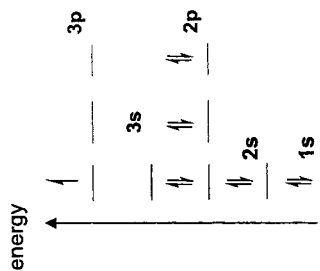
[1]

EXAMINER'S COMMENTS

The question was well answered.

A few candidates identified wrongly that the number of electrons equal to the atomic mass of Na (23.0).

- (b) Draw an energy level diagram to show the electron configuration of a sodium atom in an excited state that produces yellow light.



[1]

EXAMINER'S COMMENTS

The question was not so well attempted. Many candidates failed to identify the information given in the question – "The yellow light is produced by an excited electron in a sodium atom falling from a 3p orbital to the 3s orbital."

Examples of some incorrect responses:

- Drew the energy level diagram of the electronic configuration of Na atom in the ground state.
- Did not label the orbitals properly.
- Having a total of 12 electrons in the orbitals instead of 11 electrons.

- (c) Calculate the energy of the yellow light in

(i) J (per atom)

(ii) kJ mol⁻¹

(i) Energy, $E = \frac{(6.63 \times 10^{-34})(3.00 \times 10^8)}{5.898 \times 10^{-7}}$

$= 3.37 \times 10^{-19} \text{ J}$

(ii) Energy = $3.37 \times 10^{-19} \times 6.02 \times 10^{23}$

$= 2.03 \times 10^5 \text{ J mol}^{-1}$

$= 203 \text{ kJ mol}^{-1}$

[2]

EXAMINER'S COMMENTS

Some candidates chose the wrong data and substituted into the equation in Part (i), e.g. used 5.89 instead of 5.898.

In Part (ii), candidates did not multiply by Avogadro Constant and the value of Avogadro Constant can be obtained by the Data Booklet.

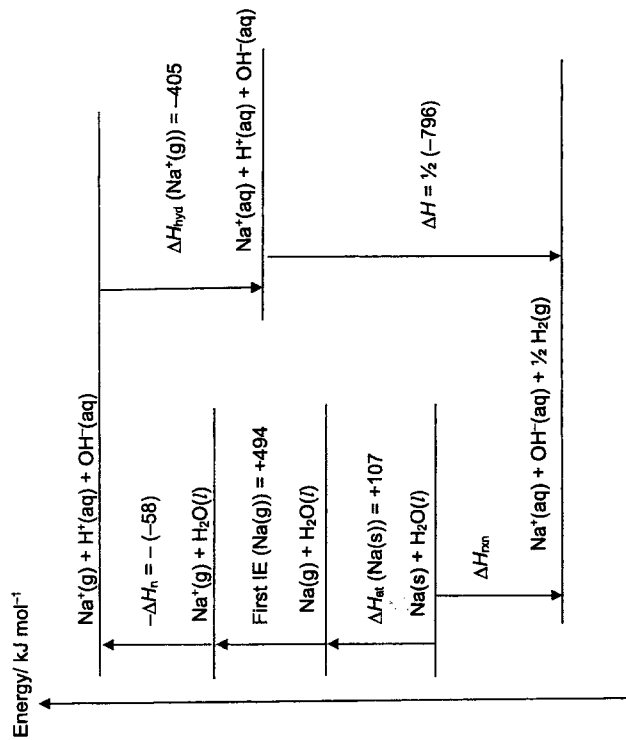
- 2 (d) Sodium can react with water to form aqueous sodium hydroxide.



The following data will be useful in this question.

Enthalpy change of atomisation of Na(s)	= +107 kJ mol ⁻¹
Enthalpy change of neutralisation	= -58 kJ mol ⁻¹
Enthalpy change of hydration of Na ⁺ (g)	= -405 kJ mol ⁻¹
Enthalpy change of 2H ⁺ (aq) → H ₂ (g)	= -796 kJ mol ⁻¹

Construct a fully labelled energy level diagram to determine the enthalpy change for the above reaction using relevant data from the above list, together with relevant data from the Data Booklet.



Enthalpy change, $\Delta H_{\text{rxn}} = +107 + 494 + 58 + (-405) + \frac{1}{2}(-796)$
 $= -144 \text{ kJ mol}^{-1}$

[5]

EXAMINER'S COMMENTS
This question was not well attempted.

Examples of incorrect responses:

- Wrongly identified the product of ΔH_{m} of Na(s), e.g. Na^(g)
 - Did not give or the wrong state symbols for some of the species
 - Could not recognise the equation of the enthalpy change of neutralisation. The correct equation should be $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ with the value of -58 kJ mol^{-1} .
 - Wrong direction of arrow to represent the change in energy was given.
- Candidates failed to recognise that \uparrow represent the endothermic process with positive ΔH and \downarrow represent the exothermic process with negative ΔH . Only \uparrow and \downarrow are accepted in energy level diagram.
- A number of candidates chose the wrong data from the Data Booklet, e.g. bond energy of O-H in the process of $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$. This shows that candidates still have not internalised the definition of some of the enthalpy changes.

- 2 (e) The melting point of Na is 98°C , whereas that of NaOH is 318°C . Explain, in terms of structure and bonding, the differences in melting point between them.

Na has giant metallic structure with metallic bonding and NaOH has giant ionic lattice structure with ionic bonding.

Larger amount of energy is required to overcome the stronger electrostatic forces of attraction/ionic bonding between Na^+ and OH^- ions than the weaker electrostatic forces of attraction/metallic bonding between Na^+ cation and sea of delocalised electrons.

[Total: 11]

EXAMINER'S COMMENTS

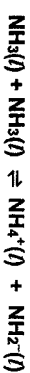
This question was well attempted.

Examples of incorrect responses:

- Did not describe the metallic bonding and ionic bonding.
- Failed to recognise the structures of Na and NaOH.
- Identified wrongly that NaOH contains hydrogen bonding, ion-dipole interactions, permanent dipole-permanent dipole attractions.
- Used the wrong words to describe the bonding, e.g. intermolecular or between NaOH molecules.
- Did not state the factor of affecting the difference in the melting point which was the strength of the bonding.
- Used lattice energy to compare the strength of metallic bonding and ionic bonding. Some candidates failed to recognise that the lattice energy is only used to compare the strength of ionic bonding between ionic compounds.

- 3 (a) Liquid ammonia, like aqueous ammonia is a conductor of electricity, but a very weak one. Liquid ammonia can exhibit this property as it can undergo self-ionisation.

- (i) Write an equation between two ammonia molecules to show this property of liquid ammonia.



[1]

- (ii) Identify the two different conjugate acid-base pairs in the reaction occurring in (a)(i).

Acid: NH_3 conjugate base: NH_2^-

Base: NH_3 conjugate acid: NH_4^+

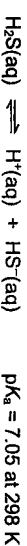
[1]

EXAMINER'S COMMENTS

Many candidates thought wrongly that the equation was meant for $\text{NH}_3(\text{aq})$ rather than $\text{NH}_3(\text{l})$. Therefore, no water must be included. Many gave NH_2^- as the conjugate base rather than NH_2^- .

For (ii), candidates need to specify which is the acid and its associated conjugate base or which is the base and its associated conjugate acid. Failure to do so that would result in penalty.

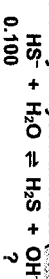
- (b) Hydrogen sulfide can act as a weak acid.



- (i) NaHS is a basic salt that undergoes salt hydrolysis. Calculate the pH of $0.100 \text{ mol dm}^{-3} \text{ NaHS}(\text{aq})$.



The anion is then hydrolysed in water (salt hydrolysis).



0.100

?

$$[\text{OH}^-] = \sqrt{K_{\text{b}} \times 0.100}$$

$$= \sqrt{\frac{K_{\text{w}}}{K_{\text{a}}} \times 0.100}$$

$$= \left(\frac{10^{-14}}{10^{-7.05}} \times 0.100 \right)^{1/2}$$

$$= 1.059 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = 14 - \text{pOH}$$

$$= 14 - [-\log(1.059 \times 10^{-4})]$$

[2]

EXAMINER'S COMMENTS

Surprisingly, many candidates failed to recognise that the Q asked for salt hydrolysis (anion hydrolysis in this case). Therefore, a basic pH was to be expected!

- (ii) The pK_a for C_6H_5SH is 6.5. Suggest an explanation for the different pK_a values for H_2S and C_6H_5SH .



For the anion or the conjugate base, $C_6H_5S^-$, the lone pair of electrons on S atom can be delocalised into the benzene ring, dispersing the negative charge on the anion and so stabilises it. This makes it less ready to accept protons. Therefore, C_6H_5SH is more acidic than H_2S and so has a lower pK_a value than H_2S . [1]

EXAMINER'S COMMENTS

Failure by candidates to indicate the lone pair of electrons on S atom specifically, rather than just electrons that could be delocalised into the benzene ring and therefore dispersing the negative charge on the conjugate base, anion $C_6H_5S^-$, resulted in penalty.

- 3 (c) A solution containing hydrogensulfite ions, HSO_3^- (aq), and sulfite ions, SO_3^{2-} (aq), can act as a buffer. The K_a of HSO_3^- (aq) is $6.73 \times 10^{-8} \text{ mol dm}^{-3}$ at 298 K.

A buffer solution is prepared by mixing 50.0 cm^3 of $0.500 \text{ mol dm}^{-3} \text{ NaHSO}_3$ and 25.0 cm^3 of $0.600 \text{ mol dm}^{-3} \text{ NaOH}$.

By finding $[SO_3^{2-}]$ and $[HSO_3^-]$ after mixing NaHSO_3 and NaOH , calculate the pH of the buffer solution formed at 298 K. Show your working clearly.



$$\text{Amount of } HSO_3^- = \frac{50.0}{1000} \times 0.500 = 0.0250 \text{ mol}$$

$$\text{Amount of } OH^- = \frac{25.0}{1000} \times 0.600 = 0.0150 \text{ mol}$$

$$\text{Amount of } HSO_3^- \text{ left after reaction} = (0.0250 - 0.0150) = 0.0100 \text{ mol}$$

$$\text{Amount of } SO_3^{2-} \text{ formed} = 0.0150 \text{ mol}$$

$$[SO_3^{2-}] = (0.0150 \times \frac{1000}{75.0}) = 0.200 \text{ mol dm}^{-3}$$

$$[HSO_3^-] = (0.0100 \times \frac{1000}{75.0}) = 0.133 \text{ mol dm}^{-3}$$

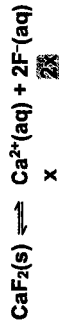
$$\begin{aligned} \text{pH} &= pK_a + \lg \left(\frac{[\text{salt}]}{[\text{acid}]} \right) \\ &= -\lg (6.73 \times 10^{-8}) + \lg \left(\frac{0.200}{0.133} \right) \\ &= 7.35 \end{aligned}$$

EXAMINER'S COMMENTS

A majority of candidates were not able to calculate the $[HSO_3^-]$ and $[SO_3^{2-}]$ correctly! And surprisingly, though the Q stated that the resulting mixture is a buffer solution three times (!), still, a majority of candidates failed to use the buffer equation to calculate the pH of the solution!

- (d) Calcium fluoride, CaF_2 , occurs naturally in the mineral *fluorspar*. It is the major sources of fluorine for the chemical industry, for making polymers (PTFE), freons and fire retardants. It is also sparingly soluble in water. In its saturated solution, the concentration of CaF_2 is $2.30 \times 10^{-4} \text{ mol dm}^{-3}$.

- (i) Write an expression for the solubility product, K_{sp} , of calcium fluoride, and calculate its value.



where $x = 2.30 \times 10^{-4} \text{ mol dm}^{-3}$

$$\begin{aligned} K_{sp} &= [\text{Ca}^{2+}][\text{F}^{-}]^2 \\ &= (x)(2x)^2 = 4x^3 \\ &= 4(2.30 \times 10^{-4})^3 \\ &= 4.87 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} \end{aligned}$$

[2]

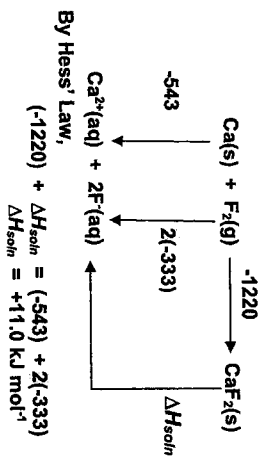
EXAMINER'S COMMENTS

A rather common error was to write $K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$ However, many students were not able to calculate a value for the K_{sp} ! Failure to multiply the concentration of F^{-} by 2 was common! And this resulted in the wrong calculated value of the K_{sp} ! Worse still, quite a number of candidates could not give the correct expression for the K_{sp} of CaF_2 ! Expression such as $K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$ or $K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$ given by candidates were not uncommon! It was simply amazing!

- 3 (d) (ii) Use only the relevant data provided below to calculate a value for the enthalpy change of solution of calcium fluoride.

enthalpy change of formation of $\text{CaF}_2(\text{s})$	$-1220 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of $\text{Ca}(\text{s})$	$+178 \text{ kJ mol}^{-1}$
enthalpy change of formation of $\text{Ca}^{2+}(\text{aq})$	-543 kJ mol^{-1}
electron affinity of fluorine atoms	-328 kJ mol^{-1}
enthalpy change of formation of $\text{F}^{-}(\text{aq})$	-333 kJ mol^{-1}

Students can use either use the energy cycle method or direct application of formula to solve this question but only making use of the relevant data given. Full credit should be given for both methods.



$$\begin{aligned}
 \Delta H_{\text{soln}} &= \sum(\Delta H_{\text{f(products)}}) - \sum(\Delta H_{\text{f(reactants)}}) \\
 &= [-543 + 2(-333)] - [-1220] \\
 &= +11.0 \text{ kJ mol}^{-1}
 \end{aligned}$$

[2]

EXAMINER'S COMMENTS

A common mistake made by candidates was to use ALL the data provided through the Q asked for the use of only the relevant data provided! Worse, many candidates also used even more data from the DBI As a result, the energy cycle drawn were irrelevant and confusing! No credit given here. This part of the Q was poorly done! Candidates must be informed and made aware of the use of relevant information only, based on the context of the Q asked!

(iii) Hence, predict whether CaF₂ will be more, or less, soluble in hot water than in cold water.

Since the enthalpy change of solution of CaF₂ is endothermic, it follows

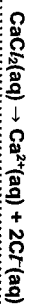
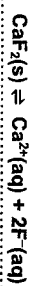
that the solubility will increase at a higher temperature; so it will be more

soluble in hot water. [1]

EXAMINER'S COMMENTS

Failure of candidates to provide reasons for the solubility of CaF₂ was penalised. Candidates have to take note of the words predict and hence! Predict is associated with giving a reason or explanation for the answer given and hence means based on the answer given in (ii). The expression, endothermic was required to obtain a mark!

3 (d) (iv) Describe and explain how the solubility of CaF₂ is affected when CaCl₂(aq) is added.



Adding CaCl₂ increases [Ca²⁺], so that the position of equilibrium

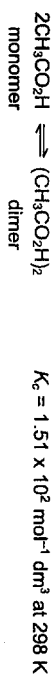
(POE) above (first equation) shifts to left due to the common ion effect. [1]

The solubility will decrease.

EXAMINER'S COMMENTS

Practically, almost all candidates failed to indicate the equation, $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$, when they wrote the position of equilibrium shifted to the left! No credit awarded here for their failure to do so!

(v) In non-polar solvents, ethanoic acid, CH₃CO₂H, can form a dimer containing two hydrogen bonds.



I A solution of 0.100 mol dm⁻³ CH₃CO₂H is allowed to reach equilibrium in a non-polar solvent at 298 K. The equilibrium concentration of the dimer is 0.0417 mol dm⁻³. Calculate the $\frac{[(\text{CH}_3\text{CO}_2\text{H})_2]}{[\text{CH}_3\text{CO}_2\text{H}]}$ ratio at equilibrium. Quote your answer to 3 significant figures.



Initial / mol dm⁻³ 0.100 0

Change / mol dm⁻³ $-2(0.0417)$ $+0.0417$

Equilibrium/ mol dm⁻³ $0.100 - 2(0.0417)$ 0.0417

$= 0.0166$

$$\frac{[(\text{CH}_3\text{CO}_2\text{H})_2]}{[\text{CH}_3\text{CO}_2\text{H}]^2} = \frac{0.0417}{0.0166} = 2.51$$

[1]

EXAMINER'S COMMENTS

Poorly done by candidates! The use of the K_c value provided to arrive at the answer of the ratio asked was necessary! Again, it had to be emphasised as in (d)(ii) that not all data given had to be used! However, some candidates did use the K_c value to calculate for the ratio. Full credit was given to those candidates too!

- II Suggest how the ΔG for this equilibrium in an aqueous solution would differ from the ΔG in a non-polar solvent. Explain your answer. [1]

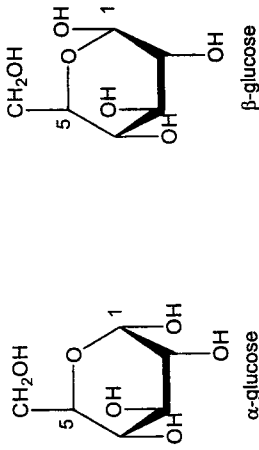
In an aqueous solution (polar water), ethanoic acid can dissociate partially into ions. In addition, hydrogen bonds can be formed between water and ethanoic acid, so decreases the feasibility of dimerisation. Therefore, ΔG will be less negative or even positive in an aqueous solution. The POE above is very much to the left. [Total: 15]

EXAMINER'S COMMENTS

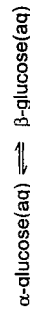
Also, poorly done by candidates! A variety of answers were given by candidates, mostly vague and unconvincing! A mere mention that in an aqueous solution (polar solvent), there is possibility of ethanoic acid dissociating into its ions or that H-bonding between it and water takes place and as a result, dimerisation of the monomer is limited, would suffice! And the corresponding effect on ΔG .

Many candidates thought incorrectly that if a reaction was spontaneous then ΔG should be positive!

- 4 D-glucose can exist in two isomers as α -glucose and β -glucose. In α -glucose, the $-\text{OH}$ group attached to carbon 1 and the $-\text{CH}_2\text{OH}$ group at carbon 5 are in a trans arrangement (opposite of the plane), while in β -glucose, the two groups are in a cis arrangement (same side of the plane).



Each of these isomers can be synthesised and isolated as pure compounds. The α -glucose has an angle of optical rotation of $+112^\circ$ while the β -glucose has an angle of optical rotation of $+19^\circ$. When either one of the isomers is dissolved in water, the α and β isomers slowly interconvert until equilibrium is established. The optical rotation changes over time and reaches $+52.5^\circ$.



- (a) Given that the optical rotation is directly proportional to the concentration of each isomer of glucose, show that the ratio of the α -glucose to β -glucose in the equilibrium mixture is 36 to 64.

Let x to be the percentage of the α -glucose

$$\frac{x}{100} (+112) + \frac{100-x}{100} (+19) = +52.5$$

$$x = 36.0$$

α -glucose : β -glucose = 36 : 64 (shown) [1]

EXAMINER'S COMMENTS

This question was not well attempted. $+52.5^\circ$ is the average optical rotation of α -glucose to β -glucose in the equilibrium mixture.

- (b) Write an expression for K_c .

$$K_c = \frac{[\beta\text{-glucose}]}{[\alpha\text{-glucose}]}$$

[1]

EXAMINER'S COMMENTS

This question was well attempted.

- (c) At higher temperature, the optical rotation is greater than $+52.5^\circ$. Deduce whether the forward reaction is exothermic or endothermic.

The optical rotation is greater than $+52.5^\circ$; this shows that there is an increase

in the concentration/amount/percentage of α -glucose in the reaction mixture:

it means the position of equilibrium has shifted to the left to absorb heat

Hence, the forward reaction is exothermic. [1]

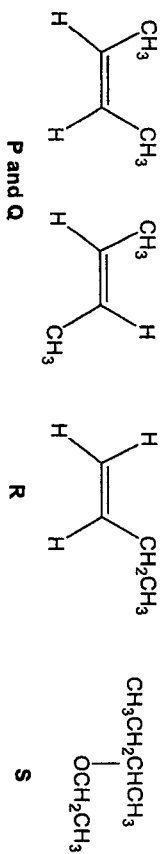
EXAMINER'S COMMENTS

This question was poorly attempted. Many candidates failed to make use of the information given, e.g. α -glucose has the larger optical rotation than the β -glucose, and hence, failed to recognise that the increase in the optical rotation was due to the shift in the equilibrium position to the left.

- 4 (d) *Cis-trans* isomerism also occurs in alkenes where the molecules contain restricted rotation of double bond. *Cis-trans* isomers of alkenes can be synthesised from the elimination reactions of halogenoalkanes.

When a mixture of beryllium hydroxide pellets and ethanol is added to optically active 2-chlorobutane, **P**, **Q**, **R** and **S** are formed. All of them do not react with PCl_5 . **P**, **Q** and **R** decolourise potassium manganate(VII), with only **R** producing an effervescence. **S** has the formula of $\text{C}_6\text{H}_{14}\text{O}$ and rotates plane-polarised light.

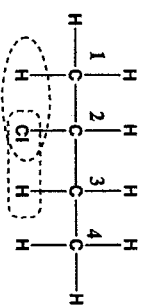
Give the structures of **P**, **Q**, **R** and **S**.



[4]

EXAMINER'S COMMENTS

This question was poorly attempted. Many candidates failed to recognise the information given by the question, e.g. "Cis-trans isomers of alkenes can be synthesised from the elimination reactions of halogenoalkanes". This showed 2-chlorobutane undergo elimination with $\text{Be}(\text{OH})_2$ and ethanol to form alkenes.

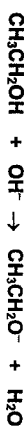


There are 2 possible ways to remove the H and Cl atoms from the 2 carbon atoms adjacent to each other. **P** and **Q** are produced when the H and Cl atoms removed from C2 and C3. **P** and **Q** are *cis-trans* isomers and hence, trigonal planar w.r.t C of C=C must be shown in the structure to differentiate **P** and **Q** isomers.

R is produced when the H and Cl atoms are removed from C1 and C2. Candidates who gave the formula of $\text{H}_3\text{CCH}_2\text{C}$ were penalised for the incorrect way to write the formula of the alkyl groups.

S is produced when 2-chlorobutane undergoes nucleophilic substitution. Based on the formula given, the Cl is replaced by OCH_2CH_3 and it can be obtained by ethanol.

- (e) The hydroxide ion from beryllium hydroxide undergoes acid-base reaction with ethanol. Write an equation to represent this.



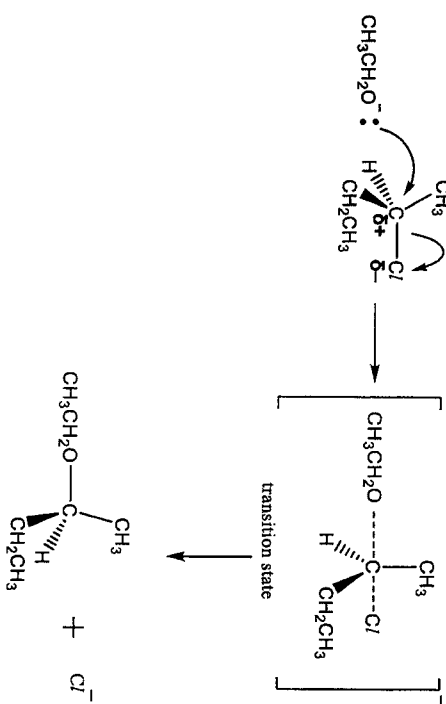
[1]

EXAMINER'S COMMENTS

Many candidates failed to identify the formula of ethanol which is $\text{CH}_3\text{CH}_2\text{OH}$. Some of them gave CH_3OH , CH_3COOH . Candidates should not molecular formula, e.g. $\text{C}_2\text{H}_6\text{O}$ to represent ethanol in the equation since the identity of the compound was given.

- (f) Outline the mechanism for the formation of **S** from 2-chlorobutane.

Name: Nucleophilic substitution, $\text{S}_{\text{N}}2$



[3]

EXAMINER'S COMMENTS

This question was poorly attempted. Many candidates failed to deduce the identity of nucleophile which could be deduced from the structure of **S**. For the candidates correctly identified the type of the mechanism, some of them did not give the name of the mechanism, did not draw the 2-chlorobutane in 3-dimensional tetrahedral shape to show the nucleophile attacking from the opposite side of the leaving group, did not draw the product in the inverted configuration or the wrong atom bonded to the chiral carbon atom.

- 4 (g) How would you expect the rate of the reaction described in (f) to change if 2-bromobutane is used?
 The rate of reaction would be faster as compared to 2-chlorobutane since the C-Br bond is weaker than C-Cl bond and so, C-Br bond would break more easily than C-Cl bond or less amount of energy is required to break C-Br bond than C-Cl bond. [1]

[Total: 12]
EXAMINER'S COMMENTS
 This question was well attempted. Many candidates were able to include all the underlined marking points in their answers.
 Some misconceptions: candidates compared the electronegativity of Cl and Br and hence, compared the electron deficiency of the carbon atom to attack the nucleophile. With this explanation, the rate of reaction would be slower for 2-bromobutane which contradicts with the fact.

- 5 This question is regarding the chemistry of chromium and chromium-containing compounds.
 (a) A metal ion, M^{n+} , oxidises Cr^{3+} to $Cr_2O_7^{2-}$. In the reaction, the M^{n+} ion is reduced to M^{2+} . In an experiment, 60.0 cm^3 of $0.040 \text{ mol dm}^{-3} M^{n+}$ was found to react with 10.0 cm^3 of $0.080 \text{ mol dm}^{-3} Cr^{3+}$.
 Determine the value of n in M^{n+} .

$$\text{Amount of } Cr^{3+} \text{ reacted} = 0.080 \times \frac{10.0}{1000} = 8.00 \times 10^{-4} \text{ mol}$$

$$\text{Amount of } M^{n+} \text{ reacted} = 0.040 \times \frac{60.0}{1000} = 2.40 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } M^{n+} \text{ reacted with 1 mole of } Cr^{3+} = \frac{2.40 \times 10^{-3}}{8.000 \times 10^{-4}} = 3.00$$

$$\text{Oxidation: } 2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$$

The oxidation of 1 mole of Cr^{3+} releases 3.00 mol of electrons

$$3M^{n+} = Cr^{3+} = 3e$$

- Since 1 mol of Cr^{3+} releases 3 mol of electrons
 Hence 3 mol of M^{n+} gains 3 mol of electrons
 1 mole of M^{n+} gains 1 mol of electrons
 \Rightarrow Oxidation number of M^{n+} decreases by 1

Since M^{n+} was reduced to M^{2+} , hence $n = +2 + 1 = 3$

[3]

EXAMINER'S COMMENTS

Most candidates solved this question by balancing the half-equation of oxidation of Cr^{3+} to $Cr_2O_7^{2-}$ and the half-equation of reduction of M^{n+} to M^{2+} and combined them as overall redox equation

Most of candidates who can't solve the question is due to their carelessness when calculating no of moles of Cr^{3+} or M^{n+} .

- (b) (i) The variety of colours shown by chromium compounds is typical of transition metals. State one other characteristic property of transition metals.

Variable / Different oxidation state [1]
[1]

EXAMINER'S COMMENTS

Most candidates could answer this question.

Those who failed to do so are the ones who stated the "physical properties of metals such as high melting point" that is not unique to transition metal. Ionic compound also has high melting point.

- (ii) Explain why the transition elements such as chromium have higher melting points as compared to the main group metals in general.

For transition metals,

..... as both the 3d and 4s electrons is involved in delocalisation.....

..... melting involves overcoming the stronger electrostatic forces of attraction between the cations and the sea of delocalised electrons, thus larger amount of energy is needed, hence transition metals have higher melting points.....

For the main group metals.....

Only the s electrons are involved in the delocalisation in metallic bonding. This results in weaker metallic bonds..... [3]

EXAMINER'S COMMENTS

Most candidates could answer this question.

Those who failed to do so are the ones who did not realize that high melting point is due to large amount of energy to overcome the strong electrostatic attraction between the metal cations and delocalized electrons.

Instead, they mistaken it as large amount of energy needed to remove electron from the metal atom itself.

- 5 (b) (iii) Like chromium, iron is a useful heterogeneous catalyst. By choosing a suitable example, describe and explain how iron performs this function.

Transition metals and their compounds are good heterogeneous catalyst because of the availability of 3d and 4s electrons for temporary bond formation with reactants.

Example: Production of ammonia via Haber Process using Fe catalyst

Temporary bonds are formed with reactant molecules, N₂ and H₂ when these are adsorbed on the Fe catalyst surface.....

This adsorption weakens the bonds in reactant molecules, thereby.....

Lowering the activation energy and increasing the surface concentration of the reactants. Reactant molecules are brought closer together and reaction can take place between the reactant molecules more easily.

The products formed are desorbed from the surface.

..... [4]

EXAMINER'S COMMENTS
Most candidates could answer this question.

Those who failed to do so are the ones who did not realize that the question required them to describe the process of heterogeneous catalysis.

Instead, they merely explain what a catalyst is in general and how it increases the chance of effective collision for reaction to occur.

Another group of candidates who failed to answer the question are the ones who have the misconception of homogeneous catalysis as heterogeneous catalysis.

[Total: 11]

- 6 Biomolecules are substances that are produced by cells and living organisms. They have a wide range of sizes and structures and perform various functions.

- (a) Proteins are a type of biomolecule. The chemical used for detecting proteins, biuret reagent, H₂NCONHCONH₂, can be formed by heating urea, (NH₂)₂CO.



Step 1: 3.88 g of impure sample of urea ((NH₂)₂CO) was heated strongly above its melting point. The ammonia liberated was absorbed in 32.0 cm³ of 2.00 mol dm⁻³ sulfuric acid.

Step 2: The resulting solution was made up to 500 cm³ with distilled water.

Step 3: 25.0 cm³ of the solution required 25.50 cm³ of 0.20 mol dm⁻³ sodium hydroxide solution for neutralisation using methyl orange as an indicator.

Calculate the percentage purity of urea in the sample.



No. of moles of NaOH in 25.50 cm³ = $0.20 \times \frac{25.50}{1000} = 5.10 \times 10^{-3}$ mol

From (3) 2NaOH \equiv H₂SO₄ (remaining)

No. of moles of H₂SO₄ in 25.0 cm³ = $\frac{5.10 \times 10^{-3}}{2} = 2.55 \times 10^{-3}$ mol

No. of moles of H₂SO₄ in 500 cm³ = $2.55 \times 10^{-3} \times \frac{500}{25} = 0.0510$ mol

Initial no. of moles of H₂SO₄ in 32.0 cm³ = $2.00 \times \frac{32.0}{1000} = 0.0640$ mol

No. of moles of H₂SO₄ reacted with NH₃ = 0.0640 – 0.0510 = 0.0130

From (2) and (1) $2\text{NH}_3 \equiv \text{H}_2\text{SO}_4$ (reacted) $\equiv 4(\text{NH}_2)_2\text{CO}$

Mass of urea, $(\text{NH}_2)_2\text{CO}$ produced = $0.0130 \times 4 \times 60$

$$= 3.12 \text{ g}$$

$$\text{Percentage purity of urea, } (\text{NH}_2)_2\text{CO} = \frac{3.12}{3.88} \times 100\%$$

$$= \underline{80.4\%}$$

[3]

EXAMINER'S COMMENTS

Most candidates could not solve this question to get the percentage purity.

Most of them failed to realize that the 32 cm^3 of 2.00 moldm^{-3} sulfuric acid is excess acid used for the reaction.

Another group of them failed to get the correct mole ratio:



- 6 (b) Haemoglobin is an example of a protein. The iron in the haemoglobin molecule is surrounded by six ligands. Five of these are nitrogen atoms from the globin protein, and one is from a water molecule. This water molecule is replaced by an oxygen molecule in oxyhaemoglobin. This equilibrium may be expressed as shown:



The iron in haemoglobin contains six 3d electrons.

- (i) What is oxidation state of the iron in haemoglobin?

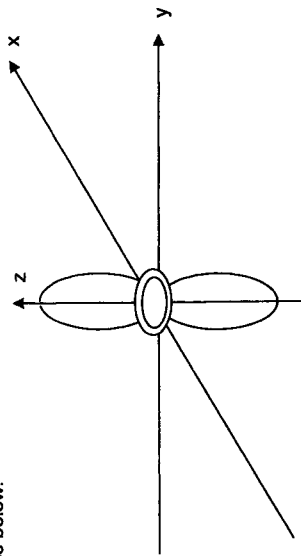
Oxidation state of iron is **+2**[1]

EXAMINER'S COMMENTS

Most candidates failed to answer this question.

Most of them misunderstood oxidation state of Fe as coordination number of Fe in the complex. They failed to obtain the oxidation state of +2 from the number of 3d electrons given in the question.

- (ii) Sketch the shape of the $3d_{z^2}$ orbitals of Fe, stating clearly the orientation and axes below.



[1]

EXAMINER'S COMMENTS

Most candidates can answer this question.

Those candidates who could not are the ones who failed to draw all 3 axes or failed to draw the "donut" or the "vertical lobes" properly.

- (iii) Oxyhaemoglobin is bright red whereas haemoglobin is close to purple. The colour is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

Suggest

- the size of d-orbital splitting in the two complexes, oxyhaemoglobin and haemoglobin,
- why oxyhaemoglobin is of a different colour from haemoglobin.

Since haemoglobin is purple, \Rightarrow light of longer wavelength is absorbed which is yellow hence the complementary colour, purple (not absorbed) will be seen. Hence, H_2O ligand causes a small d-orbital splitting / small ΔE gap between d-orbitals.

Since oxyhaemoglobin is red,

\Rightarrow light of shorter wavelength is absorbed which is green hence the complementary colour, red (not absorbed) will be seen. Hence, O_2 ligand causes a large d-orbital splitting / large ΔE gap between d-orbitals

EXAMINER'S COMMENTS

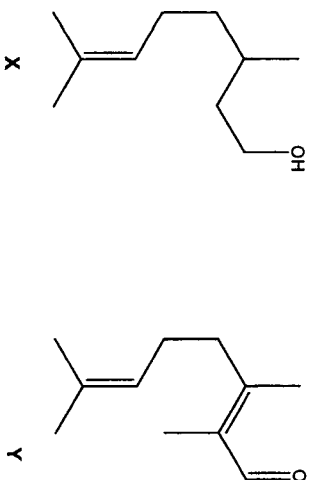
Most candidates cannot answer this question well.

Some of them failed to compare the size of d-orbital splitting for the 2 complexes as well as the complementary colours absorbed. Most of them just gave an account on why the complexes are coloured using crystal-field theory.

Quite a number of them misunderstood longer wavelength as higher wavelength and hence attributed "higher amount of energy" to yellow instead of green.

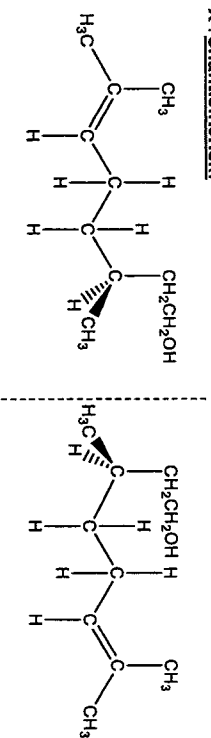
- 6 (c) A pheromone is a biomolecule that, when secreted by an individual of a species, can elicit a certain type of behaviour in other members.

The structures of two pheromones secreted by the honeybee to direct others to a food source are shown below.

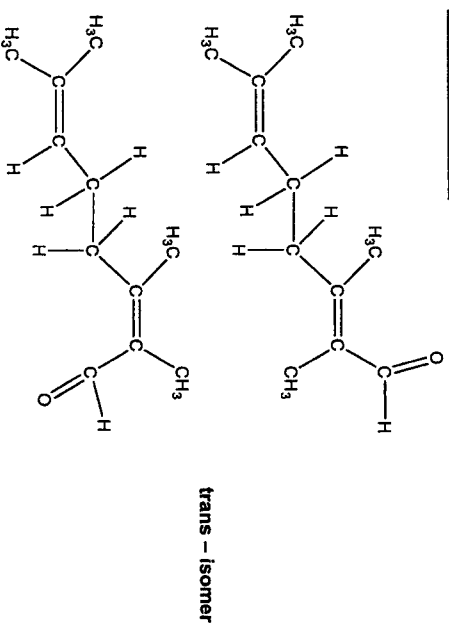


Deduce the type(s) of isomerism (if any) that may be present in each of X and Y and draw the structural formulae to illustrate various pairs of isomers.

X : enantiomerism



Y : cis-trans isomerism

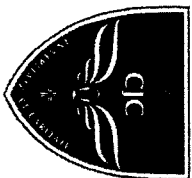


[Total: 13]

EXAMINER'S COMMENTS
Most candidates can answer this question well.

Some of them who failed to do so are the ones who failed to identify chiral carbon atom in X and the C=C double bond with 2 different substituent groups on each carbon in Y.

Some candidates misunderstood the question and give possible structural isomers for X and Y.



Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE
 NAME

CLASS

2T

CHEMISTRY

9729/03

Paper 3 Free Response

13 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

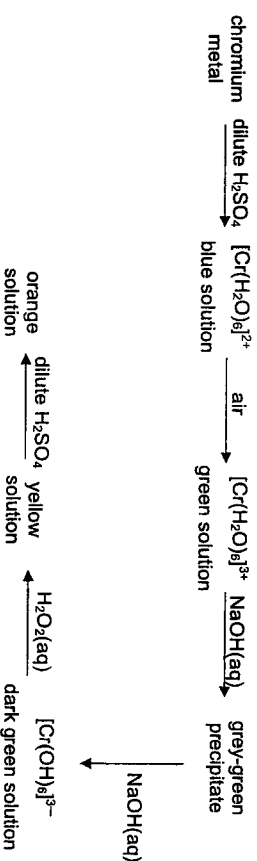
MARK SCHEME & EXAMINER'S COMMENTS

Section A

Answer all the questions in this section.

- 1 Chromium is a hard, steel-grey metal with a lustrous appearance. It is valued for its high corrosion resistance and hardness and is commonly used to manufacture alloys such as steel. Chromium plating is sometimes used to give a polished mirror finish to steel. Chromium compounds are also often used as pigments, known as chrome yellow.

- (a) The following sequence of reactions involving chromium illustrates many of the characteristics properties of transition metals.



- (i) Solutions of transition metals are frequently coloured. With reference to $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, explain fully why it forms a blue solution. [2]

In the presence of H₂O ligands, the partially filled degenerate d-orbitals of Cr²⁺ ion are split into 2 groups of non-degenerate d orbitals with a small energy gap. In the presence of visible light, d electron in a d orbital of lower energy absorbs orange light and is promoted to the higher energy d^{*} orbital (d-d^{*} electronic transition).

The complementary colour (blue) which is not absorbed appears as the colour of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ observed.

EXAMINER'S COMMENTS

Most students were only able to get the second mark for stating the correct colour absorbed.

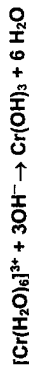
Common mistakes made are as follows:

- Missing keywords, eg 'partially filled' in the answer – note that if the d orbitals are empty (eg Sc³⁺ ion) or fully filled (eg Cu⁺ ion), there is no d-d^{*} electronic transition (no colour observed) even if splitting of the d orbitals takes place.
- Stating that the a d orbital of lower energy state is promoted instead of a d electron in the orbital of lower energy.

- (ii) Suggest the identity of the grey-green precipitate formed in the reaction between $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and aqueous sodium hydroxide. [2]

With the aid of an equation, explain fully how it is formed.

The grey-green precipitate is $\text{Cr}(\text{OH})_3$.



When OH^- ions are added to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ solution, an

precipitation/acid-base reaction occurs to form $\text{Cr}(\text{OH})_3$.

OR

The grey-green precipitate is $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$.

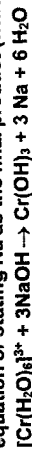


When OH^- ions are added to $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ solution, a ligand displacement reaction occurs to form $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$.

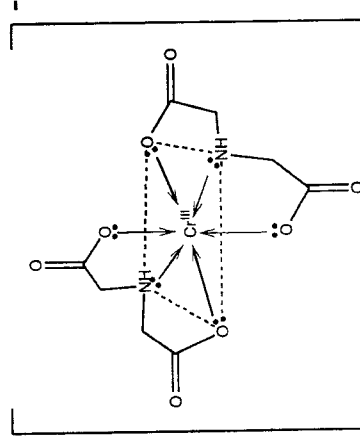
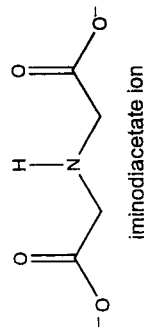
EXAMINER'S COMMENTS

Most students were able to state the correct identity of the precipitate.

Common mistakes made in the second mark are either giving an unbalanced equation or stating Na as the final product (which is not possible), for example:



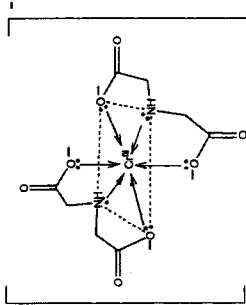
- 1 (a) (iii) Chromium(III) ions can also react with iminodiacetate ions (tridentate ligand) to form a chelating complex ion. Draw the structure of the complex ion, showing the shape clearly. [1]



Legend can also be accepted to represent ligand used.

EXAMINER'S COMMENTS

This question was very badly done. Most students left this part blank. Students are reminded that if a negatively-charged ligand is used, the individual charge is not shown in the structure of the complex, but is instead considered in the overall charge of the complex, for instance, the following drawing is wrong:



- (iv) Identify the species present in the yellow and orange solutions.
Hence write an equation to show the formation of the species in the orange solution from that in the yellow solution. [2]

Species present in yellow solution: CrO_4^{2-}

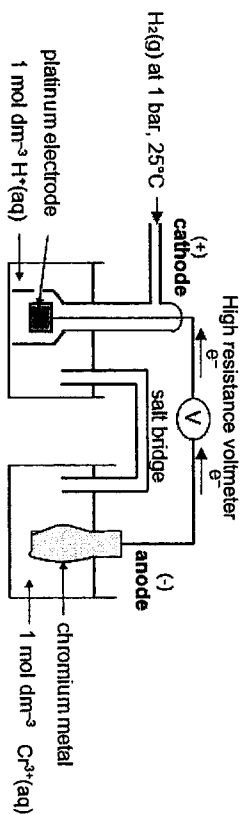
Species present in orange solution: $\text{Cr}_2\text{O}_7^{2-}$



EXAMINER'S COMMENTS

This question was very badly done. Many students just guessed and gave random identities of the two solutions, which shows they do not understand the chromium-containing species responsible for the two colours.

- 1 (b) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the $\text{Cr}^{3+}(\text{aq})/\text{Cr}(\text{s})$ half-cell, indicating the direction of electron flow. [3]

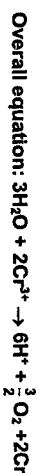


EXAMINER'S COMMENTS

This question was badly done. Students were unable to identify cathode and the anode, and thus drew the wrong direction of electron flow. In addition, there were many missing details in the answers i.e. stating of standard conditions, labelling the electrodes wrongly. Some students even drew an electrolytic cell diagram and showed poor understanding of how standard electrode potentials are obtained.

- (c) Chromium is electrolytically deposited on the cathode from a solution containing $\text{Cr}^{3+}(\text{aq})$ using inert electrodes. [2]

Calculate the volume of oxygen, at room temperature and pressure, produced at the anode when 1.00 kg of chromium is deposited on the cathode.



= 14.4 mol



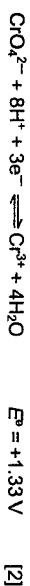
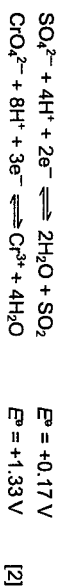
= 346 dm^3 (to 3 s.f.)

EXAMINER'S COMMENTS

Most students were able obtain the correct overall equation and find the volume of O_2 produced. Common mistakes included forgetting to convert kg into g when finding number of moles of Cr, using the ideal gas equation to solve this question.

- (d) Chrome yellow containing Na_2CrO_4 , has been used for a long time as a yellow pigment in oil paintings.

(i) Use the standard redox potentials below to explain why the yellow colour changes when the painting is exposed to an atmosphere containing sulfur dioxide.



[2]

$$E_{\text{cell}}^\circ = E_{\text{red}}^\circ - E_{\text{oxd}}^\circ$$

$$= +1.33 - (+0.17)$$

$$= +1.16 \text{ V}$$

$E_{\text{cell}}^\circ > 0$ (reaction is energetically favourable) and hence yellow colour changes

EXAMINER'S COMMENTS

Most students did not find the overall E_{cell}° to determine if the reaction is feasible. Common mistakes included explaining how the presence of SO_2 changes the position of the equilibrium according to LCP.

- 1 (d) (ii) Suggest why this colour change takes a long time. [1]

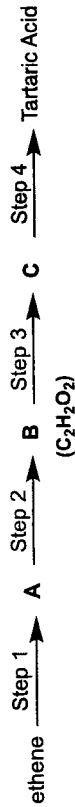
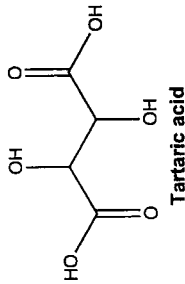
E_{act}° tells us whether a reaction is spontaneous (thermodynamically feasible) but does not predict the rate of a chemical reaction. (kinetically feasible).
Reaction has a high activation energy; low concentrations of SO_2 in atmosphere.....

[Total: 15]

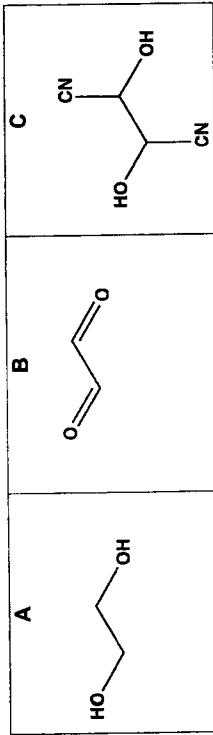
EXAMINER'S COMMENTS

This question was poorly done. A variety of answers were given, but students failed to note that the presence of SO_2 in the atmosphere is actually very low, thus this reaction does not take place under standard conditions. In addition, reactions which are energetically feasible, i.e. $E_{\text{cell}}^\circ > 0$ does not mean it may proceed, as the activation energy of the reaction may be very high.

- 2 (a) Tartaric acid is a white crystalline diprotic organic acid. It can be synthesised from ethene in four steps.



Draw the structures of the intermediates, **A**, **B** and **C**, and give the required reagents and conditions for each step of the conversion. [7]



- Step 1: ... cold, NaOH(aq) , KMnO_4
- Step 2: ... $\text{K}_2\text{Cr}_2\text{O}_7$ in dilute H_2SO_4 , heat with (immediate) distillation
- Step 3: ... HCN(aq) , trace amount of NaCN(aq)/NaOH(aq) , cold
- Step 4: ... dilute H_2SO_4 , heat

EXAMINERS' COMMENTS

With the molecular formula of compound **B** provided, it is pleasing to see that most students can deduce this. However, a fair number used KMnO_4 in Step 2 which is not accepted as it will oxidise the resultant molecule, ethanedioic acid to carbon dioxide. In addition, it is important to state the acidifying agent (H_2SO_4) or alkaline agent (NaOH) to remove ambiguity as other agents such as hydrochloric acid would result in the latter being oxidised to chlorine gas.

- 2 (b) Salts of tartaric acid are known as tartrates or hydrogen tartrates. One of these salts, potassium hydrogen tartrate, $\text{KC}_4\text{H}_5\text{O}_6$, is a weak monobasic acid and is sparingly soluble in water.

An experiment was conducted to determine the K_{sp} of the salt, $\text{KC}_4\text{H}_5\text{O}_6$. 1.00 g of the salt, $\text{KC}_4\text{H}_5\text{O}_6$ was dissolved in a beaker containing 100 cm^3 of water and was stirred constantly for 15 minutes at constant temperature until a saturated solution was produced.

20.0 cm^3 of the filtered solution was titrated against 0.035 mol dm^{-3} NaOH , using phenolphthalein as an indicator. The volume of NaOH needed for the indicator to change colour is 12.50 cm^3 .

- (i) Calculate the initial concentration of potassium hydrogen tartrate used in the titration. [1]

$$\begin{aligned} \text{Amt. of } \text{KC}_4\text{H}_5\text{O}_6 &= 0.035 \times \frac{12.50}{1000} \\ &= 4.375 \times 10^{-4} \text{ mol} \end{aligned}$$

$$[\text{KC}_4\text{H}_5\text{O}_6] = 4.375 \times 10^{-4} \div \frac{20.0}{1000} = 0.0219 \text{ mol dm}^{-3} \text{ (3 sf)}$$

- (ii) Hence, calculate the K_{sp} value of potassium hydrogen tartrate. [1]

$$K_{sp} = [\text{K}^+][\text{C}_4\text{H}_5\text{O}_6^-] = (0.0219)^2 = 4.79 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$$

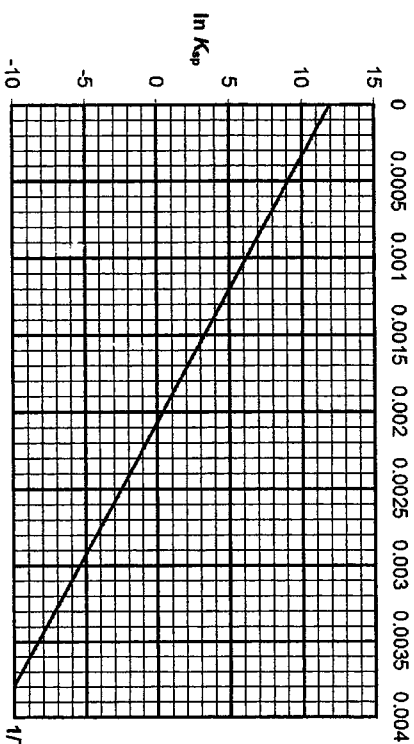
EXAMINER'S COMMENTS

Poorly answered question. It is worrying that most students that obtained an incorrect answer is due to the assumption that all the 1.00 g of potassium salt dissolved in water when it is clearly stated it is sparingly soluble in the first paragraph. Hence, back titration with NaOH was required.

- (c) The van 't Hoff equation relates equilibrium constants to enthalpy (ΔH) and entropy changes (ΔS) as follows:

$$\ln K_{sp} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

where R is the molar gas constant and T is measured in Kelvin. The titration in (b) was repeated at different temperatures and the following results were obtained.



- 2 (g) (i) Using the information provided, calculate ΔH and ΔS for the dissolution of potassium hydrogen tartrate in water. [2]

$$\text{Gradient value} = \frac{\Delta H}{R} = \frac{-12 \times 10^3}{0.0035 - 0} = 5789$$

$$\Delta H = 5789 \times 8.31 = +48110 \text{ J mol}^{-1} \\ = +48.1 \text{ kJ mol}^{-1}$$

$$\text{y-intercept value} = \frac{\Delta S}{R} = 12$$

$$\Delta S = 12 \times 8.31 = +99.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

- (ii) Hence, predict the temperature at which potassium hydrogen tartrate becomes soluble in water. [1]

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T = \Delta H / \Delta S = 48110 / 99.7 = 483 \text{ K}$$

EXAMINER'S COMMENTS

This question demonstrates the poor mathematical interpretation of the expression provided. To solve both thermodynamic constants, some students were busy solving simultaneous questions when a simple conversion using linear law was sufficient to obtain it.

- (d) At 800 K, nitrogen monoxide reacts with hydrogen as shown below in an enclosed gas tank.



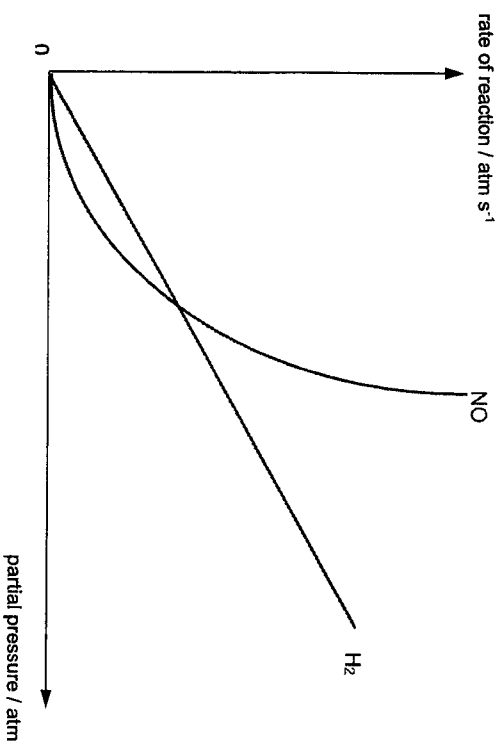
$$\text{rate} = k(P_{\text{H}_2})(P_{\text{NO}})^2$$

On the same axes, sketch suitable graphs on the same axes below to illustrate clearly how the rate of reaction would vary when partial pressures of

- (i) H_2
(ii) and NO

is increased respectively.

[1]



EXAMINER'S COMMENTS

This question is poorly attempted due to overthinking on the students' part. Some left the axis blank while others were drawing equilibrium graphs of concentration against time. It is important that candidates realise what is asked in the question before presenting their answers.

- 2 (e) Nitrogen dioxide, NO₂, is an air pollutant produced from volcanic eruptions and combustion of fossil fuels in automobile engines.

(i) Draw the dot-and-cross diagram for nitrogen dioxide, NO₂, molecule stating its shape and bond angle. [2]

Species	Dot-and-cross diagram	Shape and bond angle
NO ₂		Shape: bent Bond angle: >120° range of values (121° - 178°)

EXAMINER'S COMMENTS

Most candidates were able to draw a structure of NO₂, albeit the central nitrogen atom has 9 electrons around it. It is important for candidates to check upon drawing, especially for Period 2 elements, that it does not exceed 8 electrons, which on this occasion requires the formation of a dative covalent bond from N to O.

- (ii) A 1.00 dm³ gas cylinder is used to store 35.0 g of NO₂ at 25° C. The gas cylinder is fitted with a safety valve that will rupture when there is a great difference between the internal pressure and the atmospheric pressure.

The gas cylinder fitted with a burst disc can withstand a pressure difference of 2500 kPa.

Calculate the pressure exerted by NO₂ at 25° C in kPa. [1]

$$PV = \frac{m}{M_r}RT$$

$$P = \frac{nRT}{V}$$

$$= \frac{35.0 \times 8.31 \times 298}{46.0 \times 1.00 \times 10^{-3}}$$

$$= 1\ 884\ \text{kPa}$$

- (iii) Assuming the atmospheric pressure is 101 kPa, calculate the maximum internal pressure of the gas cylinder. [1]

Maximum pressure difference = Internal pressure – Atmospheric pressure

$$2500 = \text{Internal pressure} - 101$$

$$\text{Internal pressure} = 2500 + 101$$

$$= 2601\ \text{kPa}$$

11 turn over

- 2 (e) (iv) Hence, determine the maximum temperature that this gas cylinder can be exposed to before the burst disc ruptures. [1]

$$PV = nRT$$

$$T = \frac{PV}{nR}$$

$$= \frac{2601 \times 10^3 \times 1.00 \times 10^{-3}}{8.31 \times \frac{35.0}{46.0}}$$

$$= 411\ \text{K}$$

- (f) A gas tank contains a mixture of NO₂ and monoatomic gas A in the ratio of 4:1. At 300 K, the total pressure of the gas mixture is 100 kPa.

- (i) Given that the density of the gas mixture is 1638 g m⁻³, calculate the average relative molecular mass of the mixture to 1 decimal place. [1]

$$M_r = \frac{\rho RT}{P} = \frac{1638 \times 8.31 \times 300}{100\ 000} = 40.8$$

- (ii) Hence, calculate the A_r of monoatomic gas A and suggest its identity. [2]

Given that the mixture of NO₂ and monoatomic gas A is in the ratio of 4:1,

$$(0.8 \times 46.0) + (0.2 \times A_r \text{ of monoatomic gas A}) = 40.8$$

$$A_r \text{ of A} = 20.0$$

A is neon

EXAMINER'S COMMENTS
Other than the handful of careless mistakes involving the conversion of units, most students are able to solve these questions pretty well.

[Total: 21]

3 This question is about nitrogen containing compounds.

- (a) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:



In an experiment, student A kept the amount of $\text{Cl}_2(\text{g})$ in large excess while the initial partial pressure of $\text{NO}(\text{g})$ was varied at constant temperature of 550 K.

The table below shows the experimental results obtained.

time / s	$P_{\text{NO}} / \text{atm}$	(Rate / P_{NO}) / s^{-1}	(Rate / $(P_{\text{NO}})^2$) / ($\text{atm}^{-1} \text{s}^{-1}$)
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	1.127×10^{-4}

- (i) Suggest why the amount of $\text{Cl}_2(\text{g})$ was kept in large excess. [1]

Since the amount of $\text{Cl}_2(\text{g})$ was kept in large excess, the partial pressure of $\text{Cl}_2(\text{g})$ remains relatively constant so that any change in rate is due to the changes in the partial pressure of $\text{NO}(\text{g})$ only.

EXAMINER'S COMMENTS

This question requires students to see the reason behind keeping the amount of $\text{Cl}_2(\text{g})$ in large excess and hence link to how it affect the determination of the rate of reaction. Many students were not able to be awarded full credit.

- (ii) Define the term order of reaction. [1]

The order of reaction with respect to a reactant is defined as the power to which the concentration of a reactant is raised to in the experimentally determined rate equation.

EXAMINER'S COMMENTS

This is a recall question that was not well attempted. Students were not able to give all the keywords required.

- (iii) Using the data from the table above, deduce the order of reaction with respect to $\text{NO}(\text{g})$. [1]

$$\text{Since Rate} = k(P_{\text{NO}})^2$$

$\text{Rate}/(P_{\text{NO}})^2 = k$ is constant throughout the reaction and thus rate of reaction is directly proportional to $(P_{\text{NO}})^2$; the reaction is second order with respect to NO .

EXAMINER'S COMMENTS

This question required students to see that $\text{Rate}/(P_{\text{NO}})^2 = k$ is constant throughout the reaction and hence determine the order of reaction. Students were not able to get full credit.

3 (a) (iv)

In another experiment, the initial partial pressure of $\text{NO}(\text{g})$ was 4.2 atm and it was reacted with $\text{Cl}_2(\text{g})$ at a constant temperature of 550 K. The partial pressure of $\text{Cl}_2(\text{g})$ was recorded at time intervals of 30 seconds.

The data obtained are tabulated below.

time / s	partial pressure of $\text{Cl}_2(\text{g}) / \text{atm}$	time / s	partial pressure of $\text{Cl}_2(\text{g}) / \text{atm}$
0	0.78	300	0.49
30	0.76	330	0.46
60	0.72	360	0.44
90	0.70	390	0.42
120	0.66	420	0.39
150	0.63	450	0.38
180	0.59	480	0.36
210	0.57	510	0.34
240	0.54	540	0.33
270	0.52	570	0.32

Using the data but without plotting of any graph, deduce the order of reaction with respect to $\text{Cl}_2(\text{g})$. [1]

$$\begin{aligned} 1^{\text{st}} \ t_{1/2} &= \text{time taken for } P_{\text{Cl}_2} \text{ to decrease from } 0.78 \text{ atm to } 0.39 \text{ atm} \\ &= 420 \text{ s} \end{aligned}$$

$$\begin{aligned} 2^{\text{nd}} \ t_{1/2} &= \text{time taken for } P_{\text{Cl}_2} \text{ to decrease from } 0.76 \text{ atm to } 0.38 \text{ atm (or } 0.66 \rightarrow 0.33) \\ &= 480 - 60 \\ &= 420 \text{ s} \end{aligned}$$

Since $t_{1/2}$ is constant at 420s, the reaction is first order with respect to Cl_2 .

EXAMINER'S COMMENTS

This question required students find the half life which was not well attempted.

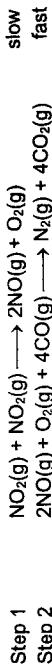
- (v) Write the rate equation for the overall reaction. Hence, calculate the rate constant, stating its units. [3]

Rate = $k(P_{NO})^2(P_{Cl_2})$
 Rate = $k'(P_{Cl_2})$ where $k' = k(P_{NO})^2$
 $t_{1/2} = 420 \text{ s} = \frac{\ln 2}{k(P_{NO})^2} = \frac{\ln 2}{k(4.2)^2}$
 $k = 9.36 \times 10^{-5} \text{ atm}^{-2} \text{ s}^{-1}$

EXAMINER'S COMMENTS

This question required students to determine the rate equation from the above parts. And hence calculate with the units stated. Common mistakes includes leaving the rate equation in terms of concentration instead of partial pressures and some thought that the rate is s^{-1} but it should be atm s^{-1}

- 3 (b) In another reaction, $2\text{NO}_2(\text{g}) + 4\text{CO}(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 4\text{CO}_2(\text{g})$, it was found that the rate equation is $\text{rate} = k[\text{NO}_2]^2$.
 A proposed mechanism for this reaction is shown.



Explain whether it is consistent with the established rate equation. [1]

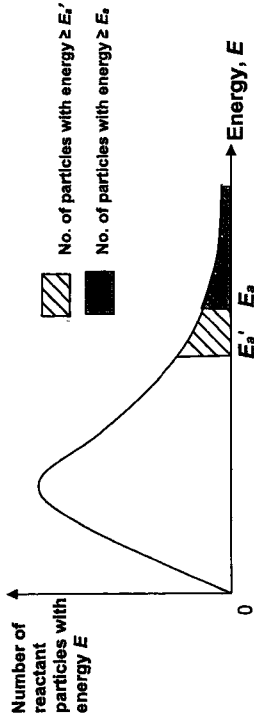
The mechanism is consistent with the established rate equation. One molecule of NO_2 reacts with one molecule of NO_2 in the slow rate determining step whereas rate equation shows 2 moles of NO_2 reacting in the slow rate determining step.

EXAMINER'S COMMENTS

This question required students to state the correlation of the number of reactants in the slow step with the rate equation. This question is fairly well attempted.

- (c) Tryptophan metabolism plays an important role in the mechanisms associated with the gut-brain axis. At least 90% of human intake of tryptophan is converted to kynurenine for further metabolism via a catalyst.

- (i) Explain how the activation energy of a reaction is affected by the presence of a catalyst, and with an appropriate sketch of a Maxwell-Boltzmann distribution curve, explain how a catalyst increases the rate of reaction. [3]



The catalyst lowers the activation energy of the reaction by providing an alternative pathway for the reaction to occur.

With a lower activation energy, according to the Maxwell-Boltzmann distribution, there will be a higher proportion of reactants with energy greater or equal to this lower activation energy, E_a . Thus, there is higher frequency of effective collisions between reactants since they possess sufficient energy for reaction. Therefore, the rate of reaction increases.

EXAMINER'S COMMENTS

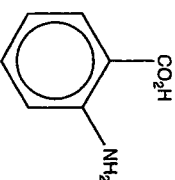
This is recall question on the Maxwell-Boltzmann distribution curve. However, this was not well attempted with many keywords or marking points missed hence not given full credit.

Common mistakes includes the wrong Maxwell-Boltzmann curve, the lack of keywords like "frequency of effective collisions".

- 3 (c) (ii) Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$. When dissolved, an aqueous solution of kynurenine is almost neutral and maintains its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid. Addition of this solution to aqueous 2,4-dinitrophenylhydrazine causes an orange precipitate to form.

Kynurenine reacts with $NaBH_4$ to form compound L, $C_{10}H_{14}N_2O_3$. Heating L with concentrated H_2SO_4 produces only M, $C_{10}H_{12}N_2O_2$. Heating M with acidified $KMnO_4$ under reflux results in the formation of compound N, $C_8H_6NO_4$, and anthranilic acid.

The molecular structure of anthranilic acid is as shown below.

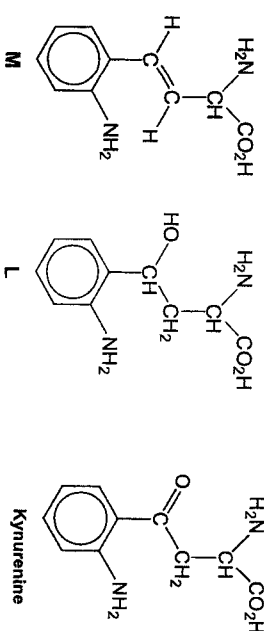
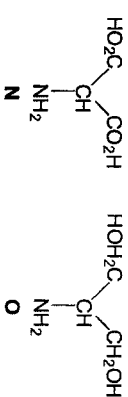


anthranilic acid

Reaction of N with $LiAlH_4$ in dry ether produces compound O, $C_8H_6NO_2$. A solution of O turns litmus paper blue.

Suggest possible structures for L, M, N, O and kynurenine. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [13]

INFORMATION	DEDUCTION
Kynurenine has the molecular formula $C_{10}H_{12}N_2O_3$	C:H is approximately 1:1. It contains a benzene ring
When dissolved, an aqueous solution of kynurenine is almost neutral	It functions as a <u>buffer</u> .
Kynurenine maintained its pH upon addition of small amounts of aqueous sodium hydroxide or hydrochloric acid	Presence of <u>carbonyl group</u>
Addition of the kynurenine to aqueous 2,4-DNPH caused an orange precipitate to form.	<u>Condensation reaction</u> .
Kynurenine reacts with $NaBH_4$ to form compound L, $C_{10}H_{14}N_2O_3$	<u>Reduction of ketone group</u> in kynurenine.
Heating L with concentrated H_2SO_4 produces only M, $C_{10}H_{12}N_2O_2$	<u>Elimination of H and OH groups</u> from L to form alkene in M. Indicate the presence of <u>OH group</u> on L.
Heating M with acidified $KMnO_4$ under reflux results in the formation of compound N, $C_8H_6NO_4$ and anthranilic acid	<u>Oxidative cleavage of C=C bond</u> occurred as 2 molecules were obtained
Reaction of N with $LiAlH_4$ in dry ether produces compound O, $C_8H_6NO_2$. A solution of O turns litmus blue.	<u>Reduction of carboxylic acid group</u> in N.



[Total: 24]

EXAMINER'S COMMENTS

This is an elucidation question that requires students to use the information to explain the type of reaction and functional group present. And hence deduce the structures.

Many students were only able to achieve partial credits.

Some of the common mistakes includes:

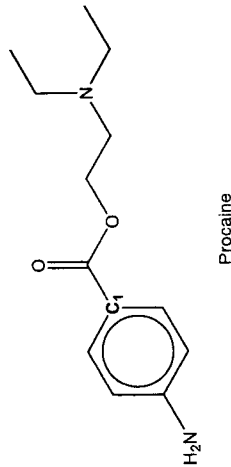
- deduction of amide groups in kynurenine,
- identification of type of reaction when L is reacted with concentrated H_2SO_4 as hydrolysis

Section B

Answer one question from this section.

- 4 An anaesthetic is a drug used to induce a temporary loss of sensation or awareness. They may be classified as general anaesthetics that result in a reversible loss of consciousness, or local anaesthetics which cause a reversible loss of sensation for a limited region of the body without necessarily affecting consciousness.

- (a) Procaine, one of the first injectable local anaesthetics used during surgery has the following structure:

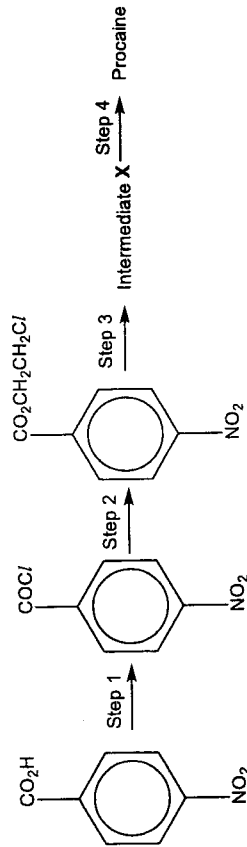


- (i) State the oxidation state of C₁ in Procaine. [1]
- 0

EXAMINER'S COMMENTS

This question was badly done. Many different values were given.

- (ii) Procaine can be made by the following reaction scheme:

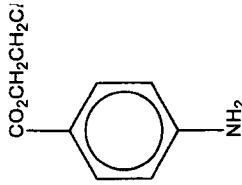


State the reagents and conditions used for steps 1, 2, 3 and 4. Draw the structure of intermediate X. [5]

- Step 1: anhydrous PCl_5 / SOCl_2 , r.t.p. OR anhydrous PCl_5 , heat
 Step 2: $\text{HOCH}_2\text{CH}_2\text{Cl}$, r.t.p.
 Step 3: 1) Sn , conc. HCl , heat under reflux; 2) NaOH(aq)
 Step 4: $\text{NH(CH}_2\text{CH}_3)_2$, heat under reflux

NOTE: Step 3 and 4 are interchangeable

Structure of intermediate X:

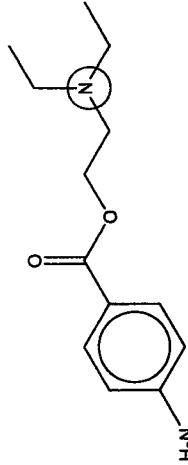
**EXAMINER'S COMMENTS**

This question was badly done.

Common mistakes made are as follows:

- Step 1: stating Cl_2 with anhydrous FeCl_3 (this is used for electrophilic substitution of Cl^+ onto the benzene ring) or Cl_2 with *uv light* (this is for free radical substitution of an alkane/alkyl group which is not present in the starting compound).
- Step 2: stating $\text{HOCH}_2\text{CH}_2\text{Cl}$ with conc H_2SO_4 and heat, which will lead to the dehydration of the alcohol (to form an alkene). Note that acyl chloride will react readily with an alcohol to form an ester, no catalyst is needed.
- Step 3: using LiAlH_4 and dry ether to reduce nitrobenzene to phenylamine (this is not possible as an azo compound is formed instead (refer to Nitrogen Compounds lecture notes Pg 17-17)).
- Step 4: giving conc NH_3 as the reactant will not lead to the structure of Procaine.

- 4 (a) (iii) One molecule of Procaine contains two nitrogen atoms, both of which can act as a base by accepting a proton. On the diagram below, circle the nitrogen atom which will be a stronger base. Explain your reasoning. [2]



The alkyl groups attached to the N atom are electron-donating groups, hence making the lone pair of electrons on the N atom more available to accept a proton.

OR

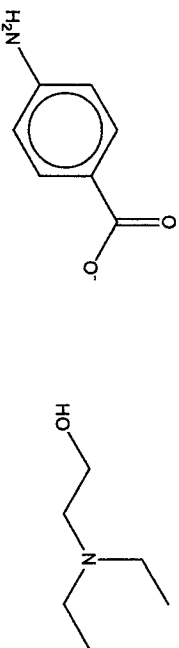
The lone pair of electrons on the N atom of phenylamine can be delocalised into the π electron system of benzene ring, thus making the lone pair of electrons less available to accept a proton

EXAMINER'S COMMENTS

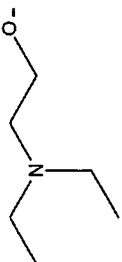
This question was well done. Many students were able to identify the correct nitrogen atom and give the correct explanation.

A small minority of student mentioned 'negative charge on nitrogen atom' or 'stabilising the negative ion' and was penalised, because the nitrogen atom will only carry a positive charge (conjugate acid) after accepting a proton.

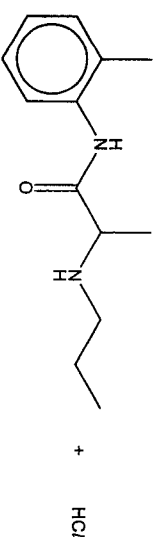
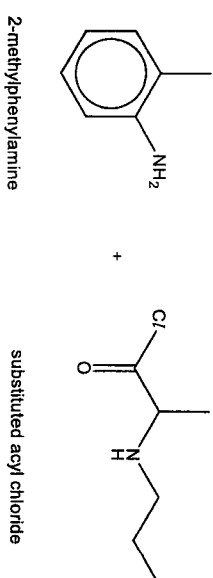
- 4 (a) (iv) Procaine undergoes hydrolysis rapidly in the small intestines where the pH is about 9. Give the structural formulae of the products obtained from the hydrolysis under such conditions. [2]

**EXAMINER'S COMMENTS**

Most students were able to draw the first structure correctly. However, many students mistakenly thought that the alcohol will react with OH⁻ ions as well and gave the following wrong product:



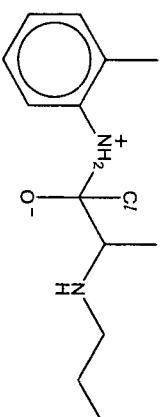
- (b) Prilocaine, an amide-based local anaesthetic, is commonly used in dentistry. Prilocaine is synthesised when the following substituted acyl chloride undergoes a condensation (addition-elimination) reaction with 2-methylphenylamine.



Prilocaine

The reaction above takes place in three steps.

The first step involves the nucleophilic addition of 2-methylphenylamine to the substituted acyl chloride to form the following dipolar ion as an intermediate.



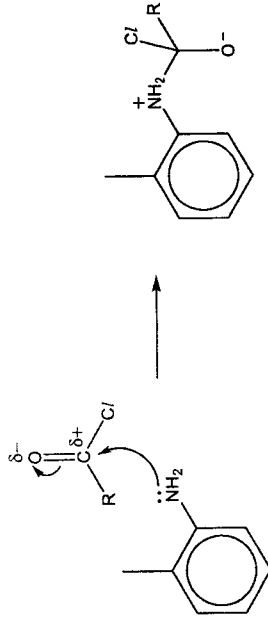
In the second step, the nitrogen atom on another molecule of 2-methylphenylamine acts as a base and accepts a proton from the dipolar ion intermediate.

In the final step, the C=O bond of the amide bond is restored when the chlorine atom leaves as a chloride ion.

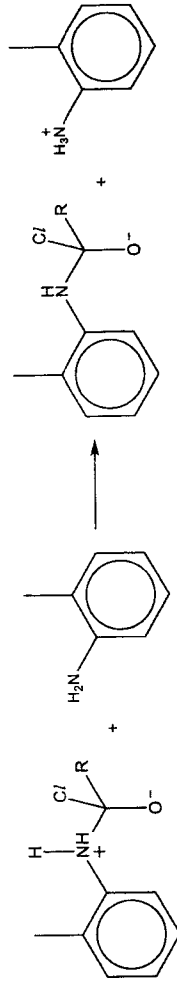
With reference to the information provided above, suggest a three-step mechanism for the formation of Prilocaine.

You may wish to represent the substituted acyl chloride as $\text{R}-\text{C}(=\text{O})-\text{Cl}$. Show all partial charges and curly arrows clearly in your answer. [3]

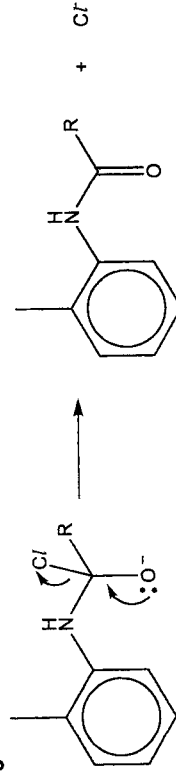
Step 1:



Step 2



Step 3

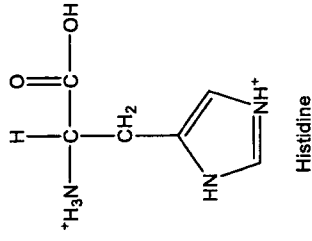
**EXAMINERS' COMMENTS**

This question was mostly left blank.

For the few students who attempted, the curly arrows were randomly positioned. Students are reminded of the need to read the information given in the question carefully which will help them to structure their answers.

- 4 (c) Limiting the intake of certain essential nutrients, either proteins or amino acids for several days before surgery may reduce the risk of serious surgical complications such as heart attack or stroke.

Histidine is an essential amino acid utilised by the body to develop and maintain healthy tissues. The structure of the fully protonated form of histidine is given below.



Histidine

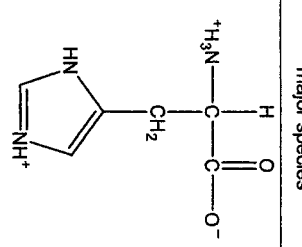
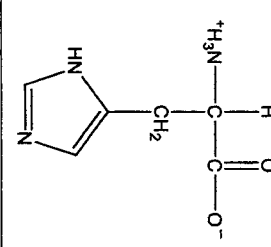
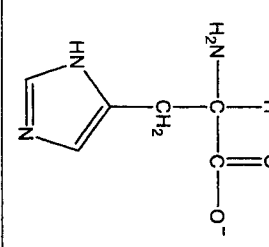
The pK_a values of the respective functional groups attached to the α -carbon in histidine are given in the following table.

functional group	pK_a value
	1.82
	6.00
	9.17

- 4 (c) (i) With reference to the given pK_a values, suggest the major species present in solutions of histidine with the following pH values:

- pH 4
- pH 8
- pH 12

[3]

pH value	major species
4	
8	
12	

EXAMINERS' COMMENTS
This question was badly done. Only a very small minority of students scored the full three marks.

- 4 (c) (ii) Histidine is also important for digestion in human body as it helps to produce gastric juices in the stomach.

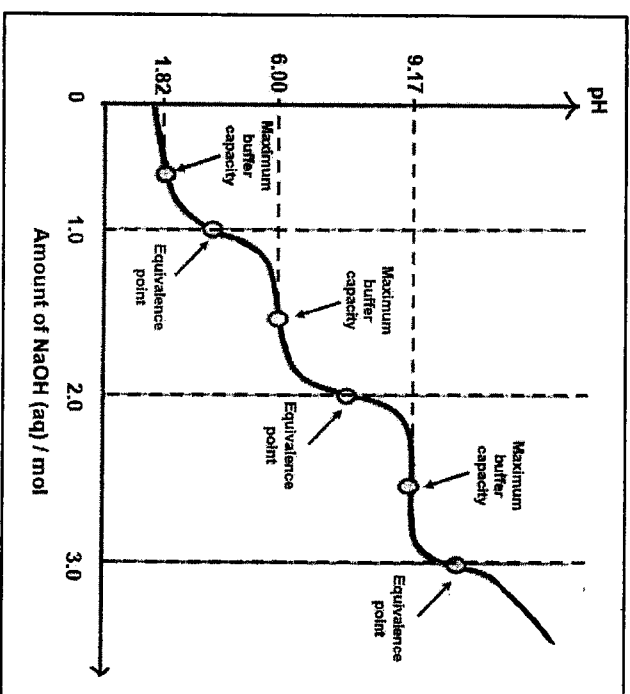
A stomach juice sample is extracted from a patient to determine the concentration of histidine by titrating it with aqueous sodium hydroxide.

Draw a labelled titration curve of pH against amount of NaOH(aq) added when one mole of fully protonated histidine is titrated with NaOH(aq)

You should clearly label the following points in your titration curve.

- amounts of NaOH required at each equivalence point
- pH values at the points of maximum buffer capacity

[3]



EXAMINERS' COMMENTS
This question was mostly left blank.

For the few students who attempted to sketch a graph, the common mistakes observed were:

- showing only one or two equivalence points
- labelling the y-axis as volume of NaOH and hence the wrong values were stated
- the pH values of at the three maximum buffer capacities were pH 4, 8 and 12, which were the values in the question in (c)(i) and is totally irrelevant

4 (c) (iii) Histidine can be converted to histamine by an enzyme called histidine decarboxylase. The enzyme undergoes partial hydrolysis to produce the following fragments:

- ala-cys-phe
- lys-asp-asp-gly
- phe-arg-lys
- ala-cys-phe-phe-arg-lys
- asp-asp-gly

Give the sequence of the nine amino acid residues of the enzyme. [1]

Reasoning:
 ala-cys-phe lys-asp-asp-gly
 ala-cys-phe-phe-arg-lys phe-arg-lys
 asp-asp-gly

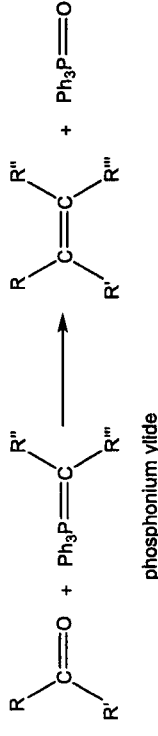
The sequence of the enzyme is ala-cys-phe-phe-arg-lys-asp-asp-gly

[Total: 20]

EXAMINERS' COMMENTS

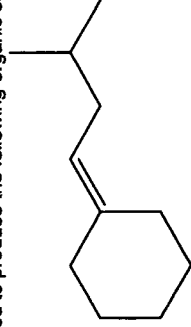
This question was well-done. Many students scored the full credit here.

5 Wittig reaction is a very important tool in organic chemistry and is particularly useful for the synthesis of alkenes, as the double bond forms specifically at the location of the original aldehyde or ketone. The Wittig reagent used is triphenyl phosphonium ylide, $\text{Ph}_3\text{P}=\text{CR}''''$, where the phenyl group is abbreviated as 'Ph'.

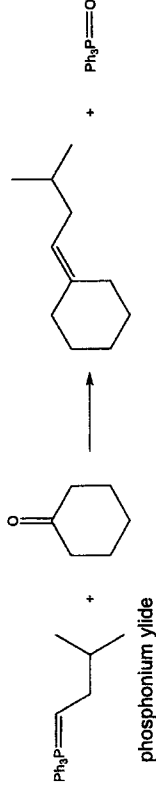


where $\text{R}, \text{R}', \text{R}'', \text{R}''' = \text{H}$ or alkyl

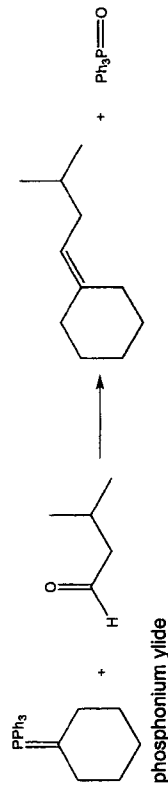
(a) Draw the structures of the carbonyl compound and the specific phosphonium ylide that can be used to produce the following organic compound.



[2]



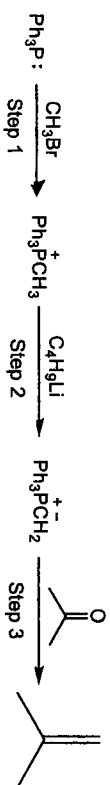
OR



EXAMINER'S COMMENTS

This question was done quite well. Most students were able to recognise the pattern and deduce the carbonyl compound and the phosphonium ylide to form the organic compound. Some even gave both the alternative answers.

- 5 (b) The synthesis of methylpropene via the Wittig reaction is shown below.



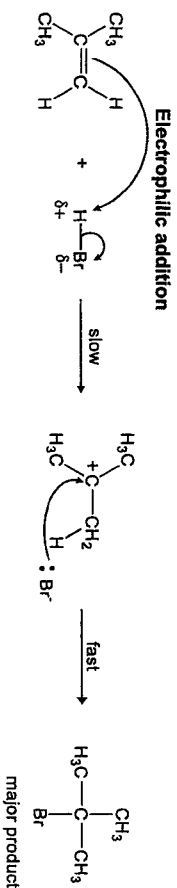
- (i) Name the type of reaction that occurs in step 1. [1]

Nucleophilic substitution

- (ii) State the role of butyl lithium, $\text{C}_4\text{H}_9\text{Li}$, in step 2. [1]

$\text{C}_4\text{H}_9\text{Li}$ acts as a base/proton acceptor

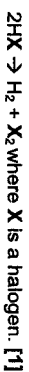
- (iii) Methylpropene undergoes a reaction with hydrogen bromide. Suggest a mechanism for this reaction and use it to predict the major product. Explain your reasoning. [3]



EXAMINER'S COMMENTS
Most students were able to get (i) correct, but did not manage to identify that butyl lithium functioned as a Bronsted-Lowry base as it has removed a proton from Ph_3PCH_3 in order to form the phosphonium ylide in (ii). Some students showed electrophilic addition mechanism of propene with HBr, instead of methylpropene with HBr. Most students managed to get the mechanism correct.

- (iv) Describe and explain the trend in the thermal stability of the hydrogen halides HCl , HBr and HI . Include an equation for the thermal decomposition reaction in your answer. [3]

Hydrogen halides decompose on heating to give hydrogen gas and halogens.



The thermal stability decreases down from HCl , HBr and HI . [1]

Down the group, as the size of the halogen atom increases.

The H-X bond length increases and is weaker.

Hence, the bond energy of H-X decreases, and thermal stability decreases

down the group. [1]

EXAMINER'S COMMENTS

This question was poorly done. Common mistakes included stating that HX is an ionic compound, and explaining that the size of the halide ion increases down the group. Many students also failed to explain that as the size of the halogen atoms increased, the effectiveness of orbital overlap decreases/bond length increases and thus bond strength weakens over the group. Many students also gave the wrong equation for the thermal decomposition of the hydrogen halides; $\text{H-X} \rightarrow \text{H}^+ + \text{X}^-$

- (b) (v) Hence, by stating relevant information from the Data Booklet, suggest how the rate of the reaction will change in (b)(iii) when hydrogen chloride is used instead of hydrogen bromide. [2]

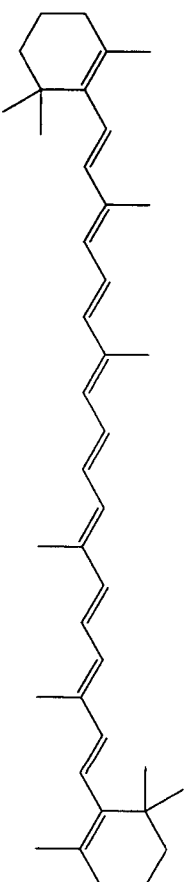
Bond energy H-Cl : 431 kJ mol^{-1}
Bond energy H-Br : 366 kJ mol^{-1}

When hydrogen halides react with alkenes, the H-X bond has to be broken... Since the breaking of H-X bond takes place in the slow, rate-determining step, the stronger H-X bond, the slower the reaction will be... Thus rate of reaction will be slower when hydrogen chloride is used instead of hydrogen bromide.

EXAMINER'S COMMENTS

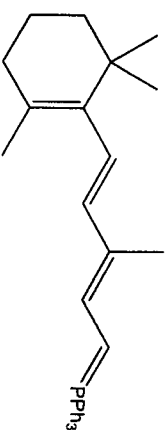
This question was done well. Many students were able to score the full marks for this section.

- 5 (c) (i) Wittig reaction is also used in the industry to synthesise β -carotene. β -carotene is a food colouring that can be extracted from the pigmentation found in red-orange plants and fruits such as carrots. It can be synthesised using excess of an aldehyde and 2 molecules of phosphonium ylide.



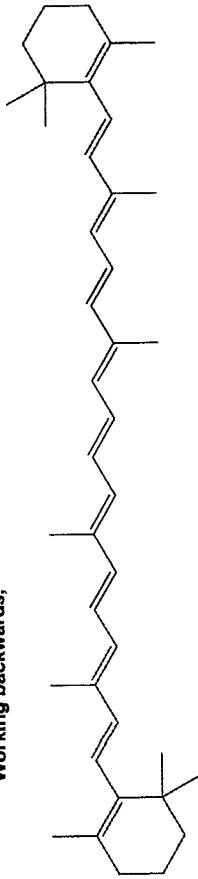
β -carotene

- (ii) The phosphonium ylide used to synthesise β -carotene is given below, where Ph represents a phenyl group.

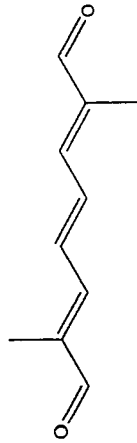


- Suggest the structure of the aldehyde that can be used to produce β -carotene. [1]

Working backwards,



Structure of the aldehyde is:




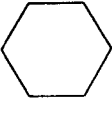
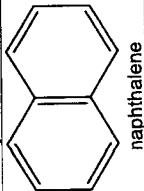
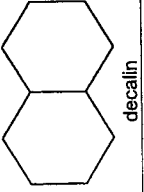
EXAMINER'S COMMENTS

This question was poorly done. Many students did not pick out information from the question, that 2 molecules of phosphonium ylide was used, and thus drew the wrong structure of the aldehyde.

- 5 (d) The long conjugated hydrocarbon chain in β -carotene leads to its intense orange colour.

A conjugated system contains a series of alternating single and double bonds, in which there is a p orbital on each atom and electrons are delocalised in the molecule. This generally lowers the overall energy of the molecule and increases its stability.

The table below contains information about cyclohexene and naphthalene. Cyclohexene contains one carbon-carbon double bond and shows chemical properties common to other alkenes. Naphthalene, $C_{10}H_8$, shows chemical properties common to aromatic compounds.

alkene	conditions for reaction with hydrogen	product	calculated enthalpy change of hydrogenation/ kJ mol^{-1}
 cyclohexene	room temperature, nickel catalyst	 cyclohexane	-118
 naphthalene	-	 decalin	?

- (i) Calculate the enthalpy change of hydrogenation of naphthalene. [1]

$$\Delta H = 5 \times (-118) = -590 \text{ kJ mol}^{-1}$$

- (ii) The actual value for the enthalpy change of complete hydrogenation of naphthalene is -335 kJ mol^{-1} . Explain why this is so, in terms of hybridisation and interactions of the orbitals in the carbon atoms within a naphthalene molecule. [2]

Each carbon atom is sp^2 hybridised and there is an unhybridised p

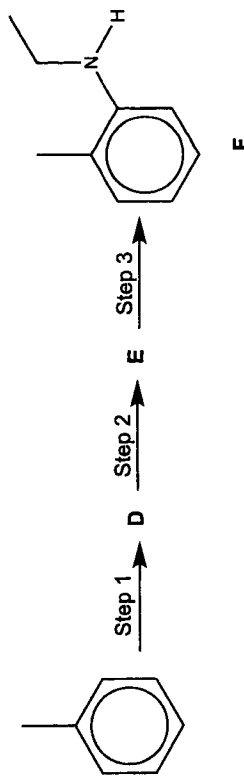
orbital on each carbon atom which overlaps sideways to form a

resonance structure, giving the molecule extra stability.

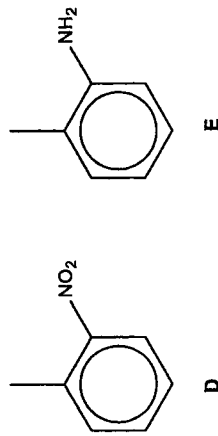
EXAMINER'S COMMENTS

This question was poorly done. Many students did not identify the type of hybridisation that C in naphthalene had, and the reason why it is more stable, when the question specifically asked for it. Moreover, the clue, "A conjugated system contains a series of alternating single and double bonds, in which there is a p orbital on each atom and electrons are delocalised in the molecule," has been also given in the question, which students could have included in their answer.

- 5 (e) Dyes possess colour as they have an extended conjugated system. Compound F is used in the manufacture of dyes and paints. It can be synthesised from methylbenzene in three steps as shown.



- (f) Suggest structures for the organic compounds D and E. [2]



(ii) Suggest reagents and conditions for each of the steps 1 and 2. [2]

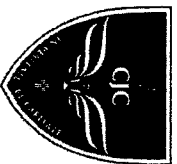
Step 1: concentrated HNO_3 , concentrated H_2SO_4 , 30°C

Step 2: (1) Sn, concentrated HCl , heat under reflux; (2) aqueous NaOH

[Total: 20]

EXAMINER'S COMMENTS

This question was mostly well attempted. Most students were able to identify the organic compounds D and E, and state the correct reagents and conditions required.



Catholic Junior College
JC2 Preliminary Examinations
Higher 2

CANDIDATE
NAME

CLASS

CHEMISTRY

9729/04

Paper 4 Practical

23 August 2022
2 hours 30 minutes

Candidates answer on the Question Paper.
Additional Materials: As listed in the Confidential Instructions

READ THESE INSTRUCTIONS FIRST

Write your name and class in the boxes above.

Give details of the practical shift and laboratory, where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

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

Answer all questions in the spaces provided on the Question Paper.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 20 and 21.

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.

Shift	
Laboratory	

For Examiner's Use	
1	/ 15
2	/ 13
3	/ 27
Total	/ 55

ANSWERS for review

This document consists of 24 printed pages and 0 blank page.

9729/04/CJC JC2 Preliminary Examinations 2022

Turn over

Answer all the questions in the spaces provided.

1 Determination of the M_r of a hydrated ethanedioate salt, using acidified potassium manganate(VII) by titration

Calcium ethanedioate is the major component of the most common type of human kidney stones. It is one of a series of salts formed from ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$. Another of these salts can be represented by the formula $\text{X}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, where X is a Group 1 metal.

Solution Q contains 64.5 g dm^{-3} of $\text{X}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in deionised water. You are not provided with Q.

FA 1 is a diluted solution of Q, in which 35.70 cm^3 of Q was made up to 250 cm^3 with deionised water in a graduated flask.

FA 2 is $0.0200 \text{ mol dm}^{-3}$ potassium manganate(VII), KMnO_4 .

FA 3 is 1.00 mol dm^{-3} sulfuric acid, H_2SO_4 .

In this question, you will perform a titration. The data from this titration will be used to determine:

- the concentration of $\text{C}_2\text{O}_4^{2-}$ ions in Q.
- the M_r of $\text{X}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and hence the identity of the metal X.

(a) Titration of FA 1 against FA 2

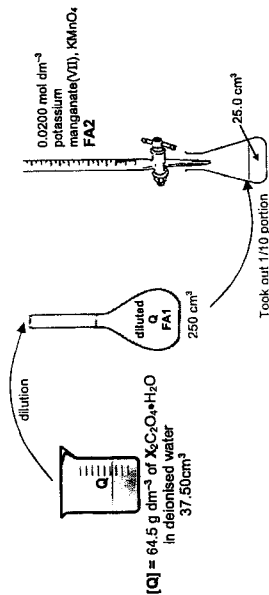
In this titration, FA 2 is run from a burette into the conical flask containing FA 1 and FA 3. Initially, the colour of the FA 2 will take some time to disappear. After some FA 2 has been added, sufficient $\text{Mn}^{2+}(\text{aq})$ ions will be present to allow the reaction to occur faster.

The end point is reached when a permanent pale pink colour is obtained.

- Fill the burette with FA 2.
- Using a pipette, transfer 25.0 cm^3 of FA 1 into the conical flask.
- Using an appropriate measuring cylinder, transfer 25.0 cm^3 of FA 3 to the same conical flask.
- Heat this solution to about 60°C .
- Run FA 2 from the burette into this flask until a permanent pale pink colour is obtained. Be careful when you titrate under the hot condition.
- Record your titration results to an appropriate level of precision, in the space provided next page.
- Repeat points 1 to 6 until consistent results are obtained.
- Turn off your Bunsen burner.

9729/04/CJC JC2 Preliminary Examinations 2022

Turn over



Titration results

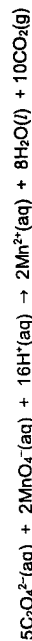
	1	2
Final burette reading /cm ³	24.95	49.90
Initial burette reading /cm ³	0.00	24.95
Volume of FA 2 used /cm ³	24.95	24.95

- Tabulate initial and final burette readings and volume used in the titration table and table has correct headers and units.
- Consistent burette readings taken ($V_{FA2} \pm 0.10 \text{ cm}^3$) and recorded to 2 d.p.
- Accuracy of titration results. [5]

(ii) From your titrations, obtain a suitable volume of FA 2 to be used in your calculations. Show clearly how you obtained this volume.
 Average volume of FA 2 = $\left(\frac{24.95+24.95}{2}\right) = 24.95 \text{ cm}^3$

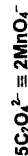
volume of FA 2 =[1]

(iii) The equation for the reaction between ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$ and manganate(VII) ions is shown below.



Calculate the amount of ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$ in 25.0 cm³ of FA 1.

Amount of $\text{MnO}_4^{-} = \left(\frac{24.95}{1000} \times 0.0200\right) = 4.99 \times 10^{-4} \text{ mol}$



Amount of $\text{C}_2\text{O}_4^{2-}$ in 25.0 cm³ of FA 1 = $\left(\frac{5}{2} \times 0.000499\right)$

= $1.25 \times 10^{-3} \text{ mol}$

amount of $\text{C}_2\text{O}_4^{2-}$ in 25.0 cm³ of FA 1 =[2]

[Turn over

(iv) Determine the concentration in mol dm⁻³, of $\text{C}_2\text{O}_4^{2-}$ in Q. (concentrated solution)

Amount of $\text{C}_2\text{O}_4^{2-}$ in 250 cm³ of FA 1

= $\left(\frac{250}{1000} \times 1.25 \times 10^{-3}\right) \text{ mol}$

= $\left(\frac{250}{1000} \times 1.25 \times 10^{-3}\right) \text{ mol}$

= 0.0125 mol

Amount of $\text{C}_2\text{O}_4^{2-}$ present in 35.70 cm³ of Q = 0.0125 mol

Concentration of $\text{C}_2\text{O}_4^{2-}$ in Q = $\left(\frac{0.0125}{35.70} \times 1000\right) \text{ mol dm}^{-3}$

= 0.349 mol dm⁻³

concentration of $\text{C}_2\text{O}_4^{2-}$ in Q = 0.349 mol dm⁻³.....[2]

(v) Use your answer to (a)(iv) to calculate the M_r of the ethanedioate salt.

Given: solution Q contains 64.5 g dm⁻³ of $\text{X}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

M_r of $\text{X}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} = \frac{64.5}{0.349} = 184.8$

M_r of the ethanedioate salt =[1]

(vi) Hence, deduce the identity of X. Show your working clearly.

[A: C, 12.0; O, 16.0; H, 1.0; Li, 6.9; Na, 23.0; K, 39.1; Rb, 85.5; Cs, 132.9; Fr, 223.0]

M_r of $\text{X}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O} = 184.8$

$2(\text{A, of X}) + 88.0 + 18.0 = 184.8$

A, of X = 39.4

So, X is ~~potassium~~

X is[2]

(b) A student performed the experiment in (a)(i) using a sample of another ethanedioate salt. The student obtained a mean titre value of 22.20 cm³.

The teacher calculated that the volume of FA 2 required should be 22.40 cm³. The teacher told the student that the total percentage error from the apparatus in the experiment was 0.4%.

Calculate the error in the student's result, based on these data. State and explain whether or not the student's result is accurate.

Experimental error = $\frac{22.40 - 22.20}{22.40} \times 100\% = 0.893\%$

Candidate states that experiment is not accurate and justifies this in terms...

of experimental error being > apparatus error.....

.....[2]

[Total: 15]

[Turn over

2 Investigation of reaction between manganate(VII) ions and ethanedioate ions

FA 2 is 0.0200 mol dm⁻³ potassium manganate(VII), KMnO₄ (same as in Q1).

FA 3 is 1.0 mol dm⁻³ sulfuric acid, H₂SO₄ (same as in Q1).

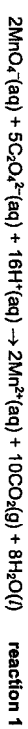
FA 4 is 0.200 mol dm⁻³ ethanedioic acid, H₂C₂O₄.

FA 5 is 0.0100 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃.

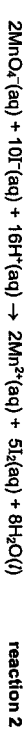
FA 6 is 0.100 mol dm⁻³ potassium iodide, KI.

You are also provided with a starch indicator.

Acidified potassium manganate(VII) oxidises ethanedioate ions, C₂O₄²⁻ as shown in **reaction 1**. The Mn²⁺ ions produced in **reaction 1** act as a catalyst for the reaction. This is an example of autocatalysis.



You are to investigate how the rate of reaction changes with [MnO₄⁻]. To do this, you will prepare a reaction mixture containing **FA 2**, **FA 3** and **FA 4**. At timed intervals, you will withdraw **five aliquots** (portions) of the reaction mixture, add them to 10 cm³ of excess KI which will “quench” the reaction by reacting away all MnO₄⁻ via a redox reaction as shown in **reaction 2**.



You will then titrate the iodine produced in the resulting solutions against sodium thiosulfate (**reaction 3**).



Your titre values will indicate the concentration of MnO₄⁻ remaining in the reaction mixture at different times. Hence, the rate of reaction between MnO₄⁻ and C₂O₄²⁻ at different times can be determined by graphical analysis of your results.

Amount of MnO₄⁻ present at that instantaneous time can be found by finding the amount of iodine that has reacted with thiosulfate.

1. At the start, before the reaction

_____ MnO₄⁻

2. 1:00 minute

_____ MnO₄⁻

3. 4:00 minute

_____ MnO₄⁻

4. 7:00 minute

_____ MnO₄⁻

5. 10:00 minute

_____ MnO₄⁻

6. 14:00 minute

_____ MnO₄⁻

You should read all of the instructions on this page and the method on the next page before you start this experiment.

Recording your results

- In an appropriate format in the space provided on **page 7** under the heading, **Results**, in (b), prepare a table to record, for each of your aliquots, the
- transfer time in minutes and seconds,
 - titration results (initial and final burette readings; and volume of **FA 5** added),
 - time, *t*, which is the transfer time converted to minutes, to one decimal place (e.g. a transfer time of 2 min 27 s becomes 2 min + 27/60 min = 2.5 min).

Make certain that your recorded results show the precision of your working.

(a) Method

Preparing the boiling tubes and burette

1. Using a 10 cm³ measuring cylinder, add about 10 cm³ of **FA 6** to each of the labelled boiling tubes, 1 to 5.
2. Fill a burette with **FA 5**.

Preparing the reaction mixture

3. Use appropriate measuring cylinders to add to the beaker labelled **reaction mixture**
 - 5.0 cm³ of **FA 3**,
 - 50.0 cm³ of **FA 4**,
 - 45.0 cm³ of deionised water.

4. Place 25.0 cm³ of **FA 2** into a 25 cm³ measuring cylinder.
5. At a convenient time, pour **FA 2** into the beaker labelled **reaction mixture**. Start the stopwatch at the instant of mixing and stir the mixture thoroughly using a glass rod.

Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch until you have collected all of your aliquots.

Removing aliquots of reaction mixture

Note: Leaving all of the titrations to be performed until after all the aliquots have been collected may cause you time problems.

6. At approximately 1 minute, use a 10 cm³ pipette to remove a 10.0 cm³ aliquot of the reaction mixture. **Immediately** transfer this aliquot into the boiling tube labelled **1** and shake the mixture. Note and record the transfer time (in minutes and seconds, to the nearest second) when half of the reaction mixture has emptied from the pipette.
7. At approximately 4 minutes, repeat point 6. Transfer this aliquot into the boiling tube labelled **2** and shake the mixture.
8. Repeat point 6 three more times at about 7 minutes, 10 minutes and 13 minutes, transferring the aliquots into the boiling tubes labelled **3** to **5**.

Titration

Note: Each titration is to be performed **once only**, so great care should be taken that you do not overshoot the end-point.

9. Pour all the contents of boiling tube **1** into a clean conical flask. Rinse this boiling tube with deionised water and add the washings to the conical flask.
10. Record the initial burette reading. Titrate the liberated I₂ in this solution with **FA 5** until the solution turns pale yellow. Then add about 1 cm³ of starch indicator. The solution will turn blue-black. Continue to titrate until the blue-black colour just disappears at the end-point. Record the final burette reading and the volume of **FA 5** added.
11. Wash this conical flask thoroughly with water.
12. Top up the burette with **FA 5**.
13. Repeat points **9** to **11** as required for each of the remaining boiling tubes.

(b) Results

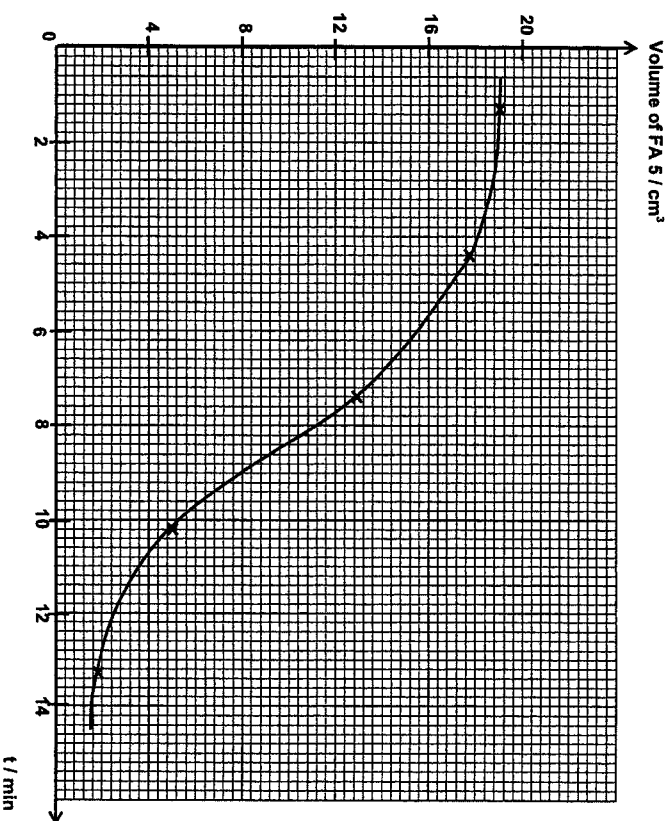
Transfer time	Final burette reading/cm ³	Initial burette reading/cm ³	Volume of FA 5 added/cm ³	t/min
1 min 20 s	19.00	0.00	19.00	120
4 min 25 s	17.70	0.00	17.70	265
7 min 25 s	30.60	17.70	12.90	445
10 min 12 s	35.60	30.60	5.00	612
13 min 20 s	37.40	35.60	1.80	800

[5]

- Tabulates transfer time, initial and final burette readings, volume of **FA 5** added and **t** in a single table with correct headers and correct units.
- Records all 5 full sets transfer times in whole no. in min and s and converts all values of **t** correctly to 1 decimal place in min.
- Records all 5 full sets of initial and final burette readings + calculates all titres correctly to 2 d.p.
- Enters all 5 full sets of data with all transfer times within range of suggested times.
- Titre for first aliquot within range + decreasing titre with increasing time, **t**.

- (c) (i) On the grid below, plot a graph of the volume of sodium thiosulfate, FA 5, on the y-axis, against time, t , on the x-axis.

Draw the most appropriate curve taking into account all of your plotted points.



- Axes correct way round + axes with correct labels with units + uses proper scale (not awkward scale) with plotted points occupying at least half of the given grid in both directions.
- All points plotted correctly to within $\pm \frac{1}{2}$ small square.
- A smooth curve (correct shape) of best-fit drawn, based on student's results.

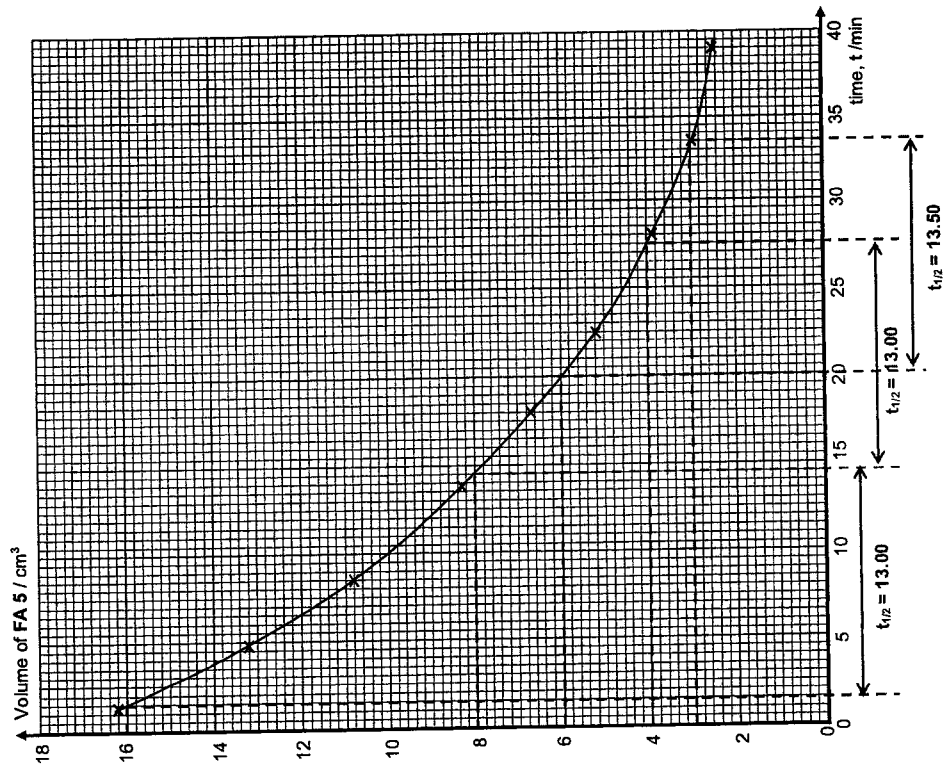
[3]

- (ii) The rate of reaction at time t is indicated by the slope of the tangent at time t . Describe and explain how the shape of the graph in (c)(i) shows that the reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is an autocatalysed reaction.
- At the start, the slope of the tangent is almost zero/small/gentle. This indicates that the rate of reaction is low due to absence of Mn^{2+} /catalyst or low concentration of Mn^{2+} /catalyst.
- As the reaction proceeds, the slope/gradient of the tangent increases. This indicates that the rate of reaction increases due to more catalyst/ Mn^{2+} is produced or concentration of Mn^{2+} /catalyst increases.
- Towards the end, the slope of the tangent decreases. This indicates that the rate of reaction decreases due to decrease in concentration of reactants.

[2]

A student performed a similar experiment in cooler conditions. In point 3, she used the same volumes of **FA 3** and **FA 4** that you used but she also added 5.0 cm^3 of a solution of manganese(II) sulfate, MnSO_4 , a source of Mn^{2+} to catalyse the reaction. She only added 40.0 cm^3 of deionised water, so the total volume used was the same as in your experiment.

- (d) On the grid below, the data from the student's experiment has been plotted and the graph line has been drawn.



Use data from the graph in (d) to determine the order of reaction with respect to $[\text{MnO}_4^-]$ in reaction 1. Draw clearly any construction lines on the graph. Explain your reasoning clearly.

Volume of $\text{S}_2\text{O}_3^{2-}$ (FA 5) required at time t is directly proportional to the $[\text{MnO}_4^-]$ left in the reaction mixture at time t .

From the graph, first $t_{1/2} = 13.00 \text{ min}$,
second $t_{1/2} = 13.00 \text{ min}$,
third $t_{1/2} = 13.50 \text{ min}$.

Indicate the $t_{1/2}$ correctly (based on working) either on the graph or in this space.

Shows clear construction lines on the graph to determine the $t_{1/2}$ (showing the initial V for each $t_{1/2}$ clearly).

Since half-lives are (approximately) constant, the reaction is first order with respect to $[\text{MnO}_4^-]$ in reaction 1.

[3]
[Total: 13]

3 Part 1: Qualitative Analysis

In this task you are to explore the chemistry of some compounds of an unknown transition element **R** and determine the identities or structures of a number of different substances.

- FB 1** is a solid sample of a common dioxide of the unknown transition element **R**.
FB 2 is dilute sulfuric acid, H_2SO_4 .
FB 3 is a solid sample of sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$.
FB 4 is a solution of pure compound **S**, which is the product that will be formed in (a)(i).
FB 5 is a dilute solution of KMnO_4 .
FB 6 is a simple hydrocarbon compound.
FB 7 is bromine water.

Carry out the following experiments. Carefully record your observations in the spaces provided. Test any gases produced.

Test	Observations
<p>(a)(i) Transfer all of the solid sample of FB 3 into a small conical flask. Add 25 cm³ of FB 2 to the flask. Gently heat the flask until the temperature of the mixture reaches about 60 °C. Swift the mixture carefully. Place the flask on the wire gauze / heat proof mat.</p>	<p>1. White solid ($\text{Na}_2\text{C}_2\text{O}_4$) eventually dissolves during the experiment.</p>
<p>Using a spatula, add FB 1 to the mixture in small portions. Between each addition, stir the mixture carefully with the thermometer and observe any changes in the temperature of the mixture.</p>	<p>2. Effervescence/bubbles after each addition (do not accept "gas evolved"). 3. CO_2 gas (collected) gives a white ppt with lime water.</p>
<p>Stop adding FB 1 to the mixture when you think the reaction is complete.</p>	<p>4. Upon addition of FB 1, temperature of mixture rises / conical flask feels hot (even though no heat is applied). 5. Temperature rise stops / temperature falls / mixture starts to cool / effervescence much less vigorous on addition of more FB 1.</p>

[Turn over

<p>Filter the mixture into a boiling tube and leave the filtrate to stand. The filtrate contains the compound S. Retain this filtrate for use in (a)(ii).</p>	<p>6. (Pale pink) filtrate turns yellow-green / pale yellow.</p>
---	--

- (a)(ii) In this part, you are to investigate the effect of the addition of aqueous sodium hydroxide, and the addition of ammonia, to separate portions of the filtrate from (a)(i) and **FB 4**.
 solution of compound **S**
- In the space below, prepare a suitable table and in it record details of the tests performed and the observations made.

Test	Observations
<p>(a)(iii) Place 2 cm³ of the filtrate from (a)(i) in a test-tube, add to it dropwise NaOH(aq), with shaking, till excess. To 2 cm³ of the filtrate from (a)(i) in another test-tube add to it dropwise $\text{NH}_3\text{(aq)}$, with shaking, till excess. Repeat the above tests using NaOH(aq) and $\text{NH}_3\text{(aq)}$ separately with FB 4, in place of the filtrate from (a)(i), solution of compound</p>	<p>Tests with the filtrate from (a)(i): 7. NaOH(aq) and $\text{NH}_3\text{(aq)}$: off-white / light brown ppt. Tests with FB 4: 8. NaOH(aq) and $\text{NH}_3\text{(aq)}$: off-white / light brown ppt. 9. NaOH(aq) and $\text{NH}_3\text{(aq)}$ with both solutions: all 4 ppts insoluble in excess. 10. NaOH(aq) and $\text{NH}_3\text{(aq)}$ with both solutions: ppts darken (on standing) / turns brown on contact with air</p>
<p>A single table to describe the procedure of adding dropwise / small volume of NaOH(aq) and $\text{NH}_3\text{(aq)}$ and then in excess, both with shaking, to separate samples of the filtrate from (a)(i) and FB 4.</p>	

[Turn over

Note that the observations for tests (b) are provided as shown below.

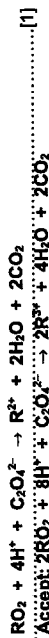
	Test	Observations
(b) (i)	Place 5 cm ³ of aqueous sodium hydroxide in a test-tube. Add 1 drop of FB 6 to this test-tube. simple hydrocarbon dilute solution of KMnO ₄ Add FB 5, dropwise with shaking, until no further change is seen. Do not exceed 40 drops.	Solution turns green / blue-green. Colour deepens as more drops are added.
(b) (ii)	Note: Eventually, this reaction will produce a precipitate of FB 1. Place 5 cm ³ of FB 2 in a test-tube. H ₂ SO ₄ (aq) Add 1 drop of FB 6 to this test-tube. simple hydrocarbon Add FB 5, dropwise with shaking, until no further change is seen. Do not exceed 40 drops.	Purple FB 5 decolourises. Colourless solution turns progressively darker brown.
(b) (iii)	Place 5 cm ³ of deionised water in a test-tube. simple hydrocarbon bromine water Add 1 drop of FB 6 to this test-tube. Add FB 7, dropwise with shaking, until no further change is seen.	Orange bromine water decolourised (solution eventually turns yellow).

[9]

Conclusions

(c) (i) In (a)(i), the reaction between FB 1 and FB 3 occurs under acidic conditions. RO₂ solid Mn₂C₂O₄

Write an ionic equation for this reaction. Use RO_2 to represent FB 1 in this equation.



(ii) Consider your observations in (a)(i). Identify the transition metal ion formed in (a)(i). Justify your choice by reference to your observations in (a)(ii).

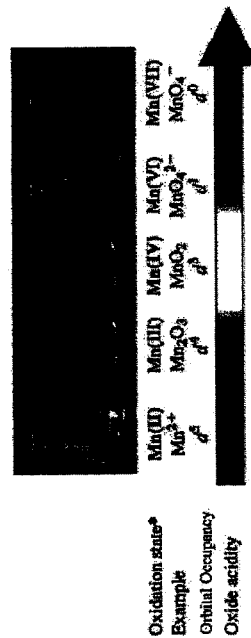
ion present is Mn^{2+}
 justification
 Off-white ppt. formed with both NaOH and NH₃, which are insoluble in excess (and which turns darker on standing in air).....[2]

(d) Consider the colour of compound FB 5 and the observations provided in (b)(i). Suggest a value for the oxidation number of R in the coloured ion produced in (b)(i). Explain your reasoning.

oxidation number of R = +5 or +6
 explanation The oxidation numbers of R / Mn in compound, FB 5 and in, FB 1, are +7 and +4 respectively.....

So, as the reaction in (b)(i) involves a change of O.N. from +7 to +4, the O.N. of the coloured ion will be in between these values.....[2]

Some Oxidation States of Manganese



*Most common states in bold face.

[Turn over

[Turn over

- (e) Compound U is the main organic product in (b)(i), when FB 6 reacts with FB 5 under alkaline conditions. The molecular formula of U is $C_6H_{12}O_2$ (difference of 20 and 2H)

(i) Deduce the molecular formula of FB 6.

simple hydrocarbon

Explain your deduction. Your explanation should be supported by evidence from the observations provided in (b).

molecular formula of FB 6 is C_6H_{12}

explanation • Br/acid decolourised, so $C=C$ present / FB 5 or $KMnO_4$ decolourised so $C=C$ present.

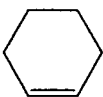
• Cold alkaline MnO_4^- oxidises $C=C$ to $C(OH)-C(OH)$ / 1,2-diol OR Mild oxidation

• Only two O atoms in molecular formula of U, so only one $C=C$ • So, FB 6 is $C_6H_{12}O_2$ (2 x OH) = $C_6H_{12}O_2$ [2]

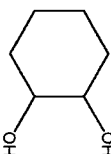
- (ii) Draw the structural formulae for FB 6 and compound U.

simple hydrocarbon

structure of FB 6



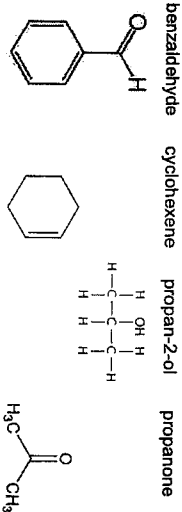
structure of U



[2]

[Turn over

- Part 2: Planning
(a) Four liquid samples labelled FC 1, FC 2, FC 3 and FC 4 are listed below.



The identity of each of the liquid samples is not known. A student carried out a series of test-tube reactions so as to distinguish the four liquid samples. The tests he performed and the corresponding observations are recorded in the table below.

Test	Observations with FC 1	Observations with FC 2	Observations with FC 3	Observations with FC 4
(i) 1. To 1 cm depth of the sample in a test-tube, add about 1 cm ³ of aqueous bromine.	Orange aqueous bromine is decolourised.	No observable change.	No observable change.	No observable change.
2. To 1 cm depth of the sample in a test-tube, add 10 drops of aqueous H_2SO_4 and 5 drops of aqueous $KMnO_4$. Place the test-tube in a hot water bath.	Purple acidified $KMnO_4$ is decolourised.	Purple acidified $KMnO_4$ is decolourised.	Purple acidified $KMnO_4$ is decolourised.	No observable change.
3. To 1 cm depth of the sample in a test-tube, add 6 drops of aqueous $NaOH$, followed by 10 drops of aqueous I_2 . Place the test-tube in a hot water bath.	No observable change.	A yellow ppt of CHI_3 is seen.	No observable change.	A yellow ppt of CHI_3 is seen.

[Turn over

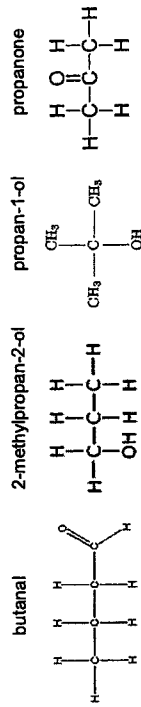
- (ii) Now, based on the student's tests and observations, identify the four liquid samples, FC 1, FC 2, FC 3 and FC 4.

In each case, give evidence to support your conclusion, by completing the table below.

	liquid sample	evidence
FC 1	Cyclohexene.	It decolourises orange $\text{Br}_2(\text{aq})$, indicating the presence of $\text{C}=\text{C}$ or alkene. It also decolourises acidified $\text{KMnO}_4(\text{aq})$ as it undergoes oxidative cleavage.
FC 2	Propan-2-ol.	It decolourises purple acidified $\text{KMnO}_4(\text{aq})$ as a secondary alcohol is oxidised. It also gives a positive iodoform reaction due to the presence of the group, $\text{CH}_3\text{CH}(\text{OH})-$.
FC 3	Benzaldehyde.	It decolourises purple acidified $\text{KMnO}_4(\text{aq})$ as an aldehyde is oxidised.
FC 4	Propanone.	It gives a positive iodoform reaction as it is a ketone with the presence of the group, $-\text{COCH}_3$.

[4]

- (b) Consider the following organic compounds.



Plan an investigation, using test-tube reactions, ~~but not the following~~ which would enable you to identify each of these four compounds.

Each compound should be identified by **only one** positive test result. It is not sufficient to identify simply by eliminating all the others.

Your plan should include:

- details of the reagents and conditions to be used,
- an outline of the sequence of steps you would follow,
- an explanation of how you would analyse your results in order to identify each compound.

Once a compound has been clearly identified, your plan should concentrate on distinguishing the remaining compounds.

YOU MUST NOT CARRY OUT THIS PLAN.

1. Add Iodine's reagent, to the 4 compounds separately in a test tube. Heat gently in a water bath. Butanal, an aldehyde will give a silver mirror, the other 3 compounds will not give a silver mirror.
.....
..... (Accept: Fehling's solution with the corresponding observation.).....
 2. Add 2,4-DNP to the remaining 3 compounds separately in a test-tube. Heat gently in a water bath. Propanone, a ketone will give an orange ppt, the other 2 compounds will not give an orange ppt.
.....
 3. Add $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ to the remaining 2 compounds separately in a test-tube. Heat gently in a water bath. Propan-1-ol being a primary alcohol, is oxidised and the orange acidified $\text{K}_2\text{Cr}_2\text{O}_7$ turns green.
.....
..... (Do not accept $\text{KMnO}_4(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ - used in (a))
 4. Add anhydrous PCl_5 to the remaining compound in a test-tube. Steamy white fumes of HCl are observed, indicating that it is an alcohol, 2-methylpropan-2-ol.
.....
..... (Accept Na metal, SOCl_2 with the corresponding observations.)
- Correct sequence of steps used:
..... 2,4-DNP is not used as the first step as it gives a positive test with both butanal and propanone. [5]
..... acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ is not used as the first step as both butanal and propan-1-ol can both be oxidised. [Total: 27]
..... PCl_5 , Na metal and SOCl_2 are not used as the first step as each gives a positive test with both the alcohols
..... [Turn over

Qualitative Analysis Notes
[ppt. = precipitate]
(a) Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH ₃ (aq)
aluminium, Al ³⁺ (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH ₄ ⁺ (aq)	ammonia produced on heating	-
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.
chromium(III), Cr ³⁺ (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(I), Cu ⁺ (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe ²⁺ (aq)	green ppt. turning brown on contact with air insoluble in excess	green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe ³⁺ (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn ²⁺ (aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn ²⁺ (aq)	white ppt. soluble in excess	white ppt. soluble in excess

[Turn over

(b) Reactions of aqueous anions

ion	reaction
carbonate, CO ₃ ²⁻	CO ₂ liberated by dilute acids
chloride, Cl ⁻ (aq)	gives white ppt. with Ag ⁺ (aq) (soluble in NH ₃ (aq))
bromide, Br ⁻ (aq)	gives pale cream ppt. with Ag ⁺ (aq) (partially soluble in NH ₃ (aq))
iodide, I ⁻ (aq)	gives yellow ppt. with Ag ⁺ (aq) (insoluble in NH ₃ (aq))
nitrate, NO ₃ ⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and Al foil
nitrite, NO ₂ ⁻ (aq)	NH ₃ liberated on heating with OH ⁻ (aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO ₂ in air)
sulfate, SO ₄ ²⁻ (aq)	gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids)
sulfite, SO ₃ ²⁻ (aq)	SO ₂ liberated with dilute acids; gives white ppt. with Ba ²⁺ (aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH ₃	turns damp red litmus paper blue
carbon dioxide, CO ₂	gives a white ppt. with limewater (ppt. dissolves with excess CO ₂)
chlorine, Cl ₂	bleaches damp litmus paper
hydrogen, H ₂	"pops" with a lighted splint
oxygen, O ₂	relights a glowing splint
sulfur dioxide, SO ₂	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl ₂	greenish yellow gas	pale yellow	pale yellow
bromine, Br ₂	reddish brown gas / liquid	orange	orange-red
iodine, I ₂	black solid / purple gas	brown	purple

[Turn over

Name:	Centre/Index Number:	Class:
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DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

Paper 1 Multiple Choice

9729/01
23 September 2022
1 hour

Additional Materials: Multiple Choice Answer Sheet

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

Write in soft pencil.

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

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

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

Read the instructions on the Answer Sheet very carefully.

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

Any rough working should be done in this booklet.

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

This document consists of **15** printed pages and **1** blank page.

1 Beams of charged particles are deflected by an electric field. Under identical conditions, the angle of deflection of a particle is proportional to its charge/mass ratio.

In an experiment, protons are deflected by an angle of $+15^\circ$ by an electric field. In another experiment under identical conditions, particle Y is deflected by an angle of -5° .

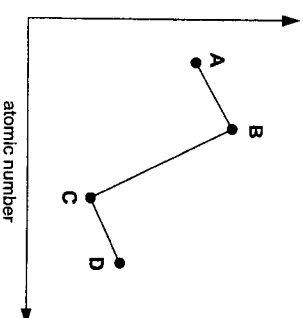
What could be the composition of particle Y?

	protons	neutrons	electrons
A	1	2	1
B	3	3	5
C	4	5	1
D	4	5	3

2 The first ionisation energies of four elements with consecutive atomic numbers below 20 are shown on the graph.

One of the elements reacts with hydrogen to form a covalent compound with formula HX . Which element could be X?

first ionisation energy / kJ mol^{-1}

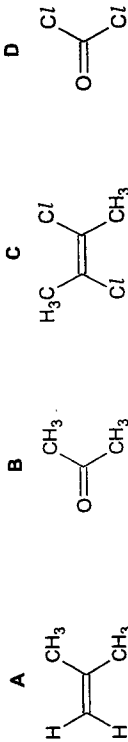


3 Which molecule does **not** have any 90° or 180° bond angles?

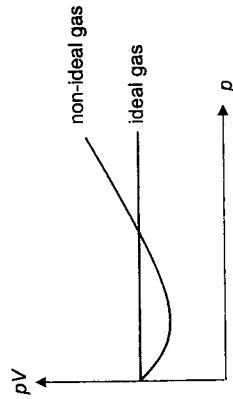
- 1 O_3
- 2 PF_5
- 3 $[PCl_4]^+$
- 4 SF_6

- A** 1 and 3 only
- B** 2 and 4 only
- C** 1, 2 and 4 only
- D** 3 only

4 Which molecule has the largest overall dipole moment?



5 The value of pV is plotted against p for two gases, an ideal gas and a non-ideal gas, where p is the pressure and V is the volume of the gas.



Which gas shows the greatest deviation from ideal gas behaviour at 273 °C?

- A** CO₂ **B** Cl₂
C CH₃OH **D** N₂H₄

6 X and Y are oxides of different elements in Period 3.

If one mole of X is added to water, the solution formed is neutralised by exactly one mole of Y.

What could be the identities of X and Y?

	X	Y
A	P ₄ O ₁₀	Al ₂ O ₃
B	SO ₃	Al ₂ O ₃
C	P ₄ O ₁₀	Na ₂ O
D	SO ₃	Na ₂ O

7 Which factor contributes to the difference in thermal stability between CaCO₃ and BaCO₃?

- A** The polarisability of the ions present in CaCO₃ is greater than that of BaCO₃.
B The melting point of CaCO₃ is lower than that of BaCO₃.
C The charge density of Ca²⁺ is higher than that of Ba²⁺.
D The lattice energy of CaCO₃ is more negative than that of BaCO₃.

8 The volatility of the Group 17 elements, chlorine, bromine and iodine, decreases down the group.

Which of the following is responsible for this trend?

- 1 bond length in the halogen molecule **B** 4 only
 2 bond strength in the halogen molecule
 3 electronegativity of the halogen atom **D** 3 and 4 only
 4 number of electrons in the halogen atom
A 1, 2, 3 and 4

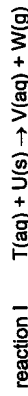
9 30 cm³ of 0.1 mol dm⁻³ sulfuric acid and 40 cm³ of 0.2 mol dm⁻³ sodium hydroxide were mixed in a Styrofoam cup.

Assume that the density and specific heat capacity of the final mixture are 1.0 g cm⁻³ and 4.2 J g⁻¹ K⁻¹ respectively.

What is the temperature change of the solution given that the standard enthalpy change of neutralisation is -57.3 kJ mol⁻¹?

- A** -1.6 °C **B** -1.2 °C **C** +1.2 °C **D** +1.6 °C

10 Which statement is correct to describe the spontaneity of reaction I?



- A** Reaction I is only spontaneous at low temperatures if the reaction is endothermic.
B Reaction I is only spontaneous at low temperatures if the reaction is exothermic.
C Reaction I is spontaneous at all temperatures if the reaction is endothermic.
D Reaction I is spontaneous at all temperatures if the reaction is exothermic.

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

Which statements are correct?

- H_2O_2 acts as both the oxidising agent and reducing agent in its decomposition.
- MnO_4^- reacts with Fe^{3+} in a 1 : 5 ratio under acidic conditions to give Fe^{2+} and Mn^{2+} .
- In an iodometric titration, I_2 is the reducing agent while $\text{S}_2\text{O}_3^{2-}$ is the oxidising agent.
- Each carbon atom in the ion, $\text{H}_2\text{C}_2\text{O}_4^-$, has an oxidation state of +3.

- A 1, 2 and 4 only B 2 and 3 only
C 1 and 3 only D 1 and 4 only

12 Nitric oxide, NO , reacts with hydrogen gas to give nitrogen and water only.

Given that rate = $k[\text{NO}]^2[\text{H}_2]$, which reaction mechanism best agrees with the experimentally determined rate law?

- A $\text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (slow)
 $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ (fast)
- B $\text{NO} + \text{H}_2 \rightarrow \text{HNO} + \text{H}\bullet$ (slow)
 $\text{HNO} + \text{H}\bullet \rightarrow \frac{1}{2}\text{N}_2 + \text{H}_2\text{O}$ (fast)
- C $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ (slow)
 $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ (fast)
- D $2\text{NO} + \text{H}_2 \rightarrow 2\text{HNO}$ (slow)
 $2\text{HNO} \rightarrow \text{N}_2 + \text{H}_2\text{O}_2$ (fast)

13 The initial rate method was used to investigate the reaction between compounds K and L which is catalysed by reagent M.

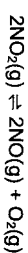
The results obtained are shown below.

experiment	initial [K] / mol dm ⁻³	initial [L] / mol dm ⁻³	initial [M] / mol dm ⁻³	relative rate / s ⁻¹
1	0.0025	0.08	0.80	0.50
2	0.0010	0.08	0.80	0.20
3	0.0050	0.08	0.40	0.25
4	0.0050	0.04	0.80	0.50

What is the rate equation for this reaction?

- A rate = $k[\text{K}][\text{L}][\text{M}]$ B rate = $k[\text{K}][\text{L}]^2[\text{M}]$
C rate = $k[\text{K}][\text{L}][\text{M}]^2$ D rate = $k[\text{K}][\text{L}]^2[\text{M}]^2$

14 Nitrogen dioxide can decompose to form nitrogen monoxide and oxygen.



When 2.50 mol of nitrogen dioxide was allowed to undergo decomposition in a 0.8 dm³ container, 0.528 mol of oxygen was present at equilibrium.

What is the numerical value of the equilibrium constant, K_c , for this reaction?

- A 0.282 B 0.353
C 2.83 D 3.54

15 The formation of sulfur trioxide from sulfur dioxide and oxygen is a reversible reaction.

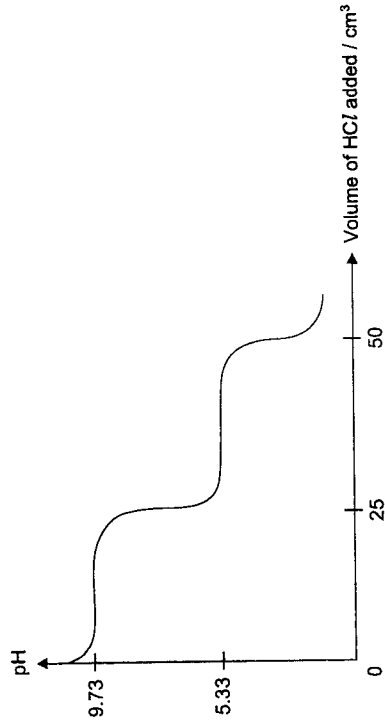


Which statements about this equilibrium are correct?

- The K_c value will be halved if the stoichiometric coefficients in the equation are halved.
- At dynamic equilibrium, the rates of the forward and backward reactions are equal to zero.
- An increase in pressure of the system will result in a greater yield of SO_3 at equilibrium.
- When temperature is reduced, the rate constant of the forward reaction, k_f , decreases to a smaller extent than that of the backward reaction, k_b .

- A 3 and 4 only B 1 and 2 only
C 2, 3 and 4 only D 1 and 3 only

16 The pH change when 1.00 mol dm^{-3} hydrochloric acid was added dropwise to 25 cm^3 of 1.00 mol dm^{-3} piperazine ($\text{C}_4\text{H}_{10}\text{N}_2$) is shown below.



From the table below, which pair of indicators can be used consecutively to detect the end-points of the titration?

indicator	range
bromothymol blue	6.0 – 7.6
ethyl orange	3.4 – 4.8
methyl red	4.8 – 6.0
thymolphthalein	9.4 – 10.6

- A Bromothymol blue followed by ethyl orange
- B Bromothymol blue followed by methyl red
- C Thymolphthalein followed by ethyl orange
- D Thymolphthalein followed by methyl red

17 A student added aqueous silver nitrate, with stirring, to three different mixtures.

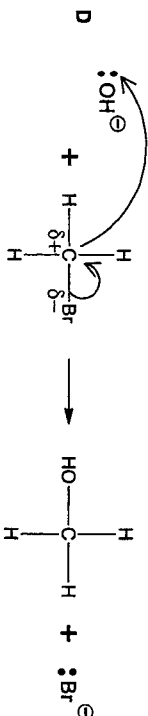
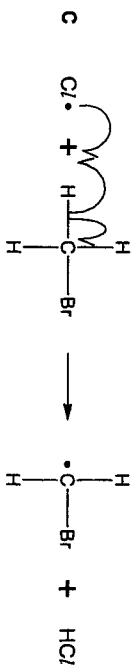
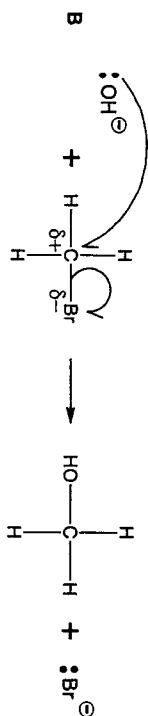
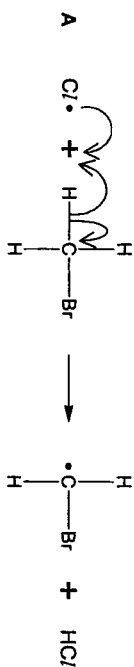
beaker	mixture
1	sodium chloride and sodium bromide
2	sodium chloride and sodium iodide
3	sodium bromide and sodium iodide

The student then added an excess of concentrated aqueous ammonia to each beaker with stirring.

Which observation is correct?

	beaker 1	beaker 2	beaker 3
A	colourless solution	yellow precipitate	yellow precipitate
B	cream precipitate	yellow precipitate	cream and yellow precipitate
C	colourless solution	cream precipitate	cream precipitate
D	yellow precipitate	cream precipitate	cream and yellow precipitate

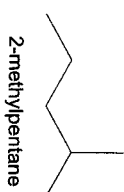
18 Which equation has the movement of electrons correctly shown using curly arrows?



19 Which statement correctly describes enantiomers?

- A A racemic mixture is optically active.
- B Enantiomers have different melting points.
- C Enantiomers exhibit the same biological behaviour in the human body.
- D Enantiomers have the same solubility in the same solvent.

20 2-methylpentane can undergo free radical substitution with chlorine in the presence of ultraviolet light.



Assume that the rate of abstraction of hydrogen atom from each carbon is the same.

Which statements are correct?

- 1 There are four equivalent secondary hydrogen atoms in 2-methylpentane.
- 2 The relative proportion of the tertiary monochloroalkane product will be the smallest.
- 3 There are three isomeric primary monochloroalkane products.
- 4 The propagation step of the reaction mechanism involves H• radicals.

- A 1, 2 and 3 only
- B 2 and 3 only
- C 2 and 4 only
- D 1 and 4 only

21 Which statement is true about the reaction between but-1-ene and aqueous bromine?

- 1 The reaction is an overall first order reaction.
- 2 Water acts as an electrophile in this reaction.
- 3 The reaction involves a trigonal planar intermediate.
- 4 1-bromobutan-2-ol will be the product with the highest yield.

- A 3 only
- B 2 and 3 only
- C 1 and 4 only
- D 3 and 4 only

22 Pyridine is analogous to benzene, and they share very similar chemical properties.



Pyridine undergoes electrophilic substitution with bromine. Which of the following accurately describes the catalyst required and the intermediate formed in this reaction?

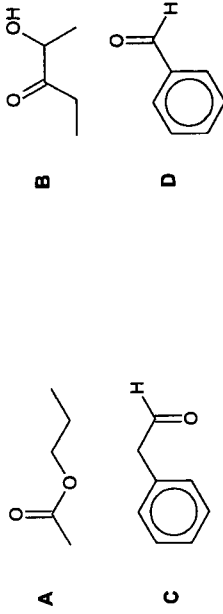
	required catalyst	intermediate formed
A	Lewis base	
B	Lewis base	
C	Lewis acid	
D	Lewis acid	

23 Which chemical test will **not** allow for the following two compounds to be distinguished?

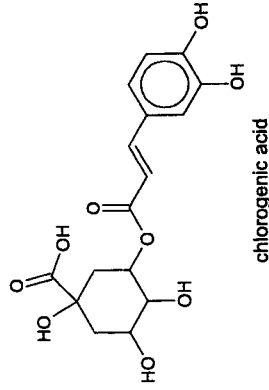


- A Add Br₂ in CCl₄
- B Add neutral FeCl₃(aq)
- C Warm with K₂Cr₂O₇(aq) and H₂SO₄(aq)
- D Warm with KOH(aq), then add excess HNO₃(aq) followed by AgNO₃(aq)

24 Compound X does not give a reddish-brown precipitate with Fehling's solution but produces a pale yellow precipitate with hot alkaline aqueous iodine. What could be the structure of compound X?



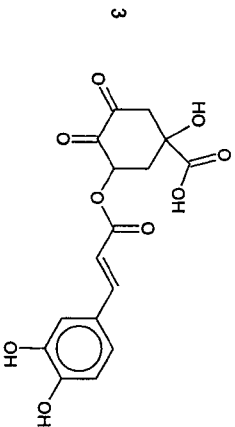
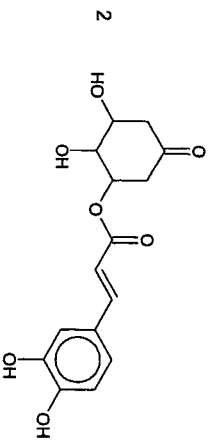
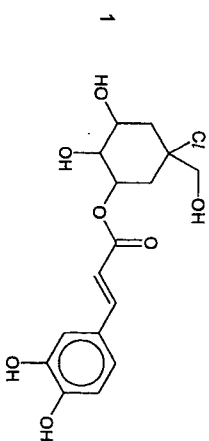
The structure of chlorogenic acid is relevant to Questions 25 and 26.



25 Which statement is true about chlorogenic acid?

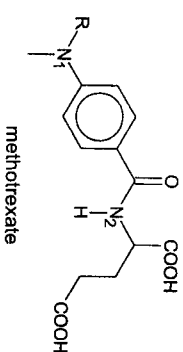
- A 1 mol of chlorogenic acid gives 2 mol of organic products when heated with excess acidified K₂Cr₂O₇(aq).
- B 1 mol of chlorogenic acid produces 1 mol of CO₂ gas when reacted with excess Na₂CO₃(aq).
- C 1 mol of chlorogenic acid will react with 6 mol of NaOH(aq) at room temperature.
- D 1 mol of chlorogenic acid will react with 6 mol of ethanoyl chloride.

26 Which compound below can be used to synthesise chlorogenic acid in either one or two steps?



- A 3 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3

27 Methotrexate is an immunosuppressant used to treat some forms of cancer.

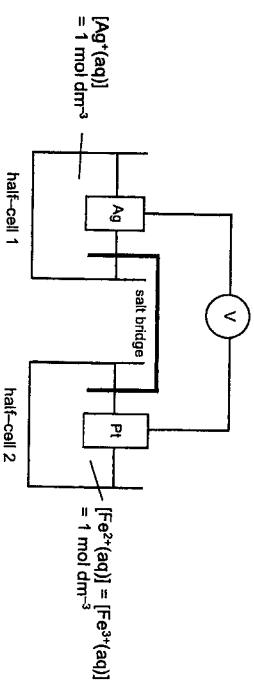


You may assume that the R group is unreactive.

Which statement is true about methotrexate?

- A N_1 can react with ethanoyl chloride to give an amide.
B Both N_1 and N_2 have lone pair of electrons that are available for donation.
C The heating of methotrexate with $H_2SO_4(aq)$ does not produce any zwitterions.
D The treatment of methotrexate with $LiAlH_4$ will result in the removal of 2 oxygen atoms from methotrexate.

28 Consider the galvanic cell below.



Excess NaCN(s) was added into half-cell 2.

Which is true about the galvanic cell above after the addition of NaCN(s)?

- A Electrons flow out of half-cell 1 and into half-cell 2.
B The cell potential becomes more positive.
C The polarity of both electrode changes.
D The cathode reduces in mass.

29 An impure piece of copper contained silver and zinc as minor impurities. It contained no other metal. In order to purify it, the impure copper was made the anode of an electrolytic cell, with a pure copper cathode and aqueous CuSO_4 as electrolyte.

Which statement is true regarding this purification of copper?

- 1 Cu^{2+} is preferentially reduced at the cathode.
 - 2 At the anode, zinc and copper are oxidised.
 - 3 The cell voltage must be adjusted such that only copper and metals with more positive E^\ominus than $E^\ominus_{\text{Cu}^{2+}/\text{Cu}}$ are preferentially oxidised.
- A** 1 only **B** 2 only
C 1 and 2 only **D** 1, 2 and 3

30 Which cation contains exactly two unpaired electrons?

- A** Fe^{3+} **B** Cu^{2+}
C Cr^{3+} **D** Ni^{2+}