Catholic Junior College

JC2 Preliminary Examination
Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY
9729/02

Paper 2 Structured Questions

26 August 2022

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 calculation 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**
Paper 2	**Q1**	**/13**
	Q2	**/11**
	Q3	**/15**
	Q4	**/12**
	Q5	**/11**
	Q6	**/13**
		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 $Cu(OH)_2$ due to the NaOH present.

EXAMINER'S COMMENTS
Qualitative Analysis – Precipitation of insoluble metal hydroxides in NaOH(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 $Cu(OH)_2$ 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 $Cu(OH)_2$ 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 $[Cu(H_2O)_6]^{2+}$ complex which already exists in $CuSO_4(aq)$, 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):

$C_6H_5COCH_3$ C_6H_5CHO $C_6H_5CH_2CHO$

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

B is $C_6H_5CH_2CHO$ [1]

EXAMINER'S COMMENTS
Fehling's Solution – test for aliphatic aldehydes

As Fehling's solution gives a red ppt only for aliphatic aldehydes, only $C_6H_5CH_2CHO$ will give a positive result. The aromatic aldehyde C_6H_5CHO will not give a red ppt, neither will the ketone $C_6H_5COCH_3$. 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 $C_6H_5COCH_3$. [2]

EXAMINER'S COMMENTS

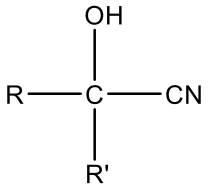
A significant number of students had the incorrect idea that the compounds were presented in order of A, B, C, in spite of the question stating that the compounds were not necessarily in this order. These students referred to the observations for each compound as "A would give [observation] while C would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

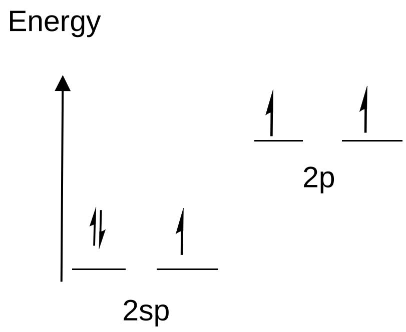
HCN, trace NaOH (or trace NaCN), 10-20 °C [1]

EXAMINER'S COMMENTS

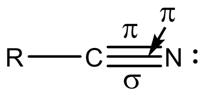
Carbonyl Compounds – Nucleophilic Addition

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).

....[1]

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:

$$:B + H_2O \rightleftharpoons BH^+ + OH^-$$

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) (sp^3 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_5FeS_4. Given that the oxidation state of S is –2 in bornite, write down the oxidation states of Cu and Fe in bornite.

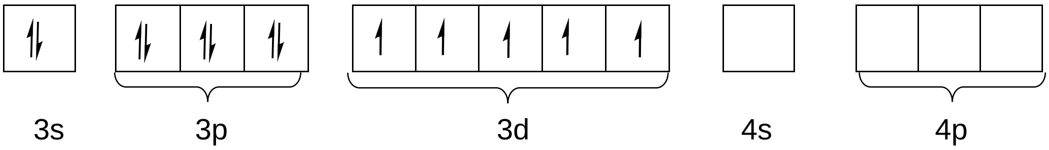
Oxidation state of Cu: .+1........

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.



[1]

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 Cu_xFeS_y.

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.

$$Cu_5FeS_4 + 26HNO_3 \rightarrow Fe(NO_3)_3 + 5Cu(NO_3)_2 + 4S + 13NO_2 + 13H_2O$$

$$Cu_xFeS_y + (6 + 4x)HNO_3 \rightarrow Fe(NO_3)_3 + xCu(NO_3)_2 + yS + (3 + 2x)NO_2 + (3 + 2x)H_2O$$

When 1 mole each of bornite and chalcopyrite were fully reacted with HNO_3, bornite produced 64.2 g more sulfur precipitate and 1.92×10^5 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:

$$13 - (3 + 2x) = \frac{1.92 \times 10^5}{24000}$$

$10 - 2x = 8$

$\therefore x = 1$

[3]

[Total: 13]

EXAMINER'S COMMENTS
Mole Concept & Stoichiometry – mole ratio, mass → mol conversion and volume → 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_5FeS_4 – first mentioned in (b)(i)) and chalcopyrite (Cu_xFeS_y – 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.

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 5.89×10^{-7} 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 5.898×10^{-7} 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 = 6.63×10^{-34} J s
c is the speed of light = 3.00×10^{8} m s^{-1}

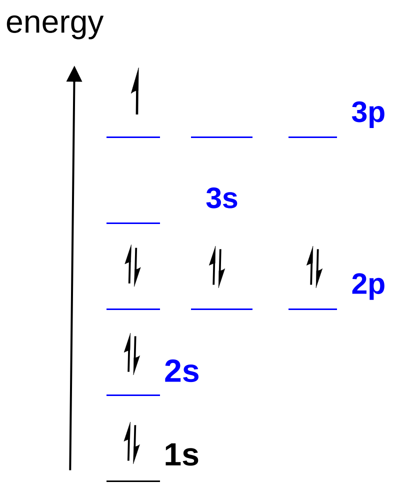
(a) State the electronic configuration of a sodium atom in the ground state.

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, $E = \dfrac{(6.63\times10^{-34})(3.00\times10^{8})}{5.898\times10^{-7}}$
= 3.37 x 10^{-19} J
(ii) Energy = 3.37 10^{-19} x 6.02 x 10^{23}
= 2.03 x 10^{5} J mol^{-1}
= 203 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.

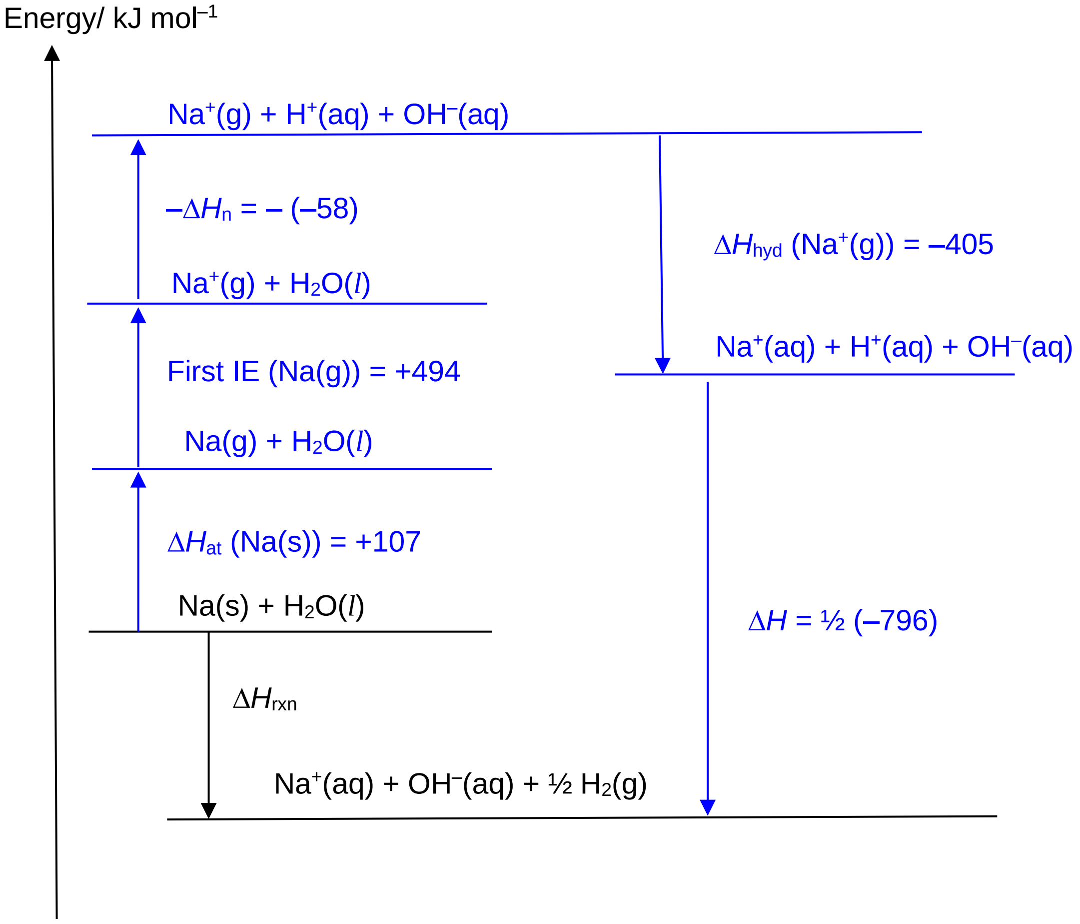
2 **(d)** Sodium can react with water to form aqueous sodium hydroxide.

$$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2} H_2(g)$$

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 $2H^+(aq) \rightarrow H_2(g)$ = –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, ΔH_{rxn} = +107 + 494 + 58 + (–405) + ½ (–796)
= **<u>–144 kJ mol^{-1}</u>**

[5]

EXAMINER'S COMMENTS
This question was not well attempted.

Examples of incorrect responses:

- **Wrongly identified the product of ΔH_{at} 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 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ 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 ↑ represent the endothermic process with positive ΔH and ↓ represent the exothermic process with negative ΔH. Only ↑ and ↓ 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 $H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$. 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. [2]

[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.

$NH_3(l) + NH_3(l) \rightleftharpoons NH_4^+(l) + NH_2^-(l)$ ....[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 $NH_3(aq)$ rather than $NH_3(l)$! 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.

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq) \qquad pK_a = 7.05 \text{ at } 298\text{ K}$$

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

$$NaHS \rightarrow Na^+ + HS^-$$
$$0.100 \text{ mol dm}^{-3}$$

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

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$
$$0.100 \qquad\qquad ?$$

$$[OH^-] = \sqrt{K_b \times 0.100}$$
$$= \sqrt{\frac{Kw}{Ka} \times 0.100}$$
$$= \left(\frac{10^{-14}}{10^{-7.05}} \times 0.100\right)^{1/2}$$
$$= 1.059 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = 14 - pOH$$
$$= 14 - [-\log(1.059 \times 10^{-4})]$$
$$= 10.0$$

[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.

$$C_6H_5SH \rightleftharpoons C_6H_5S^- + H^+$$

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* **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 x 10^{-8} mol dm^{-3} at 298 K.

A buffer solution is prepared by mixing 50.0 cm^3 of 0.500 mol dm^{-3} $NaHSO_3$ and 25.0 cm^3 of 0.600 mol dm^{-3} 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.

$$HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$$

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

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

Amount of HSO_3^- left after reaction = (0.0250 – 0.0150) = 0.0100 mol

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

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

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

$$pH = pK_a + \lg\left(\frac{[salt]}{[acid]}\right)$$

$$= -\lg(6.73 \times 10^{-8}) + \lg\left(\frac{0.200}{0.133}\right)$$

$$= 7.35$$

[2]

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 2.30×10^{-4} mol dm^{-3}.

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

$$\begin{array}{ccccc} CaF_2(s) & \rightleftharpoons & Ca^{2+}(aq) & + & 2F^-(aq) \\ & & x & & 2x \end{array}$$

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

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

[2]

EXAMINER'S COMMENTS

A rather basic and straight forward Q! 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 $K_{sp} = [Ca^{2+}][2F^-]^2$ or $K_{sp} = [Ca^+][F^-]^2$ or $K_{sp} = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$ 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 $CaF_2(s)$	–1220 kJ mol^{-1}
enthalpy change of atomisation of Ca(s)	+178 kJ mol^{-1}
enthalpy change of formation of $Ca^{2+}(aq)$	–543 kJ mol^{-1}
electron affinity of fluorine atoms	–328 kJ mol^{-1}
enthalpy change of formation of $F^-(aq)$	–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.

$$\begin{tikzcd}
Ca(s) \arrow[d, "-543"'] & + & F_2(g) \arrow[r, "-1220"] \arrow[d, "2(-333)"] & CaF_2(s) \arrow[dl, "\Delta H_{soln}"] \\
Ca^{2+}(aq) & + & 2F^-(aq) &
\end{tikzcd}$$

By Hess' Law,

$$(-1220) + \Delta H_{soln} = (-543) + 2(-333)$$
$$\Delta H_{soln} = +11.0\ \text{kJ mol}^{-1}$$

OR

$$CaF_2(s) + aq \xrightarrow{\Delta H_{sol}} Ca^{2+}(aq) + 2F^-(aq)$$
$$\Delta H_f\text{:}\quad -1220 \qquad\qquad -543 \qquad 2(-333)$$

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

[2]

EXAMINER'S COMMENTS
A common mistake made by candidates was to use ALL the data provided though the Q asked for the use of only the relevant data provided! Worse, many candidates also used even more data from the DB! 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 CaF_2 will be more, or less, soluble in hot water than in cold water.

Since the enthalpy change of solution of CaF_2 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 CaF_2 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 CaF_2, is affected when $CaCl_2(aq)$ is added.

$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$

Adding $CaCl_2$ increases $[Ca^{2+}]$, 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, $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$, 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, CH_3CO_2H, can form a dimer containing two hydrogen bonds.

$$\underset{\text{monomer}}{2CH_3CO_2H} \rightleftharpoons \underset{\text{dimer}}{(CH_3CO_2H)_2} \qquad K_c = 1.51 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ at } 298 \text{ K}$$

I A solution of 0.100 mol dm^{-3} CH_3CO_2H 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 $\frac{[(CH_3CO_2H)_2]}{[CH_3CO_2H]}$ ratio at equilibrium. Quote your answer to 3 significant figures.

	$2CH_3CO_2H$	**$\rightleftharpoons$**	**$(CH_3CO_2H)_2$**
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) =0.0166**		**0.0417**

$$\frac{[(CH_3CO_2H)_2]}{[CH_3CO_2H]} = \frac{0.0417}{0.0166} = 2.51$$

[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 not necessary! Again, it had to be emphasised as in (d)(ii) that not all data given had to use! 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 Δ*G* for this equilibrium in an aqueous solution would differ from the Δ*G* in a non-polar solvent. Explain your answer.

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, Δ*G* will be less negative or even positive [1] **in an aqueous solution. The POE above is very much to the left**.

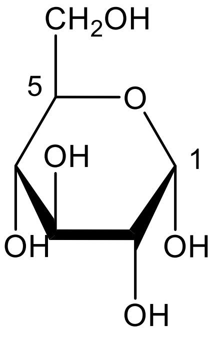
[Total: 15]

EXAMINER'S COMMENTS

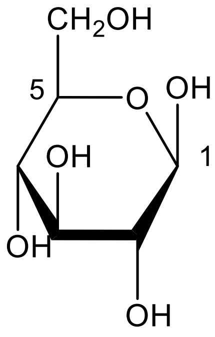
Also, poorly done by candidates! A variety of answers were given by candidates, mostly vague and unconvincing! A mere mention that in an aqueous solution (polar solvent), there is possibility of ethanoic acid dissociating into its ions or that H-bonding between it and water takes place and as a result,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

Many candidates thought incorrectly that if a reaction was spontaneous then Δ*G* should be positive!

4 D-glucose can exist in two isomers as α-glucose and β-glucose. In α-glucose, the –OH group attached to carbon 1 and the $–CH_2OH$ 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).



α-glucose



β-glucose

Each of these isomers can be synthesised and isolated as pure compounds. The α-glucose has an angle of optical rotation of +112° while the β-glucose has an angle of optical rotation of +19°. 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°.

$$\alpha\text{-glucose(aq)} \rightleftharpoons \beta\text{-glucose(aq)}$$

[Turn over

(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]

EXAMINERS COMMENTS
This question was not well attempted. +52.5º 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 +52.5º. Deduce whether the forward reaction is exothermic or endothermic.

The optical rotation is greater than +52.5º, 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.

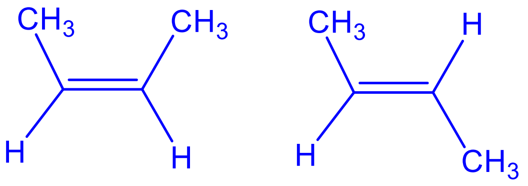
Hence, the forward reaction is exothermic. [1]

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.

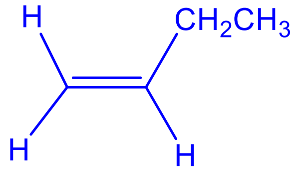
4 **(d)** *Cis-trans* isomerism also occurs in alkenes where the molecules contain restricted rotation of double bond. *Cis–trans* isomers of alkenes can be synthesised from the elimination reactions of halogenoalkanes.

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 $C_6H_{14}O$ and rotates plane-polarised light.

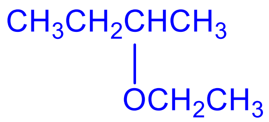
Give the structures of **P**, **Q**, **R** and **S**.



P and Q



R



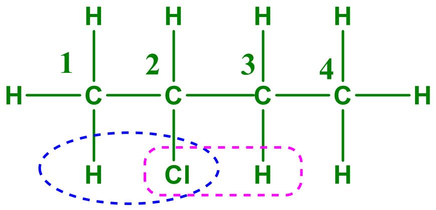
$$CH_3CH_2\underset{\substack{|\\ OCH_2CH_3}}{C}HCH_3$$

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 $Be(OH)_2$ 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 wrt C of C=C must be showed 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 H_3CH_2C 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.

$CH_3CH_2OH + OH^- \rightarrow CH_3CH_2O^- + H_2O$

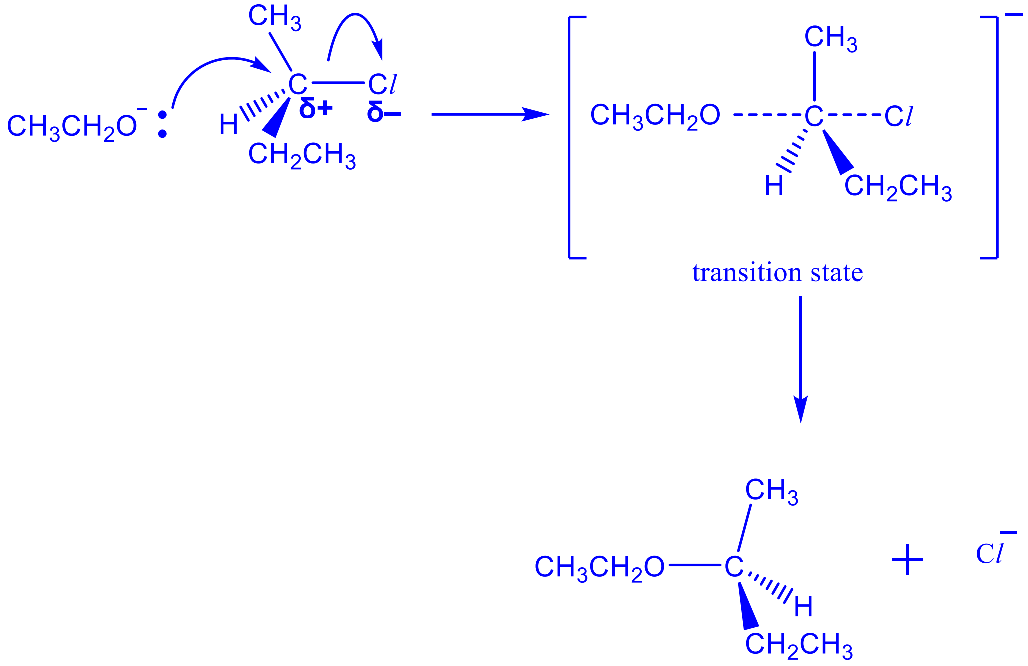
……………………………………………………………………………………………[1]

EXAMINER'S COMMENTS

Many candidates failed to identify the formula of ethanol which is CH_3CH_2OH. Some of them gave CH_3OH, CH_3COOH. Candidates should not molecular formula, e.g. C_2H_6O 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, S_N2



[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–C*l* bond and so, C–Br bond would break more easily than C– C*l* bond or less amount of energy is required to break C–Br bond than C– C*l* 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 mol dm^{-3} **M**$^{n+}$ was found to react with 10.0 cm^3 of 0.080 mol dm^{-3} Cr^{3+}.

Determine the value of n in **M**$^{n+}$.

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

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

Amount of M^{n+} reacted with 1 mole of Cr^{3+} = $\frac{2.400 \times 10^{-3}}{8.000 \times 10^{-4}}$ = $\underline{3.00}$

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

The oxidation of 1 mole of Cr^{3+} releases <u>3.00 mol of electrons</u>

$3M^{n+} \equiv Cr^{3+} \equiv 3e$

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 = $\underline{3}$

[3]

<u>EXAMINER'S COMMENTS</u>
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.

<u>Variable / Different oxidation state</u> **[1]**
………………………………………………………………………………………….[1]

<u>EXAMINER'S COMMENTS</u>
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, N_2 and H_2 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, $H_2NCONHCONH_2$, can be formed by heating urea, $(NH_2)_2CO$.

$$2(NH_2)_2CO \rightarrow H_2NCONHCONH_2 + NH_3$$

Step 1: 3.88 g of impure sample of urea $(NH_2)_2CO$ was heated strongly above its melting point. The ammonia liberated was absorbed in 32.0 cm^3 of 2.00 mol dm^{-3} sulfuric acid.

Step 2: The resulting solution was made up to 500 cm^3 with distilled water.

Step 3: 25.0 cm^3 of the solution required 25.50 cm^3 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.

$2(NH_2)_2CO \rightarrow H_2NCONHCONH_2 + NH_3$ --- (1)
$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$ --- (2)
$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ --- (3)

No. of moles of NaOH in <u>25.50 cm^3</u> = $0.20 \times \frac{25.50}{1000}$ **= 5.10×10^{-3} mol**

From (3) **2NaOH ≡ H_2SO_4 (remaining)**

No. of moles of H_2SO_4 in <u>25.0 cm^3</u> = $\frac{5.10 \times 10^{-3}}{2}$ **= 2.55×10^{-3} mol**

No. of moles of H_2SO_4 in <u>500 cm^3</u> = $2.55 \times 10^{-3} \times \frac{500}{25}$ **= 0.0510 mol**

<u>Initial</u> no. of moles of H_2SO_4 in <u>32.0 cm^3</u> = $2.00 \times \frac{32.0}{1000}$ **= 0.0640mol**

No. of moles of H_2SO_4 reacted with NH_3 = 0.0640 – 0.0510
= 0.0130

From (2) and (1) **$2NH_3 \equiv H_2SO_4$ (reacted) $\equiv 4(NH_2)_2CO$**

Mass of urea, $(NH_2)_2CO$ produced = 0.0130 x 4 x 60

= 3.12 g

Percentage purity of urea, $(NH_2)_2CO$ $= \frac{3.12}{3.88} \times 100\,\%$

= <u>80.4 %</u>

[3]

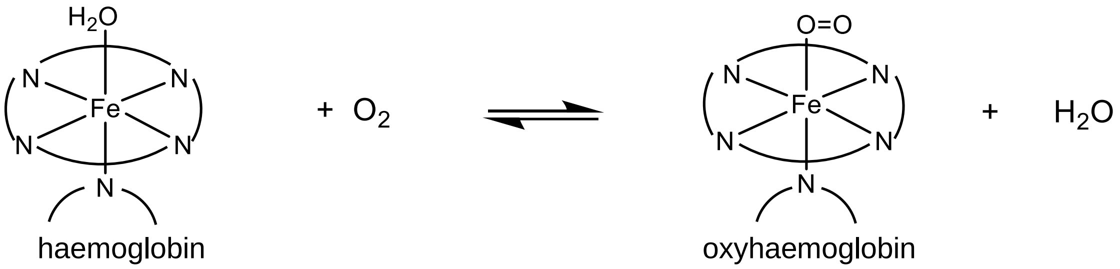
<u>EXAMINER'S COMMENTS</u>

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:
$2NH_3 \equiv H_2SO_4$ (reacted) $\equiv 4(NH_2)_2CO$

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?

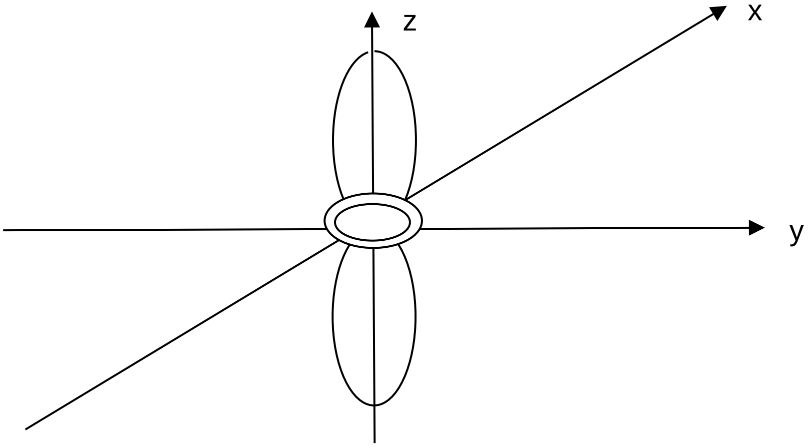
Oxidation state of iron is **<u>+2</u>** ....[1]

<u>EXAMINER'S COMMENTS</u>

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**

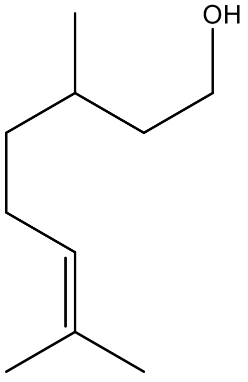
EXAMINER'S COMMENTS
Most candidates cannot answer this question well.

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.

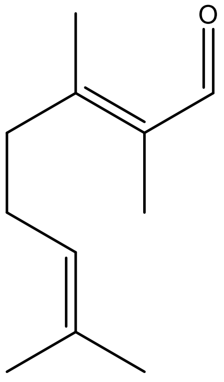
Quite a number of them misunderstood longer wavelength as higher wavelength and hence attributed "higher amount of energy" to yellow instead of green.

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.



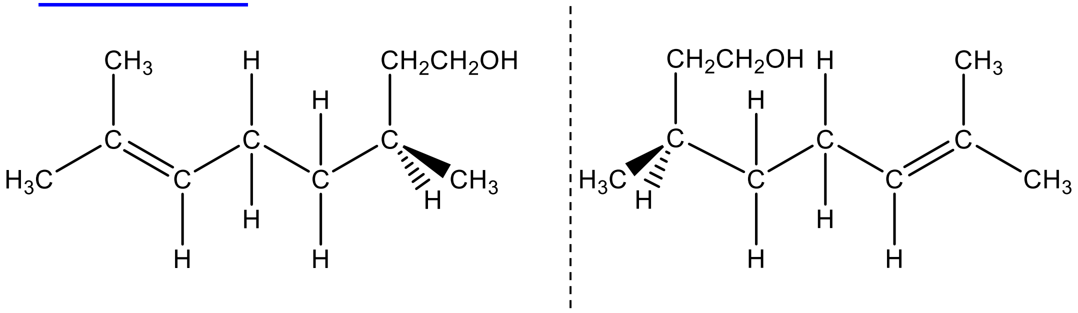
X



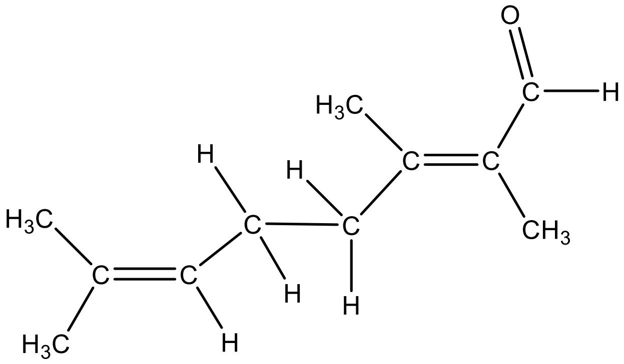
Y

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.

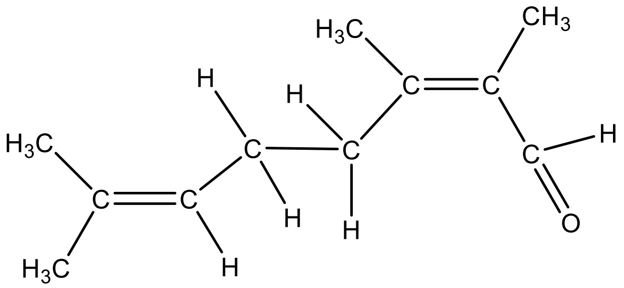
X : **enantiomerism**



Y : **cis-trans isomerism**



trans – isomer



cis-isomer

[4]

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.

[Total: 13]