CHEMISTRY Preliminary
Examination

CHEMISTRY
Higher 2

9647/01

Paper 1 Multiple Choice

29 August 2016
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 fluids.
Write your name, index number and tutorial class on the Answer Sheet in the spaces provided unless this has been done for you.

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

Read the instructions on the Answer Sheet very carefully.

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

This document consists of **17** printed pages and **1** blank page.

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Section A

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

1 3.00 g of an impure sample of calcium carbonate was heated strongly until there was no change in mass. 200 cm^3 of carbon dioxide, measured at room conditions, was obtained.

What is the percentage purity of calcium carbonate?

A 27.8 % **B** 29.8 % **C** 30.4 % **D** 35.8 %

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

Which underlined element in the following species has the +6 oxidation number?

A $\underline{Re}OCl_4$

B $H_2\underline{P}_2O_7^{2-}$

C $\underline{Ti}Cl_4$

D $\underline{Sb}Cl_5^{2-}$

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

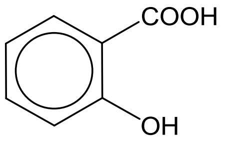
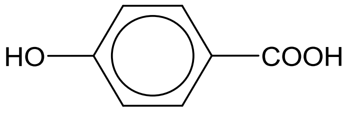
Deuterium, ${}^{2}_{1}D$, is an isotope of hydrogen.

Which of the following species has more electrons than protons, and more neutrons than protons?

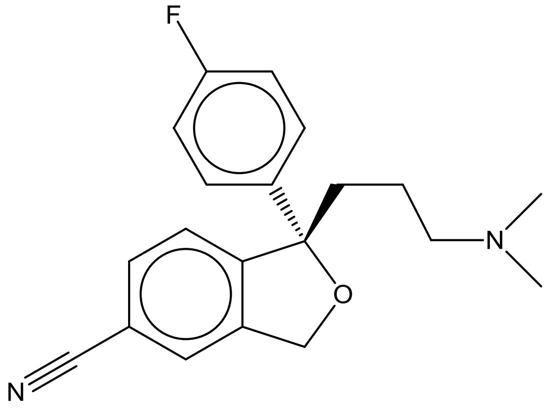
A D_3O^+ **B** ND_4^+

C OD^- **D** AlD_4^-

4 In which of the following pairs does the first compound have a higher melting point than the second compound?

	first compound	second compound
A	Mg_3N_2	Al_2O_3
B	NH_2OH	H_2O
C	CH_3OCH_3	$(CH_3)_2NH$
D		

5 Which of the following bonds is **not** present in the following molecule?



escitalopram

A a σ bond formed by sp^3–sp^2 overlap between two C atoms

B a σ bond formed by sp–sp overlap between C and N atoms

C a σ bond formed by sp^2–sp^2 overlap between two C atoms

D a σ bond formed by sp^3–sp^2 overlap between C and N atoms

6 Which of the following sets of compounds and ions is arranged in **increasing** bond angles?

A NO_2^+ < CO_3^{2-} < SO_4^{2-}

B IF_4^- < N_2O_4 < N_3^-

C ICl_2^- < H_2S < NO_2

D SCl_2 < C_2H_2 < CH_2Cl_2

7 0.50 g of a volatile liquid was placed in a syringe with a frictionless piston. The syringe was slowly warmed up till 91.0 °C at atmospheric pressure. The volume occupied in the syringe was 200.0 cm^3 when all the liquid was vaporised.

Assuming the vapour behaves as an ideal gas, what is the relative molecular mass of the liquid?

A 18.7 **B** 74.9 **C** 93.5 **D** 149.8

8 The enthalpy change when solid calcium chloride dissolves in water is –120 kJ mol^{-1}. 250 g of water is placed in an insulated cup containing 11.1 g of calcium chloride.

If the solution has the same specific heat capacity as liquid water, what is the rise in temperature of the solution?

A $\dfrac{11.1 \times 120}{250 \times 4.18}$ K

B $\dfrac{11.1 \times 120 \times 10^3}{111 \times 250 \times 4.18}$ K

C $\dfrac{250 \times 4.18}{11.1 \times 120 \times 10^3}$ K

D $\dfrac{11.1 \times 120}{111 \times 250 \times 4.18}$ K

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

The standard half-cells of four metals Mg, **P**, **Q** and **R** and their respective cations in solution were connected in pairs and the potential difference recorded.

The results obtained are as shown.

positive electrode	negative electrode	e.m.f. /V
P	Mg	+1.60
Q	Mg	+2.22
Q	**R**	+2.55

Which of the following is the **decreasing** order of reducing power for the four metals?

A **R** > Mg > **P** > **Q**

B **R** > Mg > **Q** > **P**

C **Q** > **P** > Mg > **R**

D **P** > **Q** > Mg > **R**

10 Which of the following statements is always true for a chemical reaction that has reached chemical equilibrium?

A The yield of the product(s) is greater than 50%.

B The rate of the forward reaction is greater than the backward reaction.

C The amounts of reactants and products do not change.

D Both forward and backward reactions have stopped.

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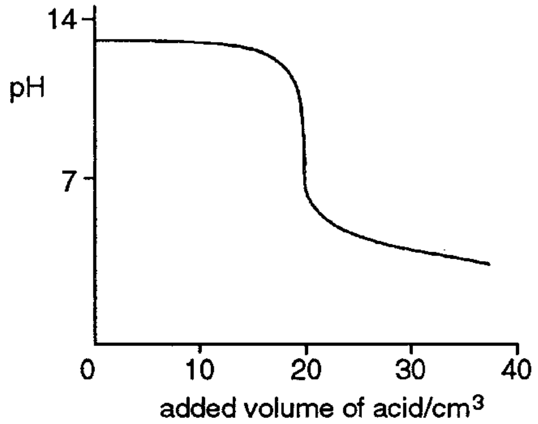
11 The graph shows the change in pH when 0.10 mol dm^{-3} acid is gradually added to *V* cm^3 of 0.10 mol dm^{-3} alkali.



Which of the following combinations could have given these results?

	V	alkali	acid
A	10	$Sr(OH)_2$	CH_3CO_2H
B	20	$Ba(OH)_2$	HC*l*
C	10	$Ca(OH)_2$	H_2SO_4
D	20	NaOH	$HO_2C–CO_2H$

12 Nitrogen oxide reacts with hydrogen gas as shown in the equation below.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The reaction was determined to be second order with respect to NO and first order with respect to H_2. In an experiment, 2.0 mol dm^{-3} of excess NO was used to react with H_2, the concentration of H_2 decreased to 6.25% of its original value in 24 minutes.

How many minutes will it take for the concentration of H_2 to decrease to 6.25% of its original value if the experiment was repeated using an excess of 4.0 mol dm^{-3} of NO?

A 1.5 **B** 4.5 **C** 6.0 **D** 9.0

13 **Figure 1** shows the melting points of eight consecutive elements whereas **Figure 2** shows the third ionisation energies of another set of eight consecutive elements, inclusive of element **Z** in **Figure 1**.

Which of the options in **Figure 2** correspond to element **Z** in **Figure 1**?

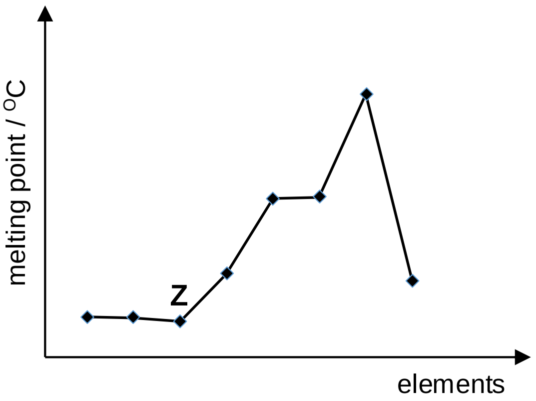


Figure 1

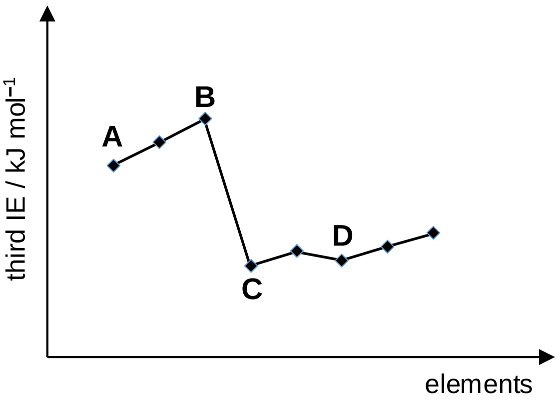


Figure 2

14 An equimolar amount of $MgCl_2$, PCl_5 and KCl were separately added to three beakers, each containing 50 cm^3 of water.

Which option correctly shows the resultant solutions arranged in **increasing** pH?

A $MgCl_2$, PCl_5, KCl

B PCl_5, $MgCl_2$, KCl

C KCl, $MgCl_2$, PCl_5

D PCl_5, KCl, $MgCl_2$

15 Which of the following properties would **not** be expected for Group II elements or their compounds?

A Barium sulfate has a higher temperature of decomposition than magnesium sulfate.

B Barium oxide in water produces a solution which reacts with dilute hydrochloric acid to give a solution with a pH of approximately 7.

C Beryllium forms compounds with the least covalent character.

D Upon heating the nitrates of Group II elements, the volume of nitrogen dioxide evolved is four times as great as the volume of oxygen.

16 Interhalogen compounds contain atoms of two or more different halogens. The interhalogen IC*l* was reacted with excess aqueous sodium hydroxide for a period of time.

What is the relative proportion of each ion present in the solution after this reaction?

	Cl^-	I^-	IO^-	IO_3^-
A	1	1	0	0
B	1	0	1	0
C	1	2	3	1
D	3	2	0	1

17 Which statement about hydrogen halides is **incorrect**?

A The acidity of hydrogen halides increases down the group.

B The reducing power of hydrogen halides increases down the group.

C The halogens, with the exception of fluorine, react with hydrogen to form hydrogen halides which have permanent dipole – permanent dipole interactions.

D The thermal stability of hydrogen halides increases down the group due to a larger electron cloud that is more polarisable.

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

Which of the following is **not** true about the first row transition metals and their compounds?

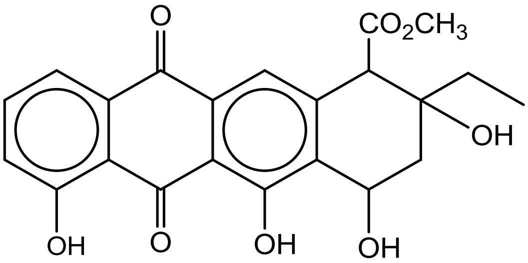
A $Fe(CN)_6^{3-}$ does not oxidise I^-.

B $Fe_2(CO_3)_3$ can be prepared by reacting $FeCl_3$(aq) with Na_2CO_3(aq).

C On addition of H_2O_2(aq) to hot acidified $K_2Cr_2O_7$(aq), a green solution is formed.

D On addition of $Co(NO_3)_3$ to water, a gas that relights a glowing splint is produced.

19 Aklavinone is a tetracycline antibiotic.



aklavinone

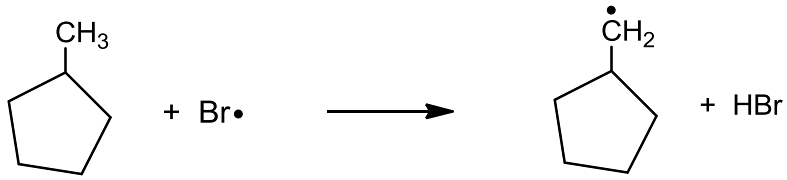
Which combination of the number of chiral centres and of the number of sp^2 and sp^3 hybridised carbon atoms does it possess?

	number of chiral centres	number of sp^2 hybridised carbon	number of sp^3 hybridised carbon
A	3	14	8
B	3	15	7
C	5	14	8
D	5	15	7

20 Methylcyclopentane reacts with bromine in the presence of UV light.

Which statement is true about this reaction?

A A possible rate determining step for this reaction is



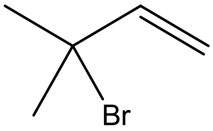
B There are three possible monosubstituted products.

C Methylcyclopentane will react slower with chlorine than bromine in the presence of UV light.

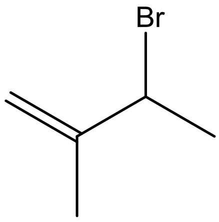
D A by-product formed in this reaction is hydrogen.

21 Which is the main product formed when one mole of 2–methylbuta–1,3–diene is allowed to react with one mole of HBr at room temperature for a prolonged period of time?

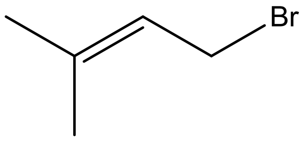
A



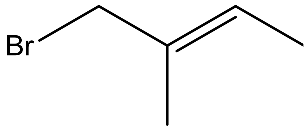
B



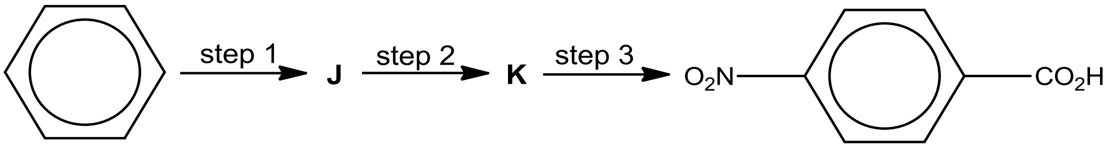
C



D



22 Which of the following could be the reagents and conditions for the three steps used in the synthesis shown below.



	step 1	step 2	step 3
A	concentrated HNO_3 and concentrated H_2SO_4, heat	CH_3Cl and $AlCl_3$	$KMnO_4$ and H_2SO_4, heat
B	$CH_3(CH_2)_2Cl$ and $AlCl_3$	$K_2Cr_2O_7$ and H_2SO_4, heat	concentrated HNO_3 and concentrated H_2SO_4, heat
C	CH_3Cl and $AlCl_3$	concentrated HNO_3 and concentrated H_2SO_4, heat	$K_2Cr_2O_7$ and H_2SO_4, heat
D	$CH_3(CH_2)_2Cl$ and $AlCl_3$	concentrated HNO_3 and concentrated H_2SO_4, heat	$KMnO_4$ and H_2SO_4, heat

23 A student investigated four different fuels. Each fuel was used separately to raise the temperature of 1 dm^3 of water from 20 ^oC to 100 ^oC. Each fuel undergoes complete combustion. All other conditions were kept the same in each experiment.

Which fuel will produce the smallest amount of carbon dioxide in these experiments?

	fuel	standard enthalpy change of combustion/ kJ mol^{-1}
A	ethane	1560
B	ethanol	1367
C	methanol	715
D	propane	2220

24 The main reason that phenol is a better Brønsted acid than cyclohexanol is

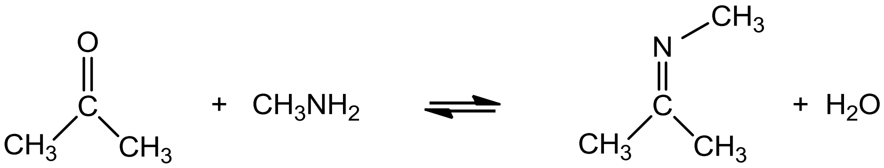
A that it is a better proton donor.

B the cyclohexyl group is an electron donating group by induction, which destabilises the anion formed during the dissociation.

C phenol is able to stabilise the anion formed during the dissociation by resonance, where the electrons are delocalised in the phenyl ring.

D the phenyl group is an electron withdrawing group by induction, which stabilises the anion formed during the dissociation.

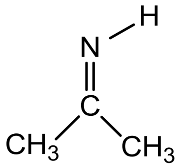
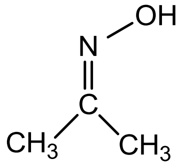
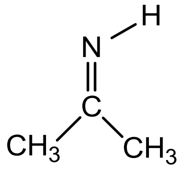
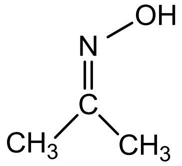
25 Propanone reacts with methylamine to form an imine as shown in the equation.



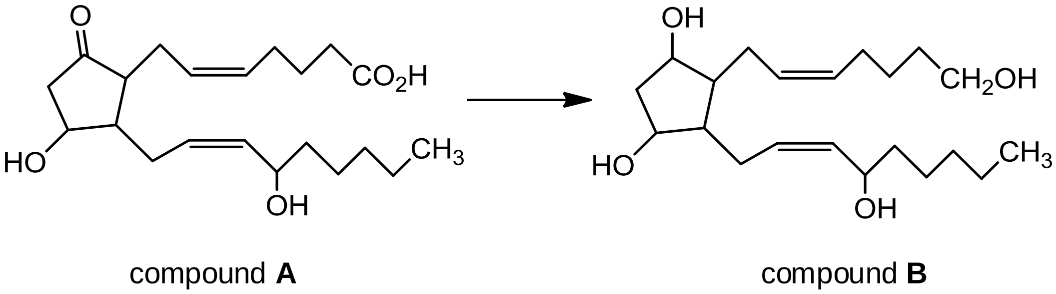
imine

Similarly, propanone also reacts with hydroxylamine, NH_2OH, to form an oxime.

Which of the following best describes the type of reaction that has occurred and the structural formula of the oxime?

	type of reaction	structural formula of the oxime
A	nucleophilic addition	
B	nucleophilic addition	
C	condensation	
D	condensation	

26 Compound **A** is an example of a prostaglandin, which belongs to a group of physiologically active lipid compounds having diverse hormone-like effects in animals.



Which reagent will convert compound **A** to compound **B** efficiently?

A $NaBH_4$

B $LiAlH_4$/dry ether

C H_2/Pt

D Sn/concentrated HC*l*

27 Lactic acid, $CH_3CH(OH)CO_2H$, is found in sour milk.

Which of the following equations represent a possible reaction with lactic acid?

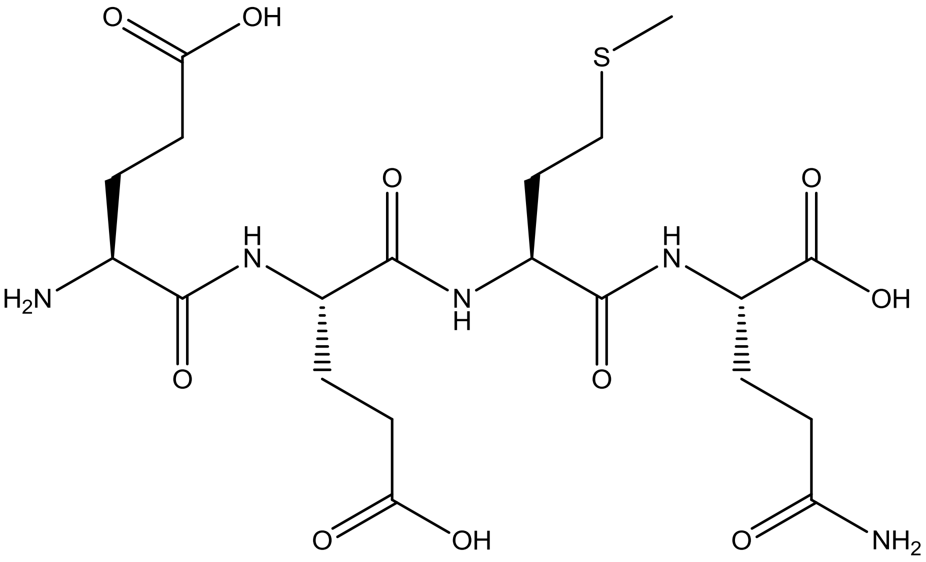
A $CH_3CH(OH)CO_2H + CH_3OH \rightarrow CH_3CH(OCH_3)CO_2H + H_2O$

B $CH_3CH(OH)CO_2H + CH_3CO_2H \rightarrow CH_3CH(OCOCH_3)CO_2H$

C $CH_3CH(OH)CO_2H + PCl_5 \rightarrow CH_3CH(Cl)CO_2H + POCl_3 + HCl$

D $CH_3CH(OH)CO_2H + 4I_2 + 7NaOH \rightarrow (CO_2^-Na^+)_2 + CHI_3 + 5NaI + 6H_2O$

28



The tetrapeptide above is a fragment of SNAP-25, a substrate of Botulinum toxin (Botox).

How many moles of NaOH will react with 1 mole of the tetrapeptide when it is heated under reflux with aqueous sodium hydroxide until no further reaction occurs?

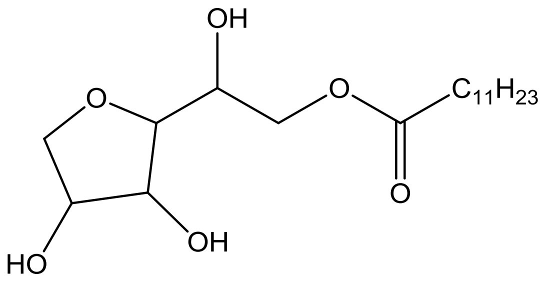
A 3

B 5

C 6

D 7

29 The demand for ‘natural’ shampoos and detergents has led to the development of more biodegradable detergents such as sorbitan monolaurate, which is made from plants.



sorbitan monolaurate

Which of the following statements about sorbitan monolaurate is correct?

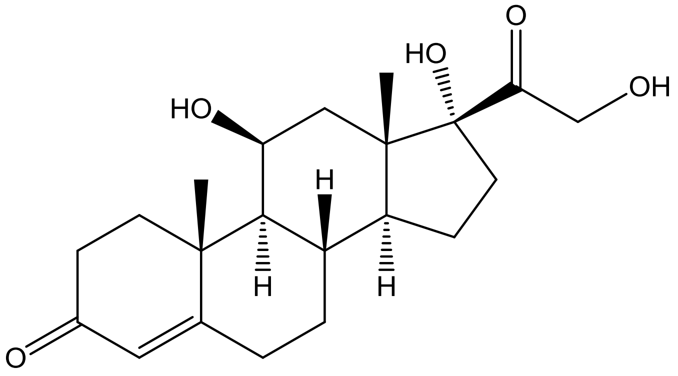
A It is optically inactive.

B It can react with concentrated sulfuric acid on heating.

C There will be an orange precipitate formed upon adding 2,4–dinitrophenylhydrazine to the compound.

D There will be no colour change on heating the compound with acidified potassium dichromate(VI) solution.

30 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.



hydrocortisone

Which of the following statements about hydrocortisone is correct?

A When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing seven carbonyl groups.

B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

C When treated with cold dilute $KMnO_4$, it forms a compound containing two additional hydroxy groups.

D When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing seven hydroxy groups.

Section B

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

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

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

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

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

31 Epsom salt is a sedative for the nervous system. Its active ingredient is magnesium sulfate which is soluble in water. The corresponding barium sulfate is insoluble in water.

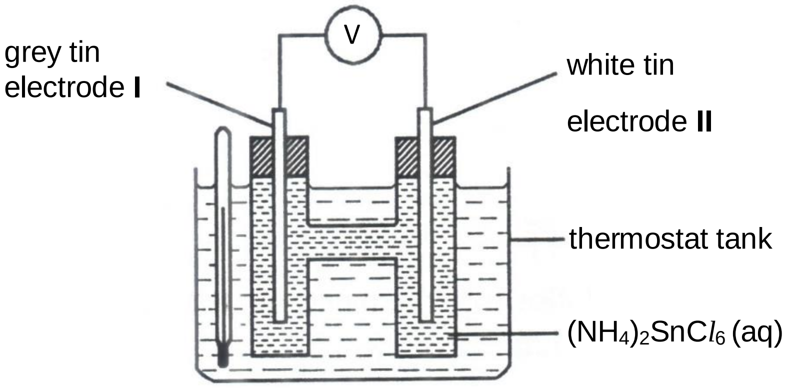
What factors account for the difference in solubility between magnesium sulfate and barium sulfate?

1 Magnesium sulfate has a higher solubility product than barium sulfate.

2 Magnesium ions have a higher enthalpy of hydration than barium ions.

3 Magnesium sulfate has a larger magnitude of lattice energy than barium sulfate.

32 The diagram shows a set-up used to find the transition temperature at which white tin and grey tin are in equilibrium. This was found to be 15 ºC. Above 15 ºC, grey tin from electrode **I** dissolves and is deposited on electrode **II** as white tin.



Which of the following statements about the set-up are true?

1 At 15 ºC, no current flows.

2 Below 15 ºC, electrons flow through the external circuit from **I** to **II**.

3 The conversion of white tin to grey tin is an endothermic process.

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

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

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

33 The pK_a values of some ammonium ions at 298 K are given below.

ammonium ion	pK_a
$CH_3NH_3^+$	10.66
$(CH_3)_3NH^+$	9.81

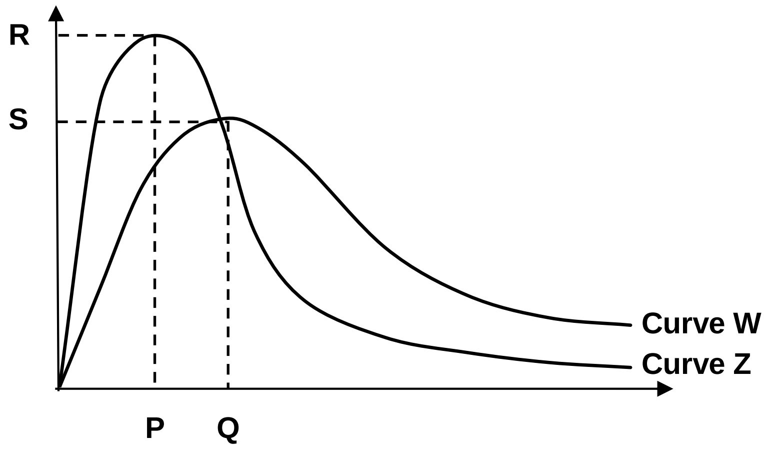
Based on the data given, which of the following statements are correct?

1 The pH of 0.1 mol dm^{-3} of $(CH_3)_3NH^+Cl^-$ is 5.4.

2 $(CH_3)_3N$ is more basic than CH_3NH_2 due to the presence of more electron donating alkyl groups.

3 1 mol of $(CH_3)_3N$ requires more HC*l* for complete neutralisation than 1 mol of CH_3NH_2.

34 Curve **Z** represents the distribution of energies of the gaseous molecules for an uncatalysed reaction.



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

1 Curve **W** will be the distribution curve obtained when the reaction is catalysed and **Q** represents the most probable energy of the molecules.

2 Curve **W** will be the distribution curve obtained at a higher temperature and **S** represents the most probable energy of the molecules.

3 Curve **Z** will be the distribution curve obtained when the reaction is uncatalysed and **P** represents the most probable energy of the molecules.

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

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

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

35 Sulfur burns in chlorine gas to form disulfur dichloride, S_2Cl_2. In excess chlorine gas, the following equilibrium is established.

$$S_2Cl_2 + Cl_2 \rightleftharpoons 2SCl_2$$

Which statements regarding S_2Cl_2 and its equilibrium with SCl_2 are **correct**?

1 S_2Cl_2 dissolves in water to give a solution with pH greater than 7.

2 S_2Cl_2 is a liquid at room temperature.

3 The sulfur atoms have a bent geometry in both S_2Cl_2 and SCl_2.

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

Which of the following statements are true for green aqueous solution of $V_2(SO_4)_3$?

1 Zn metal can reduce V^{3+}(aq) to V^{2+}(aq).

2 The solution appears green as the d-orbitals are split by the presence of the sulfate ions.

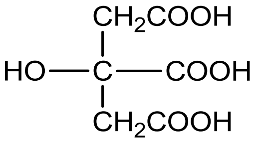
3 V^{3+}(aq) can serve as a homogeneous catalyst in the reaction between iodide ions and peroxodisulfate ions.

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

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

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

37 Unripe fruits often contain polycarboxylic acids. These are acids with more than one carboxylic acid group in their molecule. One such acid is citric acid shown below.



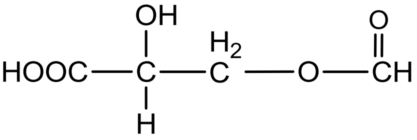
$HO-\underset{CH_2COOH}{\overset{CH_2COOH}{C}}-COOH$

Another polycarboxylic acid present in unripe fruit is a colourless crystalline solid, **W**, which has molecular formula of $C_4H_6O_5$.

A sample of **W** of mass 1.97 g was dissolved in water and the resulting solution titrated with 1.00 mol dm^{-3} NaOH. 29.4 cm^3 of 1.00 mol dm^{-3} NaOH was required for complete neutralisation.

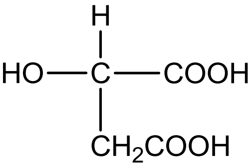
What could **W** be?

1



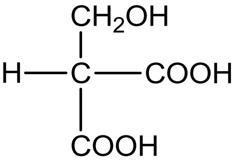
$HOOC-\underset{H}{\overset{OH}{C}}-\overset{H_2}{C}-O-\overset{O}{\overset{\|}{C}}H$

2



$HO-\underset{CH_2COOH}{\overset{H}{C}}-COOH$

3



$H-\underset{COOH}{\overset{CH_2OH}{C}}-COOH$

38 Which of the following statements are always true of the isoelectronic point, pI, of an amino acid?

1 It is the pH where the zwitterionic form of the amino acid is most dominant.

2 It is the pH where the amino acid does not migrate when placed in an electric field.

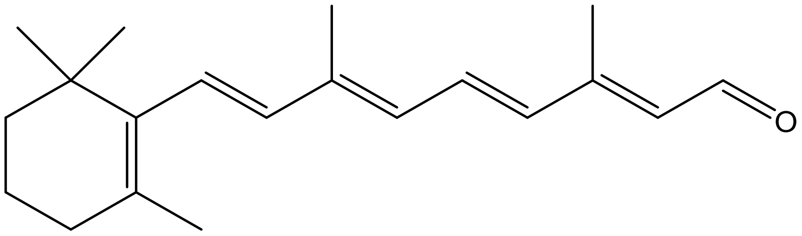
3 It is the average of the first two pK_a values.

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

A	**B**	**C**	**D**
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

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

39 The rod cells in the retina at the back of the eye contain an alcohol called retinol which is responsible for their sensitivity to light. Retinol is oxidised by an enzyme-catalysed reaction to retinal with the following structure:



retinal

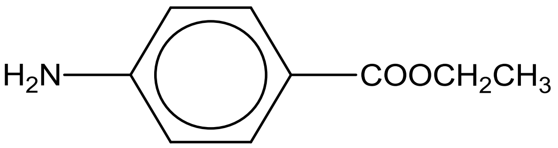
Which of the following statements about retinal are correct?

1 It can react with NH_2NH_2.

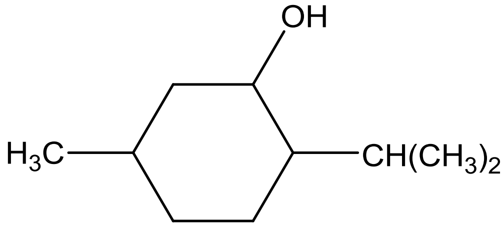
2 The molecular formula of retinal is $C_{20}H_{28}O$.

3 Oxidative cleavage of retinal gives two different organic products.

40 Benzocaine and menthol are local anaesthetics used in sunburn ointments and skin lotions. Their structures are shown below:



benzocaine



menthol

Which of the following reagents and conditions can be used to distinguish between the two compounds?

1 aqueous bromine, dark

2 iodine in aqueous sodium hydroxide, heat

3 acidified aqueous potassium manganate(VII), heat

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Answers:

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

Index No.	Name	Form Class	Tutorial Class	Subject Tutor

CHEMISTRY Preliminary Examination

CHEMISTRY
Higher 2

9647/02

Paper 2 Structured Questions

16 August 2016
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, glue or correction fluid.

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

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

For Examiner's Use	
Question no.	**Marks**
1	
2	
3	
4	
5	
6	
7	
TOTAL	

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

[Turn over

1 Planning (P)

The solubility of a metal hydroxide, $M(OH)_2$ at a particular temperature is defined as the mass of metal hydroxide that dissolve in 100 g of water.

A saturated solution of the metal hydroxide is one in which no more solid can dissolve at this fixed temperature. At 25°C, the solubility of metal hydroxide is approximately less than 2g /100g of water.

You are to plan an experiment using the method of gravimetric analysis to achieve these objectives:

1. determine the solubility product, K_{sp} of the metal hydroxide accurately;
2. determine how the solubility of the metal hydroxide in sodium hydroxide is affected by the concentration of hydroxide ions.

(a) **(i)** Write an equation with state symbols to show the dissolution of the metal hydroxide in water.

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

(ii) Suggest and explain how the solubility of the metal hydroxide varies with the concentration of hydroxide ions.

……………………………………………………………………………………………

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

(b) You are provided with:

- pure solid metal hydroxide
- 2.0 mol dm^{-3} of sodium hydroxide
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of a saturated metal hydroxide solution
- the preparation of a suitable range of diluted sodium hydroxide solutions
- an outline of how the results could be used to calculate the solubility of metal hydroxide and its K_{sp} and show how the solubility of metal hydroxide in sodium hydroxide varies with the concentration of hydroxide ions
- the risks involved and safety precautions taken

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…………………………………………………………………………………………[8]

(c) Suggest another experimental method to determine how the solubility of metal hydroxide changes with the presence of sodium hydroxide. Suggest the results to be collected.

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……………………………………………………………………………………………………[2]

[Total: 12]

2 **A**, **B** and **C** are three organic molecules which share the same molecular formula, $C_8H_9NO_2$.

You are to make use of the data about the reactions of **A**, **B** and **C** given in the table below to deduce their identities.

reaction	reagent used	**A**	**B**	**C**
1	$KMnO_4$(aq), H_2SO_4(aq) heat	purple colour remains	purple MnO_4^- decolourised	purple MnO_4^- decolourised
2	excess Br_2 (aq)	white solid formed with M_r = 308.8	no visible reaction	white solid formed with M_r = 308.8
3	NaOH (aq) at room temperature	dissolves to give a colourless solution	dissolves to give a colourless solution	does not dissolve at all
4	Na_2CO_3 (aq)	no visible reaction	effervescence seen	no visible reaction
5	HC*l* (aq) at room temperature	does not dissolve at all	dissolves to give a colourless solution	dissolves to give a colourless solution

(a) **(i)** Deduce the molecular formula of the white solid formed from **A** in reaction **2**.

……………………………………………………………………………………… [1]

(ii) What type of reaction takes place in reaction **2** for **A**?

……………………………………………………………………………………… [1]

(iii) Hence list the possible functional groups present in **A** based on reaction **2** alone.

……………………………………………………………………………………… [2]

(b) **(i)** List the functional groups that are being tested for in reaction **3**.

……………………………………………………………………………………… [2]

(ii) Identify the gas that is being produced in reaction **4** for **B** and how you would confirm its identity.

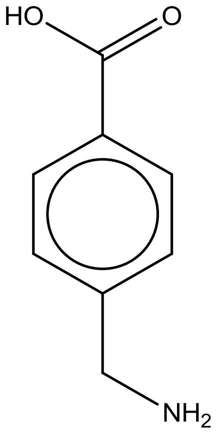
…………………………………………………………………………………………

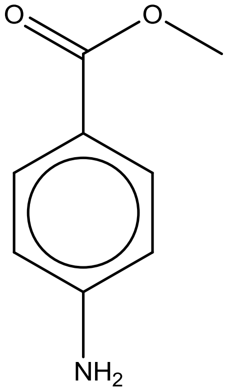
………………………………………………………………………………………… [2]

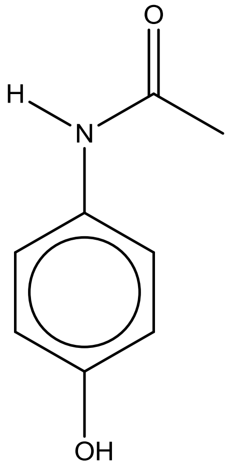
(iii) Which of the functional groups you have named in **b(i)** is confirmed by reaction **4**?

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

(c) You now have enough information to determine the identities of **A**, **B** and **C**. Below are three possible structures of **A**, **B** and **C** (not in order).





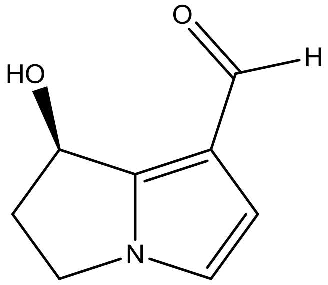


Draw the structural formula of the three compounds in the boxes below.

A	
B	
C	

[3]

(d) Hydroxydanaidal is an insect pheromone synthesised by male tiger moths from heliotrine in plants. It is an isomer of the three organic molecules above and is made up of two five-membered rings.



hydroxydanaidal

In order for a ring to be aromatic, it has to fulfil the following criteria:

- The ring must have 4n+2 electrons in the delocalised p–orbital cloud (where n is a positive integer).
- The ring must be planar.
- Every atom in the ring must be able to participate in delocalising the electrons.

(i) Given that the N atom is sp^2 hybridised, what is the number of p electrons in the right ring of hydroxydanaidal?

.... [1]

(ii) Hence state if the right ring is aromatic.

.... [1]

(iii) Suggest reagents and conditions for a reaction that that will distinguish hydroxydanaidal from the three isomers **A**, **B** and **C**.

.... [1]

[Total: 15]

3 Group VII elements can form oxoanions of XO_n^- which are strong oxidising agents. One such example is bromate(V) anion, BrO_3^- which can oxidise iodide to form iodine, and itself reduced to bromide.

(a) Write a balanced ionic equation for the reaction between bromate(V) and iodide.

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

(b) A student wished to analyse the amount of iodine and the bromide ions produced from the above reaction and hence he carried out the following procedures.

1) Add 25.0 cm^3 of 0.150 mol dm^{-3} potassium bromate(V) solution to excess potassium iodide (3 grams) and 5 cm^3 of 1 mol dm^{-3} H_2SO_4 in a 250 cm^3 conical flask.

2) Add sufficient chloroform, $CHCl_3$, to the above solution immediately and transfer the mixture to a separating funnel.

3) Separate the organic and aqueous layers and add barium nitrate solution to the aqueous layer in a beaker.

4) Filter the above mixture and add silver nitrate to the filtrate in the conical flask.

5) To the resultant mixture in the conical flask in step 4, add sufficient concentrated ammonia and filter once again.

(i) What is the purpose of adding chloroform in step 2?

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………………………………………………………………………………… [1]

(ii) What is the reason for adding barium nitrate in step 3?

…………………………………………………………………………………...

………………………………………………………………………………… [1]

(iii) A mixture of two precipitates will be formed when silver nitrate is added into step 4. Suggest the identities of the precipitates.

………………………………………………………………………………… [1]

(iv) Describe clearly what the student will observe in step 5 after he added in concentrated ammonia and performed a filtration. Explain the chemistry behind his method.

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………………………………………………………………………………… [3]

(c) Explain why fluorine does not form oxoanions such as FO_3^-.

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…………………………………………………………………………………………………

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

[Total: 8]

4 Compound **X** and compound **Y** are oxides formed from period 3 elements.

When water is added to both oxides, only **X** dissolves but not **Y**. However, **Y** will dissolve when it is added to the aqueous solution of **X** and NaOH (aq) separately.

It is known that aqueous solution of **X** can react with solid potassium hydroxide in a ratio of 1:3.

Identify compound **X** and **Y**, and explain the above reactions with the aid of balanced equations.

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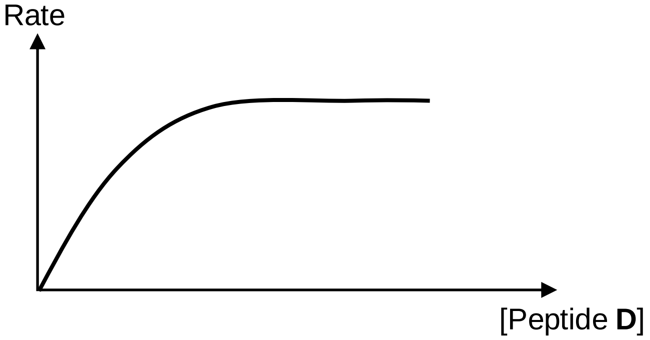
[Total: 7]

5 Chymotrypsin is a digestive enzyme found in the small intestines that can hydrolyse peptide bonds within proteins. It is also used as a form of treatment for sports injuries to reduce pain and inflammation. The three main amino acids involved in the catalytic activity are histidine, aspartic acid and serine.

(a) The graph shows the results of an investigation of the initial rate of hydrolysis of peptide **D** by the enzyme chymotrypsin. In the experiments, the initial concentration of peptide **D** was varied but that of chymotrypsin was kept constant.



Explain the difference in the rate of hydrolysis at high and low concentrations of peptide **D**.

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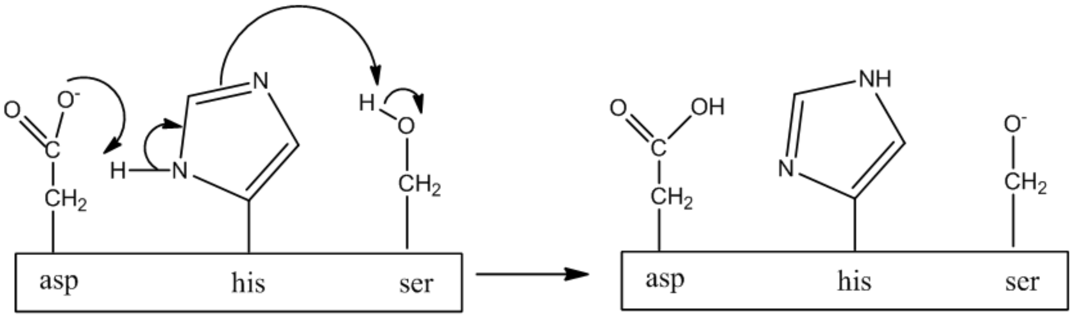
…………………………………………………………………………………………… [2]

(b) The first step of the mechanism of the action of chymotrypsin is shown:



(i) In an aqueous external environment, suggest and explain whether the three amino acids are orientated inward or outward of the compact structure.

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

…………………………………………………………………………………… [2]

(ii) State the roles of histidine in the mechanism shown above.

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

(iii) Explain with reference to the mechanism, how a low pH might affect the enzymatic activity of chymotrypsin.

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

……………………………………………………………………………………………… [2]

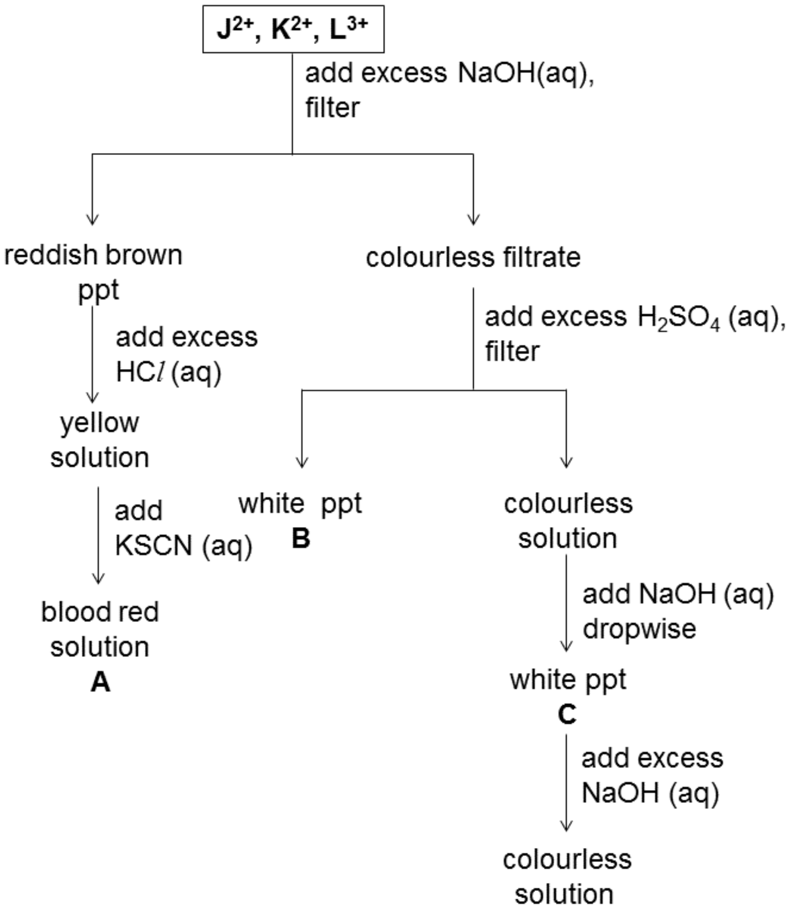
(iv) Draw the structural formula of a tripeptide with the sequence *ser-his-asp*, showing the form which it would exist at pH 4.5 given the pK_a of the R-group in his = 6.04 and pK_a of the R-group in asp = 3.90.

[2]

[Total: 9]

6 Three unknown cations **J**$^{2+}$, **K**$^{2+}$ and **L**$^{3+}$ are analysed according to the flowchart below.

J, **K** and **L** can be any one of the following: Al, Mn, Fe, Co, Ni, Pb, Zn, Sc.



(a) Identify the three cations and the three unknowns **A**, **B** and **C**. [6]

cations

J^{2+}: …………………………

K^{2+}: …………………………

L^{3+}: …………………………

unknowns

A: …………………………

B: …………………………

C: …………………………

(b) Vanadium(II) chloride, VCl_2 is prepared by the thermal decomposition of vanadium(III) chloride, VCl_3.

(i) Write the electronic configuration of a vanadium atom.

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

(ii) Hence explain why the third ionisation energy of vanadium is higher than the second ionisation energy.

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(iii) Predict, with reason, which of the chlorides of vanadium, VCl_2 or VCl_3 will have a higher melting point.

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

[Total: 9]

7 Nitryl fluoride, NO_2F is a colourless gas which acts as a strong oxidising agent and fluorinating agent.

(a) Draw a dot-and-cross diagram of NO_2F.

[1]

(b) It is known that NO_2F can be produced from nitrogen dioxide and fluorine according to the equation below.

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

The rate equation for the reaction was also found to be Rate = $k[NO_2][F_2]$.

(i) Propose a two-step mechanism consistent with the above equation, indicating the rate determining step.

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……………………………………………………………………………………………… [2]

(ii) Given that the reaction is exothermic, sketch a labelled energy profile diagram for the complete reaction path including the formation of the intermediate species.

[3]

(c) When NO_2 and excess F_2 were mixed together, $[NO_2F]$ varies with time, as shown in the table below. The initial $[NO_2]$ used is 0.400 mol dm^{-3}.

t / min	$[NO_2F]$ / mol dm^{-3}	$\frac{\Delta[NO_2F]}{\Delta t}$ / mol dm^{-3} min^{-1}	$[NO_2]$ / mol dm^{-3}
0.25	0.150	0.60	0.250
0.50	0.245		
0.75	0.300		
1.00	0.340		
1.25	0.360		
1.50	0.375	0.06	0.025

(i) Explain why it is necessary to use excess fluorine in this experiment to confirm the order with respect to nitrogen dioxide.

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

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

(ii) The rate at a particular time can be approximated using:

$$\text{rate} = \frac{\Delta[NO_2F]}{\Delta t}$$

Complete the table above by calculating $\frac{\Delta[NO_2F]}{\Delta t}$ (to 2 decimal places) and the $[NO_2]$ left (to 3 decimal places) at the respective timings. [2]

(iii) Hence, plot a graph of $\frac{\Delta[NO_2F]}{\Delta t}$ against $[NO_2]$ to confirm and explain that the reaction is first order with respect to NO_2.

0

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……………………………………………………………………………………………[3]

[Total: 12]

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Index No.	Name	Form Class	Tutorial Class	Subject Tutor

CHEMISTRY Preliminary Examination

CHEMISTRY
Higher 2

9647/02

Paper 2 Structured Questions

16 August 2016
2 hours

Candidates answer on the Question Paper
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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For Examiner's Use	
Question no.	**Marks**
1	
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3	
4	
5	
6	
7	
TOTAL	

This document consists of **12** printed pages.

[Turn over

1 Planning (P)

The solubility of a metal hydroxide, $M(OH)_2$ at a particular temperature is defined as the mass of metal hydroxide that dissolve in 100 g of water.

A saturated solution of the metal hydroxide is one in which no more solid can dissolve at this fixed temperature. At 25°C, the solubility of metal hydroxide is approximately less than 2g /100g of water.

You are to plan an experiment using the method of gravimetric analysis to achieve these objectives:

1. determine the solubility product, K_{sp} of the metal hydroxide accurately;
2. determine how the solubility of the metal hydroxide in sodium hydroxide is affected by the concentration of hydroxide ions.

(a) **(i)** Write an equation with state symbols to show the dissolution of metal hydroxide in water. [1]

$M(OH)_2(s) + aq \rightleftharpoons M^{2+}(aq) + 2OH^-(aq)$ [1]

(ii) Suggest and explain how the solubility of the metal hydroxide varies with the concentration of hydroxide ions. [1]

The solubility of metal hydroxide **decreases** when the concentration of sodium hydroxide **increases** as there is **common ion effect or explanation of eqm shifting to the left when concentration of hydroxide increases (LCP)**.

(b) You are provided with:

- pure solid metal hydroxide
- 2.0 mol dm^{-3} of sodium hydroxide
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of a saturated metal hydroxide solution
- the preparation of a suitable range of diluted sodium hydroxide solutions
- an outline of how the results could be used to calculate the solubility of metal hydroxide and its K_{sp} and show how the solubility of metal hydroxide in sodium hydroxide varies with the concentration of hydroxide ions
- the risks involved and safety precautions taken [8]

Method 1:

1. Using a 50 cm^3 burette/ 100 cm^3 measuring cylinder/ 50 cm^3 pipette, place 100 cm^3 of distilled water into a pre-weighted 250 cm^3 dry and clean conical flask/beaker (M1 g) placed in a thermostated water bath controlled at a fixed temperature. Weigh again with the distilled water inside to obtain the total mass of the distilled water and beaker, M2 g.

2. Add about 2-4g (> solubility and depending on volume of solution used) mass of solid metal hydroxide to the solution and stir with a glass rod. Stir the mixture continuously until no more solid dissolves to ensure a saturated solution is obtained.

Let the mass of metal hydroxide be M3 g.

3. Allow reaction mixture to stand/ leave for a long time to reach equilibrium.

4. Pre-weigh the dry filter paper, M4 g. Filter the mixture with the use of a filter paper and filter funnel into a beaker. Discard the filtrate. Weigh the mass of the filter paper and solid, M5 g.

5. Wash the residue with some cold water and dry the filter paper with residue in an oven/IR lamp. Temperature should be pre-set to 60°C (lower than the decomposition temperature and to prevent the filter paper from burning). Let the filter paper cool down in a dessicator. Weigh the filter paper and its contents.

6. Repeat the process of heating, cooling and weighing till constant mass of the filter paper and its contents is obtained.

Mass of dissolved solute = M3 – (M5 – M4) = X g

(mass of solid $M(OH)_2$ added - mass of residue)

Mass of solvent = M2 – M1 = Y g

Solubility of metal hydroxide in 100g of water = X/ Y x 100 (g/100g of water)

OR

Method 2:

1. Measure about 100 cm^3 (any volume) of water using a measuring cylinder and place it in a dry and clean beaker placed in a themostated water bath.

2. Add about 2g (> solubility and depending on volume of solution used) mass of solid metal hydroxide to the solution and stir with a glass rod. Stir the mixture continuously until no more solid dissolves to ensure a saturated solution is obtained.

3. Allow reaction mixture to stand/ leave for a long time to reach equilibrium.

4. Using an electronic weighing balance, measure and record the mass of an empty, dry crucible/beaker. This is recorded as M1 g.

5. Using a dry filter funnel and filter paper, filter the suspension and collect the saturated filtrate in the crucible. Measure the mass of the filtrate and crucible. The mass obtained is M2 g.

6. Using a Bunsen burner, heat the solution until all the liquid is evaporated off and constant mass is obtained, cool it and re-weigh the beaker with its contents (M3 g).

Mass of dissolved solute = (M3 – M1) = Xg
Mass of solvent = (M2 – M1) = Yg
Solubility of metal hydroxide in 100g of water = 100 x *X/Y*

6. Repeat the experiment with another mass of metal hydroxide to get reliable results.

7. Conversion of solubility in g/ 100 g of water to mol dm^{-3} assume density of water = 1g cm^{-3}

Calculate the K_{sp} of metal hydroxide as $K_{sp} = [M^{2+}][OH^-]^2$.

Results:

	$M(OH)_2(s)$	$\rightleftharpoons$	$M^{2+}(aq)$	+	$2OH^-(aq)$
Equilibrium concentration **(mol dm^{-3})**			x		2x

In a saturated solution,
$K_{sp} = [x][2x]^2 = 4x^3$

Preparation of standard solutions of sodium hydroxide

Volume of NaOH / cm^3	Volume of water / cm^3	Initial concentration of NaOH (mol dm^{-3})	Final concentration of NaOH (mol dm^{-3})
50	100	2	1
50	100	1	0.5

7. Prepare at least three standard solutions of sodium hydroxide of different concentration (2 mol dm^{-3}, 1 mol dm^{-3} and 0.5 mol dm^{-3}).
8. Use of a burette to transfer 50 cm^3 of the 2 mol dm^{-3} sodium hydroxide solution into a 100 cm^3 volumetric flask. Measuring cylinder is not accepted.
9. Top up to the mark with distilled water. Stopper, invert and shake to obtain a homogeneous solution of 1 mol dm^{-3} sodium hydroxide.
10. Repeat steps 1-3 using 50 cm^3 of the 1 mol dm^{-3} sodium hydroxide to obtain a stock solution of 0.5 mol dm^{-3} sodium hydroxide.

OR vary the volume of water and sodium hydroxide used (keeping total volume constant), use the same concentration of sodium hydroxide to obtain diluted solutions

To investigate how the solubility of metal hydroxide varies with the concentration of sodium hydroxide:

11. Repeat steps 1- 6 using the other three standard solutions of sodium hydroxide of concentration (2 mol dm^{-3}, 1 mol dm^{-3} and 0.5 mol dm^{-3}).
12. Calculate the solubility of metal hydroxide for the three concentrations of sodium hydroxide and tabulate how the solubility of metal hydroxide change with concentration of sodium hydroxide.
    Solubility of metal hydroxide in sodium hydroxide = g / 100g of solvent
13. Observe the trend that when concentrations of sodium hydroxide used decreases, the solubility of metal hydroxide increases.

Risk and safety precaution
Metal hydroxide and sodium hydroxide is corrosive and toxic in nature. Minimise contact by using gloves and goggles.

OR

Use oven/heat resistant gloves or tongs to handle the hot beaker/crucible.

OR Cool hot crucible before handling OR wear gloves when heating.

(c) Suggest another experimental method to determine how the solubility of metal hydroxide changes with the presence of sodium hydroxide. Suggest the results to be collected. [2]

Titrimetric method. Prepare a saturated solution of metal hydroxide in sodium hydroxide of known concentration and titrate the solution with standard HCl solution.

Results to be collected are: Initial burette reading/ final burette reading / titre volume

[Total: 12]

2 **A**, **B** and **C** are three organic molecules which share the same molecular formula, $C_8H_9NO_2$.

You are to make use of the data about the reactions of **A**, **B** and **C** given in the table below to deduce their identities.

reaction	reagent used	**A**	**B**	**C**
1	$KMnO_4$(aq), H_2SO_4(aq) heat	purple colour remains	purple MnO_4^- decolourised	purple MnO_4^- decolourised
2	excess Br_2 (aq)	white solid formed with M_r = 308.8	no visible reaction	white solid formed with M_r = 308.8
3	NaOH (aq) at room temperature	dissolves to give a colourless solution	dissolves to give a colourless solution	does not dissolve at all
4	Na_2CO_3 (aq)	no visible reaction	effervescence seen	no visible reaction
5	HCl (aq) at room temperature	does not dissolve at all	dissolves to give a colourless solution	dissolves to give a colourless solution

(a) **(i)** Deduce the molecular formula of the white solid formed from **A** in reaction **2**. [1]

$C_8H_7NO_2Br_2$

(ii) What type of reaction takes place in reaction **2** for **A**? [1]

Electrophilic substitution

(iii) Hence, list the possible functional groups present in **A** based on reaction **2** alone. [2]

Phenol, phenylamine

(b) **(i)** List the functional groups that are being tested for in reaction **3**. [2]

phenol and carboxylic acid

.

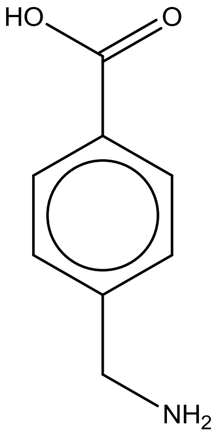
(ii) Identify the gas that is being produced in reaction **4** for **B** and how you would confirm its identity. [2]

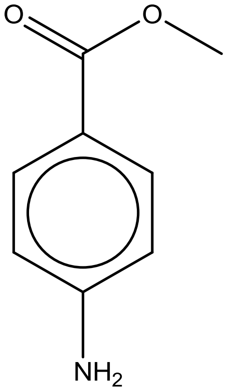
CO_2.
Pass the gas through a solution of $Ca(OH)_2$. It should form a white precipitate.

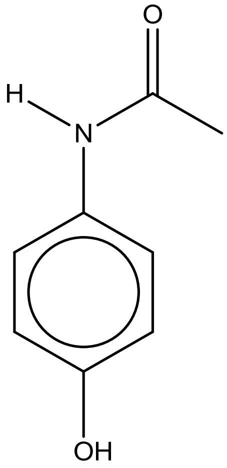
(iii) Which of the functional groups you have named in **b(i)** is confirmed by reaction **4**? [1]

Carboxylic acid

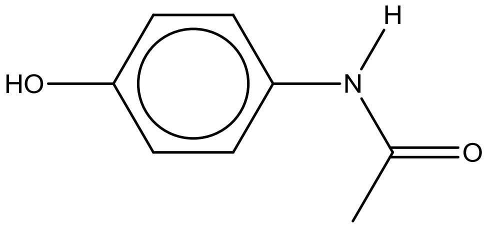
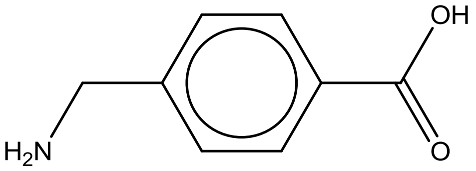
(c) You now have enough information to determine the identities of **A**, **B** and **C**. Below are three possible structures of **A**, **B** and **C** (not in order).

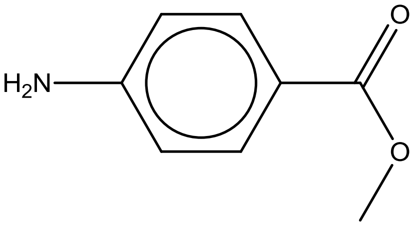




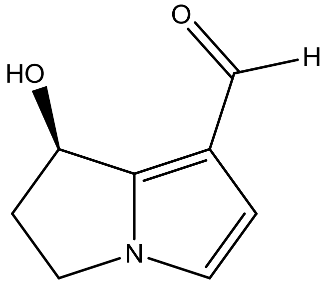


Draw the structural formula of the three compounds in the boxes below. [3]

A	
B	
C	

	 1m for each structure

(d) Hydroxydanaidal is an insect pheromone synthesised by male tiger moths from heliotrine in plants. It is an isomer of the three organic molecules above and is made up of two five-membered rings.



hydroxydanaidal

In order for a ring to be aromatic, it has to fulfil the following criteria:

- The ring must have 4n+2 electrons in the delocalised p–orbital cloud (where n is a positive integer)
- The ring must be planar
- Every atom in the ring must be able to participate in delocalising the electrons.

(i) Given that the N atom is sp^2 hybridised, what is the number of p electrons in the right ring of hydroxydanaidal? [1]

6 [1]

(ii) Hence, state if the right ring is aromatic. [1]

Yes.

(iii) Suggest reagents and conditions for a reaction that that will distinguish hydroxydanaidal from the three isomers **A**, **B** and **C**. [1]

Add Tollens' reagent and warm/heat.
Add 2,4-DNPH or Brady's Reagent.
If student stated in (ii) that it is not aromatic then accept: Add Fehling's solution and warm/heat as ecf

[Total: 15]

3 Group VII elements can form oxoanions of XO_n^- which are strong oxidising agents. One such example is bromate(V) anion, BrO_3^- which can oxidise iodide to form iodine, and itself reduced to bromide.

(a) Write a balanced ionic equation for the reaction between bromate(V) and iodide. [1]

$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$ [1]

(b) A student wished to analyse the amount of iodine and the bromide ions produced from the above reaction and hence he carried out the following procedures.

1) Add 25.0 cm^3 of 0.150 mol dm^{-3} potassium bromate(V) solution to excess potassium iodide (3 grams) and 5 cm^3 of 1 mol dm^{-3} H_2SO_4 in a 250 cm^3 conical flask.

2) Add sufficient chloroform, $CHCl_3$, to the above solution immediately and transfer the mixture to a separating funnel.

3) Separate the organic and aqueous layers and add barium nitrate solution to the aqueous layer in a beaker.

4) Filter the above mixture and add silver nitrate to the filtrate in the conical flask.

5) To the resultant mixture in the conical flask in step 4, add sufficient concentrated ammonia and filter once again.

(i) What is the purpose of adding chloroform in step 2? [1]

It is to extract iodine into the organic layer as iodine is more soluble in $CHCl_3$ due to the formation of effective interaction (induced dipole - induced dipole).

(ii) What is the reason for adding barium nitrate in step 3? [1]

It is to remove sulfate as barium sulfate so that it will not interfere with the reaction when silver nitrate is added.

(iii) A mixture of two precipitates will be formed when silver nitrate is added into step 4. Suggest the identities of the precipitates. [1]

AgBr and AgI

(iv) Describe clearly what the student will observe in step 5 after he added in concentrated ammonia and performed a filtration. Explain the chemistry behind his method. [3]

Cream ppt of AgBr dissolves to give a colourless filtrate and yellow ppt of AgI is obtained as the residue.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \text{ ----- (1)}$$

When concentrated NH_3 is added, the soluble complex of $[Ag(NH_3)_2]^+$ is formed, lowering the concentration of Ag^+.

Hence the eqm (2) position shifts to the RHS, causing AgBr to dissolve.

$$AgBr\ (s) \rightleftharpoons Ag^+(aq) + Br^-(aq)\ \text{-----}\ (2)$$

OR

The ionic product $[Ag^+][Br^–]$ become smaller than K_{sp}.

However the K_{sp} values of AgI(s) is extremely low such that its ionic product $[Ag^+][I^–]$ still exceed its K_{sp} [1], hence AgI remains insoluble even when concentrated NH_3 is added.

(c) Explain why fluorine does not form oxoanions such as $FO_3^–$. [1]

1. F does not have 3d orbitals that are energetically accessible for electrons to occupy / for expansion of octet to occur.

2. Fluorine is too / highly electronegative to have a positive oxidation number OR cannot form dative bonds (if student include answer 1)

3. Fluorine is a small atom such that 3 oxygen atoms around it would result in too much electronic repulsion / steric hindrance.

[Total: 8]

4 Compound **X** and compound **Y** are oxides formed from period 3 elements.

When water is added to both oxides, only **X** dissolves but not **Y**. However, **Y** will dissolve when it is added to the aqueous solution of **X** and NaOH (aq) separately.

It is known that aqueous solution of **X** can react with solid potassium hydroxide in a ratio of 1:3.

Identify compound **X** and **Y**, and explain the above reactions with the aid of balanced equations.

Compound X: P_4O_{10} / phosphorus (V) oxide / phosphorus pentoxide
Compound Y: Al_2O_3 / aluminium oxide

Only X is soluble in water but not Y:

$P_4O_{10}\ (s) + 6H_2O\ (l) \rightarrow 4H_3PO_4\ (aq)$

ECF from identity of compound X for P_2O_5

Al_2O_3 has high lattice energy / strong ionic bonds and hence is not able to dissolve in water.

Y will dissolve when added to the aqueous solution of X and NaOH (aq) separately:

Al_2O_3 is <u>amphoteric</u> and will react with both acids and alkalis.

$Al_2O_3\ (s) + 2H_3PO_4\ (aq) \rightarrow 2AlPO_4\ (aq) + 3H_2O\ (l)$

OR

$Al_2O_3 + 6H^+ \rightarrow Al^{3+} + 3H_2O$

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$
OR
$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-$

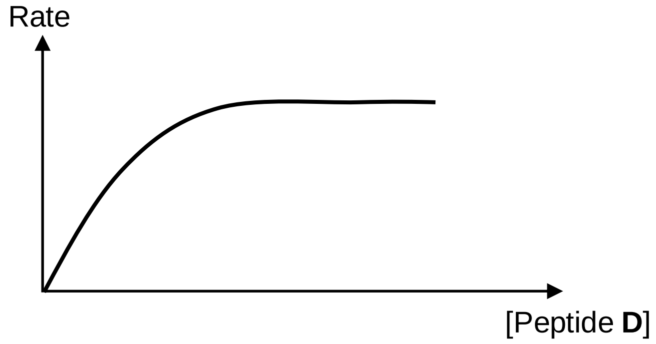
Reactions of solutions of X with potassium hydroxide:

$H_3PO_4(aq) + 3KOH(s) \rightarrow K_3PO_4(aq) + 3H_2O(l)$
OR
$3H^+(aq) + 3KOH(s) \rightarrow 3K^+(aq) + 3H_2O(l)$

[Total: 7]

5 Chymotrypsin is a digestive enzyme found in the small intestines that can hydrolyse peptide bonds within proteins. It is also used as a form of treatment for sports injuries to reduce pain and inflammation. The three main amino acids involved in the catalytic activity are histidine, aspartic acid and serine.

(a) The graph shows the results of an investigation of the initial rate of hydrolysis of peptide **D** by the enzyme chymotrypsin. In the experiments, the initial concentration of peptide **D** was varied but that of chymotrypsin was kept constant.

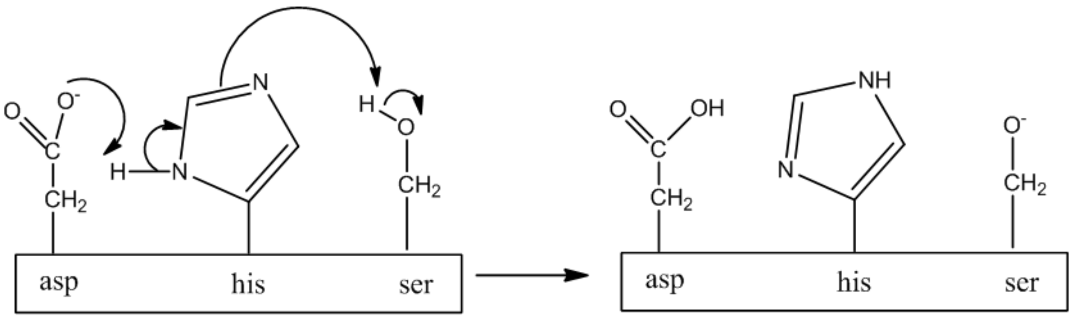


Explain the difference in the rate of hydrolysis at high and low concentrations of peptide **D**. [2]

At low concentration of peptide D, substrates do not saturate or occupy all the available active sites. Rate of reaction will be directly proportional to [substrate] or first order reaction with respect to substrate.

At high concentration of peptide D, substrates saturate or occupy all the available active sites. Rate of reaction will be independent of [substrate] Or zero order reaction with respect to substrate.

(b) The first step of the mechanism of the action of chymotrypsin is shown:



(i) In an aqueous external environment, suggest and explain whether the three amino acids are orientated inward or outward of the compact structure. [2]

Three amino acids are orientated outward of the compact structure as they contain the polar hydroxyl and amine group which are able to form hydrogen bonds/ ion-dipole with water molecules/ catalytic activity as there is binding to substrate .

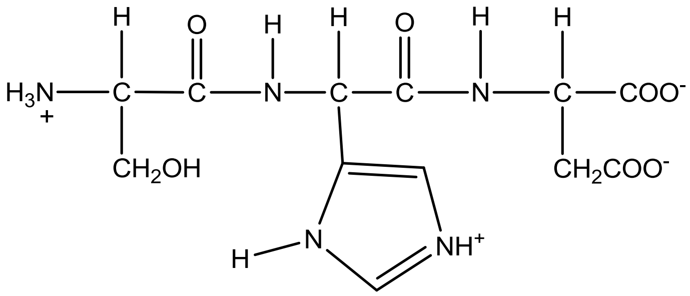
(ii) State the roles of histidine in the mechanism shown above. [1]

It is both an acid (proton donor) and a base (proton acceptor). Or protonate and deprotonate.

(iii) Explain with reference to the mechanism, how a low pH might affect the enzymatic activity of chymotrypsin. [2]

At low pH, excess H^+ will react with the basic amine group of histidine OR it will react with the COO^- group of asp OR ionic bonds are disrupted, hence this will lead to changes in enzyme shape and cause denaturation/ lose enzymatic activity/ mechanism will not work.

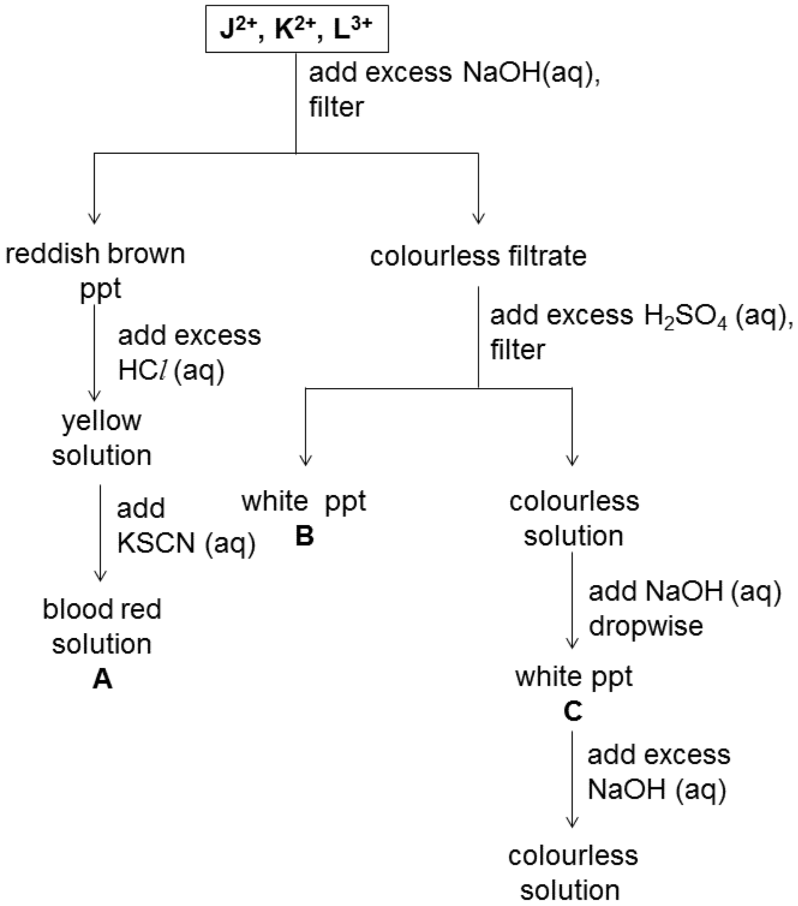
(iv) Draw the structural formula of a tripeptide with the sequence *ser-his-asp*, showing the form which it would exist at pH 4.5 given the pK_a of the R-group of his = 6.04 and pK_a of the R-group of asp = 3.90. [2]



[Total: 9]

6 Three unknown cations $\mathbf{J}^{2+}$, $\mathbf{K}^{2+}$ and $\mathbf{L}^{3+}$ are analysed according to the flowchart below.

J, **K** and **L** can be any one of the following: Al, Mn, Fe, Co, Ni, Pb, Zn, Sc.



(a) Identify the three cations and the three unknowns **A**, **B** and **C**. [6]

Cations

$\mathbf{J}^{2+}$: Pb^{2+} or $[Pb(H_2O)_6]^{2+}$

$\mathbf{K}^{2+}$: Zn^{2+} or $[Zn(H_2O)_6]^{2+}$

$\mathbf{L}^{3+}$: Fe^{3+} or $[Fe(H_2O)_6]^{3+}$

Unknowns

A : $[Fe(SCN)(H_2O)_5]^{2+}$

B : $PbSO_4$

C : $Zn(OH)_2$

Identity of J and K can be switched.

(b) Vanadium (II) chloride, VCl_2 is prepared by the thermal decomposition of vanadium (III) chloride, VCl_3.

(i) Write the electronic configuration of the vanadium atom. [1]

V: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

(ii) Hence, explain why the third ionisation energy of vanadium is higher than the second ionisation. [1]

The second electron removed is from the 4s orbital whereas the third electron is removed from the 3d orbital. The third electron removed is from an inner principal quantum shell, which experiences greater nuclear attraction and hence, requires more energy to remove.

(iii) Predict, with reason, which of the chlorides of vanadium, VCl_2 or VCl_3 will have a higher melting point. [1]

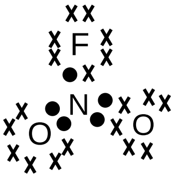
$$\text{Lattice energy } \boldsymbol{\alpha} \left| \frac{q_+ q_-}{r_+ + r_-} \right|$$

VCl_3 will have a higher melting point. As V^{3+} has a smaller ionic radius and a higher charge, VCl_3 will have a more exothermic lattice energy requiring more energy to melt. [1]

[Total: 9]

7 Nitryl fluoride, NO_2F is a colourless gas which acts as a strong oxidising agent and fluorinating agent.

(a) Draw a dot-and-cross diagram of NO_2F. [1]



(b) It is known that NO_2F can be produced from nitrogen dioxide and fluorine according to the equation below.

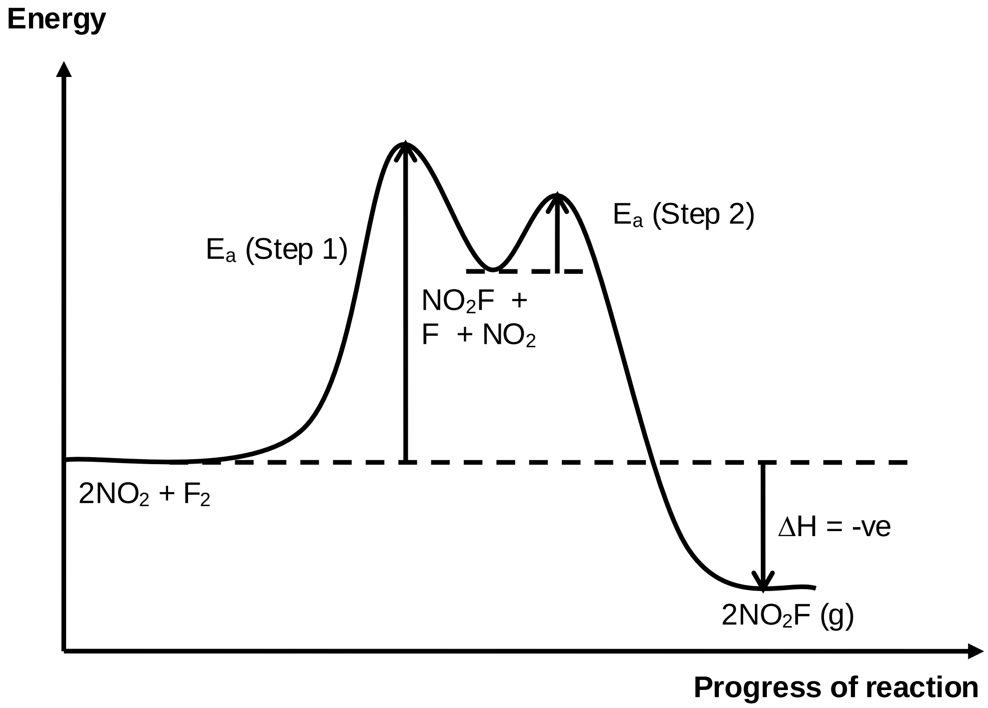
$$2NO_2\,(g) + F_2\,(g) \longrightarrow 2NO_2F\,(g)$$

The rate equation for the reaction was also found to be Rate = $k[NO_2][F_2]$.

(i) Propose a two-step mechanism consistent with the above equation, indicating the rate determining step. [2]

$NO_2\,(g) + F_2\,(g) \longrightarrow NO_2F\,(g) + F\,(g)$ (slow; rate determining step)
$NO_2\,(g) + F\,(g) \longrightarrow NO_2F\,(g)$

(ii) Given that the reaction is exothermic, sketch a labelled energy profile diagram for the complete reaction path including the formation of the intermediate species. [3]



(c) When NO_2 and excess F_2 were mixed together, $[NO_2F]$ varies with time, as shown in the table below. The initial $[NO_2]$ used is 0.400 mol dm^{-3}.

t / min	$[NO_2F]$ / mol dm^{-3}	$\frac{\Delta[NO_2F]}{\Delta t}$ / mol dm^{-3} min^{-1}	$[NO_2]$ / mol dm^{-3}
0.25	0.150	0.60	0.250
0.50	0.245	**0.38**	**0.155**
0.75	0.300	**0.22**	**0.100**
1.00	0.340	**0.16**	**0.060**
1.25	0.360	**0.08**	**0.040**
1.50	0.375	0.06	0.025

(i) Explain why it is necessary to use excess fluorine in this experiment to confirm the order with respect to nitrogen dioxide. [1]

This is to keep the concentration of fluorine relatively constant during the experiment so that the rate depends only on the concentration of NO_2. / pseudo first order wrt NO_2.

(ii) The rate at a particular time can be approximated using rate = $\frac{\Delta[NO_2F]}{\Delta t}$.
Complete the table above by calculating $\frac{\Delta[NO_2F]}{\Delta t}$ (to 2 decimal places) and the $[NO_2]$ left (to 3 decimal places) at the respective timings. [2]

(iii) Hence, plot a graph of $\frac{\Delta[NO_2F]}{\Delta t}$ against $[NO_2]$ to confirm and explain that the reaction is first order with respect to NO_2. [3]

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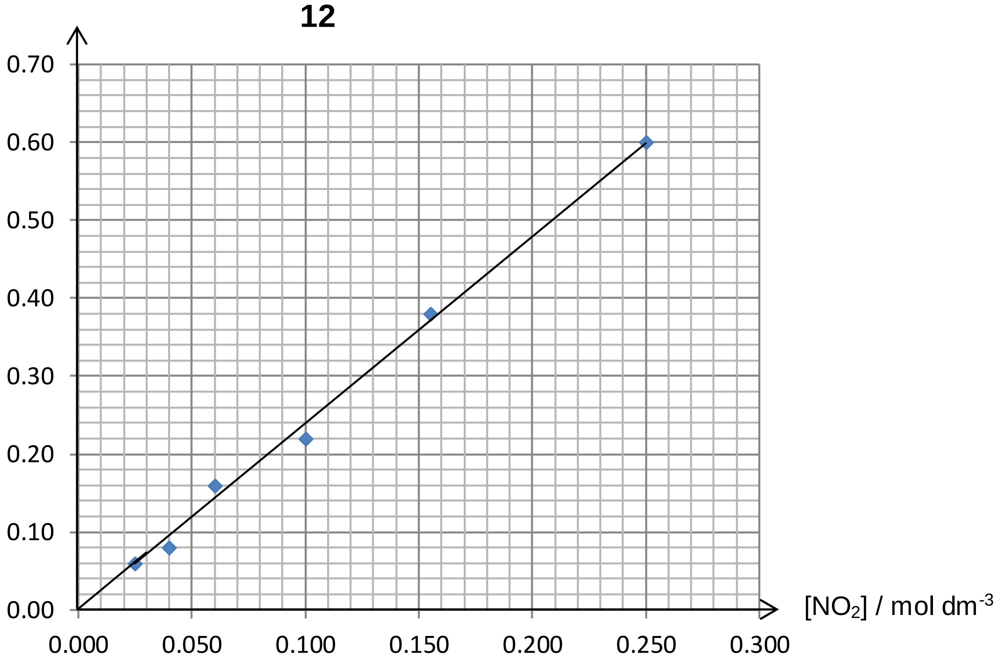
$\frac{\Delta[NO_2F]}{\Delta t}$ / mol dm^{-3} min^{-1}



As a straight line graph passing through the origin is obtained, OR the rate is directly proportional to the concentration of NO_2, hence the reaction is first order with respect to NO_2.

[Total: 12]

CHEMISTRY Preliminary Examination

CHEMISTRY
Higher 2

9647/03

Paper 3

23 August 2016
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Answer any **four** questions. Start each question on a new sheet of writing paper.
A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

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

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

1 Besides reducing carbon dioxide emission, CO_2 levels in the atmosphere can be lowered through a process known as carbon capture and sequestration (CCS). One form of naturally occurring CCS is the conversion of CO_2 into plant biomass during photosynthesis.

Scientists have also devised chemical methods of CCS. The processes for isolating carbon dioxide and for storing it has been the focus of some research.

(a) Amine gas treating has been studied as a reaction for the first part of the CCS process. This method uses aqueous solutions of various alkylamines to capture carbon dioxide from the waste gases of industrial productions.

(i) Monoethanolamine (MEA) and dimethylethanolamine (DMEA) are two alkylamines that are commonly used in amine gas treating.

base	pK_b
$HOCH_2CH_2N(CH_3)_2$ (DMEA)	3.73
$HOCH_2CH_2NH_2$ (MEA)	4.52
$C_6H_5NH_2$	9.13

Explain the difference in pK_b values in the table. [3]

(ii) The aqueous solution containing 32% MEA by weight can neutralise up to 0.5 mol CO_2 per mole of the amine. Assume that density of the solution is 1 kg dm^{-3}.

Calculate the pH of 32% MEA solution. [3]

(b) **(i)** Another alkylamine, dimethylpiperazine (DMP), has the molecular formula $C_6H_{14}N_2$.

1 mole of DMP can be formed from 2 moles of N-methyl-2-chloroethylamine under suitable conditions.

1. State the conditions needed for this reaction.
2. Write a balanced equation for the conversion of N-methyl-2-chloroethylamine into DMP, showing the structural formulae of N-methyl-2-chloroethylamine and DMP. [2]

(ii) Under room conditions, N-methyl-2-chloroethylamine reacts with

1. $ClCH_2CO_2H$ and
2. CH_3COCl

Name the type of reaction that occur and suggest the structure of the compound formed in each reaction. [3]

(c) CO_2 that is captured from amine gas treating needs to be sequestered so that it does not return into the atmosphere.

Carbon sequestration has been attempted using mineral carbonation. In this method, liquid CO_2 is buried under a volcanic rock known as basalt. Over a period of time, CO_2 reacts with metal oxides in the rock to form $MgCO_3$ and $CaCO_3$. This method allows a large amount of CO_2 in the atmosphere to be trapped as solid thus reducing its effect as a greenhouse gas.

(i) In volcanic areas, underground temperatures rises with increasing depth. Two types of carbonates found in these areas are rhodochrosite $MnCO_3$ and calcite $CaCO_3$.

By quoting suitable data from the Data Booklet, explain whether $MnCO_3$ or $CaCO_3$ decomposes more readily in the presence of geothermal heat. [3]

(ii) Magnesite, $MgCO_3$, forms an equilibrium with CO_2 when it is trapped underground in high temperature.

Reaction 1 $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$ $\Delta H_r = +117 \text{ kJ mol}^{-1}$

Suggest how mineral carbonation can be maintained despite high temperature and justify your answer. [2]

(iii) Fosterite, Mg_2SiO_4, is a component of basalt that reacts with CO_2 in the following reaction.

Reaction 2 $Mg_2SiO_4(s) + 2CO_2(g) \longrightarrow 2MgCO_3(s) + SiO_2(s)$ $\Delta H_r < 0$

enthalpy change of combustion of Mg(s) = -607 kJ mol^{-1}

enthalpy change of formation of $Mg_2SiO_4(s)$ = $-59.5 \text{ kJ mol}^{-1}$

enthalpy change of formation of $SiO_2(s)$ = -911 kJ mol^{-1}

Using the information above and relevant data from the *Data Booklet*, draw an energy level diagram and hence calculate the enthalpy change of **reaction 2**. [4]

[Total: 20]

2 **(a)** The primary fermentation of grape juice produces wine and carbon dioxide. Sometimes, a secondary fermentation takes place a few months after the primary fermentation is finished and the wine has been bottled. This secondary fermentation converts 2-hydroxybutanedioic acid (malic acid) in the wine into 2-hydroxypropanoic acid (lactic acid). There are two benefits: the carbon dioxide produced can be used to make the wine sparkling; the conversion of the malic acid into lactic acid decreases the acidity of the wine.

$$HOOCCH_2CH(OH)COOH \longrightarrow CH_3CH(OH)COOH + CO_2$$

A typical concentration of malic acid in wine is 0.05 mol dm^{-3}.

(i) Calculate the volume of carbon dioxide produced at room temperature and pressure conditions when 1.0 dm^3 of wine undergoes secondary fermentation. [1]

(ii) A typical wine bottle has a capacity of 1.5 dm^3. Using the ideal gas equation, calculate the pressure the carbon dioxide produced would exert inside the air gap of the bottle containing 1.3 dm^3 of wine at room temperature. [1]

(iii) In fact, the pressure inside the bottle is much less under these conditions. Explain why this differs from the pressure you calculated in **(a)(ii)**. [1]

(b) Another way by which the acidity in wine can be decreased is by an acid-catalysed ester formation:

$$\text{ethanol + acid} \rightleftharpoons \text{ester + water}$$

Wine consists of ethanol and water. A 1.0 dm^3 of wine typically contains 10% of ethanol by mass and a 0.10 mol dm^{-3} concentration organic acid, assuming density of wine is 1 g cm^{-3}.

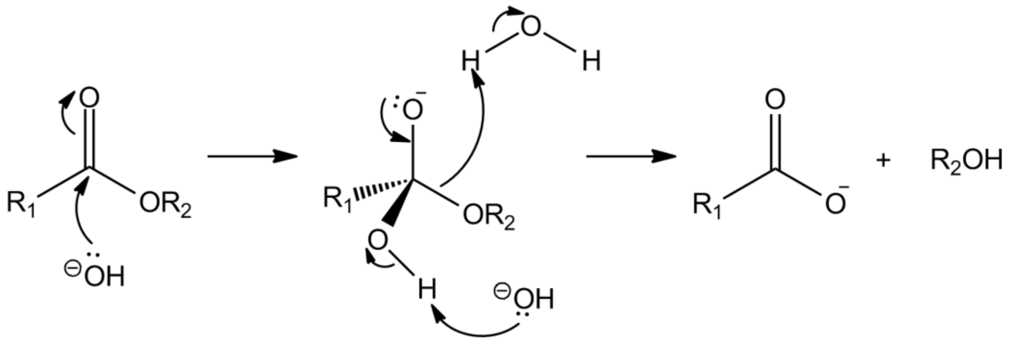
(i) Calculate the value for the equilibrium constant K_c for the ester formation, given that 17.4% of acid is converted to ester. [3]

(ii) Maturation is the process where the wine evolves to a state of readiness for bottling or drinking. Before the wine is ready to be kept in a dark and cool environment at an ambient temperature below 20 °C in barrels for storage, they will equilibrate to form ester. Suggest two reasons why wine needs several months to mature before this reaction takes place significantly. [2]

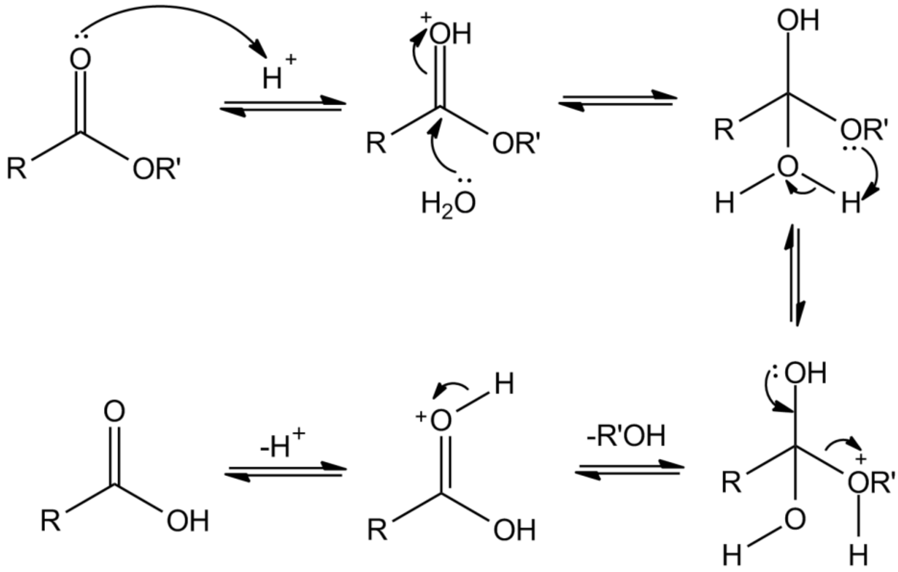
(c) Describe a laboratory test to distinguish between 2-hydroxybutanedioic acid (malic acid) and 2-hydroxypropanoic acid (lactic acid). State the reagents and conditions you would use and any observations that you would make for each compound. Write the equation for any reaction that occurs. [3]

(d) Typically, esters can be hydrolysed in dilute acid or alkali.

The mechanism of both hydrolysis methods are shown as follow:



alkaline hydrolysis



acidic hydrolysis

In alkaline hydrolysis, the hydroxide anion attacks the electron deficient carboxyl carbon.

In acid hydrolysis, the acid protonates the carboxyl oxygen to render the carboxyl carbon more electrophilic towards nucleophilic attack by water.

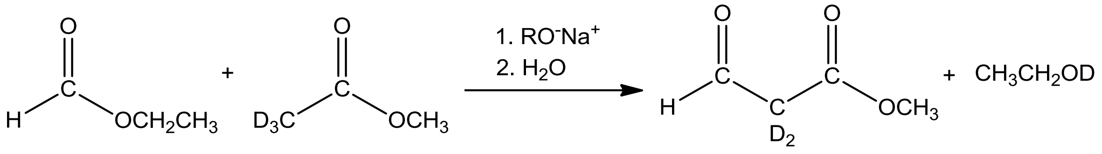
(i) What is the role of

1. OH^- in step 1 of alkaline hydrolysis
2. H^+ in acidic hydrolysis respectively? [2]

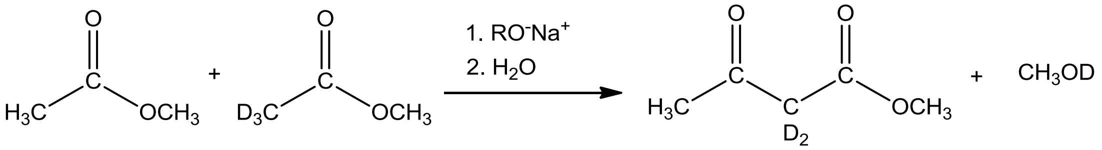
(ii) What is the role of water in acid hydrolysis? [1]

(iii) Outline the two advantages of alkaline hydrolysis. [2]

(e) Claisen condensation is a carbon–carbon bond forming reaction that can occur between two esters in the presence of a strong base, resulting in a β–keto ester. In the mixture of methyl ethanoate and ethyl methanoate, the following Claisen condensation products are formed.

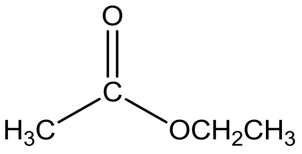


and

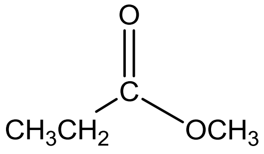


(Deuterium, $^{2}_{1}D$, is an isotope of hydrogen.)

Predict the structures of β–keto esters formed when ethyl ethanoate is mixed with methyl propanoate under suitable reaction conditions.



ethyl ethanoate



methyl propanoate

[4]

[Total: 20]

3 **(a)** The characteristic properties of transition metals include coloured ions, complex formation, variable oxidation states and catalytic activity.

Transition metals are used extensively as heterogeneous catalysts in industrial processes. An example is the use of iron as a catalyst in the Haber process to manufacture ammonia.

(i) Explain what is meant by the term *heterogeneous*. [1]

(ii) State, in the correct order, three essential steps for the mechanism of heterogeneous catalysis. [2]

(iii) The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its efficiency as a heterogeneous catalyst.

Suggest a reason why transition metals which adsorb weakly are usually not good heterogeneous catalysts. [1]

(iv) A catalyst containing molybdenum(VI) was analysed for its molybdenum content by reducing a sample to the molybdenum(III) state. When titrated with acidified potassium manganate(VII), the molybdenum(III) was oxidised back to molybdenum(VI).

A 0.330 g sample of the catalyst, after reduction, required 27.50 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) to convert the molybdenum(III) into molybdenum(VI).

Calculate the percentage by mass of molybdenum in the catalyst. [2]

(b) **(i)** The chemistry of the transition metal, tungsten, has certain similarities to that of sulfur. Both elements reach their maximum +6 oxidation states when combined with the electronegative element, oxygen.

Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}. A common mineral is Scheelite which is calcium tungstate, $CaWO_4$.

Draw the structure showing the bonding in the WO_4^{2-} ion and give the O–W–O bond angle. [2]

(ii) Tungsten(VI) oxide, WO_3, is used in electrochromic windows which change colour when an electrical voltage is applied.

In electrochromic windows, a voltage is applied between a transparent layer of tungsten(VI) oxide and a source of ions such as a lithium salt, and the following reaction takes place during which some of the lithium ions are incorporated into the structure of the oxide:

$$WO_3 + xLi^+ + xe^- \longrightarrow Li_xWO_3$$

The product, Li_xWO_3, is known as a tungsten bronze and its colour depends on the value of x. The value of x can vary from 0 to 1; a typical value giving blue-black colour is when x = 0.3.

Calculate the average oxidation state of the tungsten when x = 0.3. [1]

(iii) A complex of tungsten, $W(CO)_6$, has zero oxidation state for tungsten. It reacts with $CH_3^-Li^+$ as shown by the following equation:

$$CH_3^-Li^+ + W(CO)_6 \longrightarrow Li^+[W(CO)_5(COCH_3)]^-$$

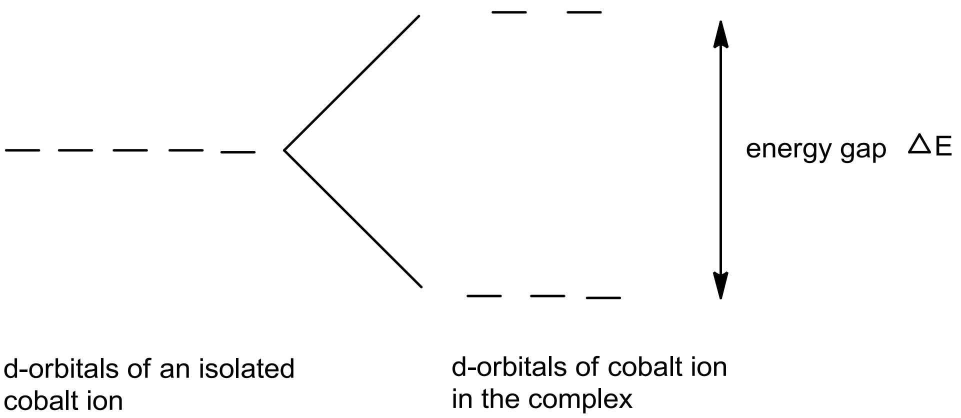
The reaction is nucleophilic addition where CH_3^- is a nucleophile.

Illustrate the shape of $[W(CO)_5(COCH_3)]^-$ by drawing the displayed formula of the anionic complex. [1]

(c) CoF_6^{3-} and $Co(NH_3)_6^{3+}$ are two octahedral complexes which are blue and yellow in colour respectively.

The colours of the two complexes are different due to different ligands which cause splitting of the five 3d orbitals by different amount.

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



In the 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In the 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary before the higher energy d-orbitals are used.

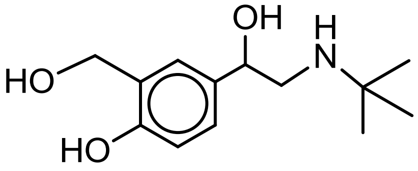
CoF_6^{3-} is a 'high spin' complex while $Co(NH_3)_6^{3+}$ is a 'low spin' complex.

(i) Draw two diagrams like the one above to show the electronic configurations of cobalt ions in CoF_6^{3-} and $Co(NH_3)_6^{3+}$ respectively. [2]

(ii) Hence, explain which of the two complexes will have a larger energy gap, ΔE. [1]

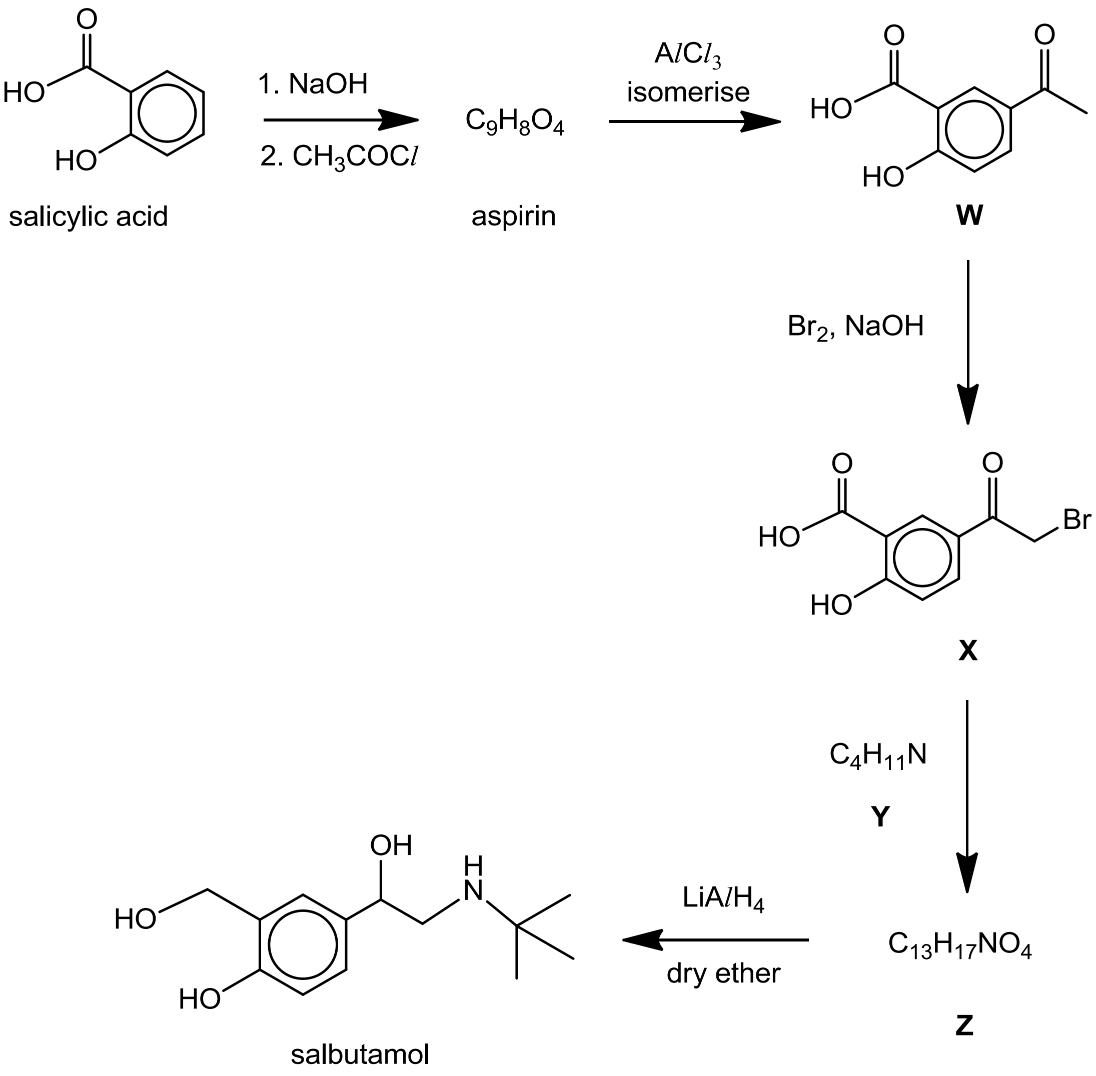
(iii) Explain why electrons usually prefer to occupy orbitals singly, rather than in pairs. [1]

(d) Salbutamol is an anti-asthma drug which is prepared from aspirin, which in turn is prepared from salicylic acid.



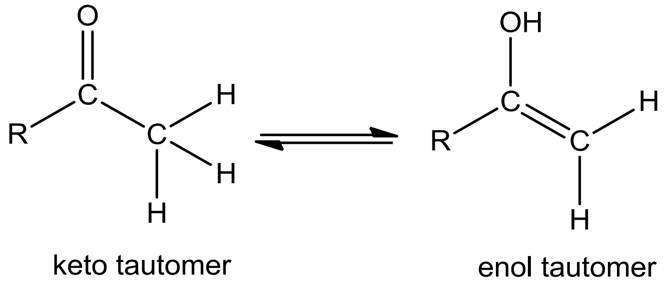
salbutamol

The following reaction scheme shows the synthesis of salbutamol from salicylic acid.



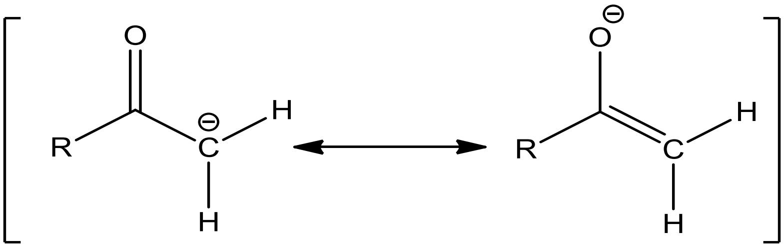
(i) Draw the structures of aspirin, product **Z** and reagent **Y.** [3]

(ii) A carbonyl compound with a hydrogen atom on its α–carbon rapidly equilibrates with its corresponding enol form as shown.



This rapid inter-conversion between the keto and enol form is a special kind of isomerism known as tautomerism.

In the presence of strong bases, the hydrogen atom on its α–carbon is abstracted to form a resonance-stabilised enolate anion as shown below:



two resonance structures of the enolate anion

Resonance structures differ only in the position of their electrons.

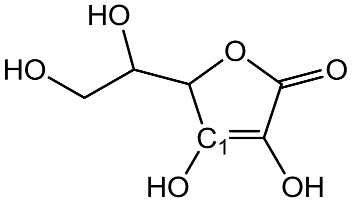
The mechanism for the reaction from product **W** to form product **X** using Br_2 and NaOH involves the intermediate, enolate anion. The two steps are:

- The first step involves an acid-base reaction between the hydroxide ion and the methyl group to give the enolate anion.
- Using its resonance structure with the C=C bond, the enolate anion undergoes electrophilic attack by Br_2 to give product **X**.

Based on the information given, describe the mechanism for the reaction to form product **X** from product **W**. In your answer, show any relevant charges, lone pairs of electrons and arrows to show movement of electrons. [3]

[Total: 20]

4 This question concerns ascorbic acid (vitamin C, $C_6H_8O_6$) and its chemistry. The structure of ascorbic acid is provided below.



ascorbic acid

(a) Ascorbic acid can be used in the synthesis of other compounds, with the use of $Si(CH_3)_3Cl$ as a protecting group for the alcohol groups.

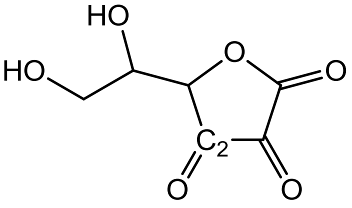
(i) In water, $Si(CH_3)_3Cl$ hydrolyses at a much faster rate than $C(CH_3)_3Cl$.

Explain the difference in the ease of hydrolysis. [2]

(ii) State and describe the mechanism for the hydrolysis of $C(CH_3)_3Cl$ in water. You should include in your answer:

- Dipoles of relevant covalent bonds
- Curly arrows
- Label for the slow step [3]

(b) Dehydroascorbic acid (DHA), $C_6H_6O_6$, with its structure shown below, is the oxidised product of ascorbic acid.



dehydroascorbic acid

(i) State the oxidation number of:

- the carbon labelled C_1 in ascorbic acid.
- the carbon labelled C_2 in DHA. [2]

(ii) Write a balanced half equation, showing their structural formulae, for the reduction of DHA to ascorbic acid. [1]

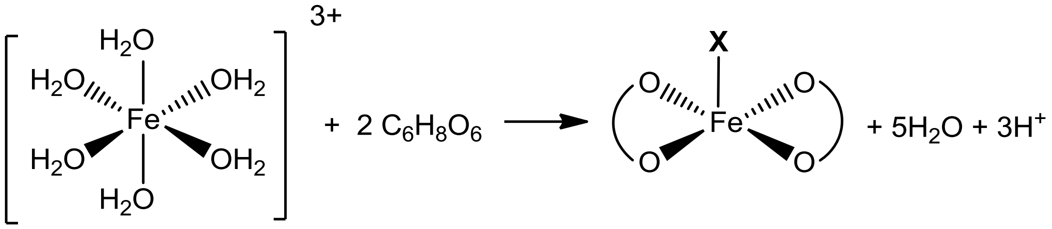
(iii) The electrode potential of ascorbic acid at pH 2 is +0.281 V. Explain how the electrode potential value changes as the pH increases. [2]

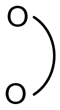
(c) Electrolysis of an aqueous solution of $Fe(ascorbate)_2$ buffered at pH 2 was carried out, with 22.4 cm^3 of hydrogen gas obtained at room temperature and pressure. Ascorbate is the conjugate base of ascorbic acid.

(i) Using information from the *Data Booklet*, determine the minimum voltage required to run this electrolysis. [2]

(ii) Calculate the mass of the product obtained at the anode. [2]

(d) To 50 cm^3 of an aqueous solution of ascorbic acid, 200 cm^3 of ethanol was added. Some FeCl_3 was dissolved in this solution and the solid, Fe(ascorbate)$_2$**X** with an M_r of 422.8, was filtered off. The equation is as follows:



Note:  represents the ascorbate ligand

(i) Suggest the role of ethanol in the preparation of the precipitate. [1]

(ii) Determine the identity of the ion **X**. [1]

(iii) The formation of Fe(ascorbate)$_2$**X** from Fe(H_2O)$_6^{3+}$ involves a ligand substitution between H_2O and the ascorbate ion as shown in the equation above.

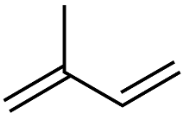
Explain the sign of the entropy change for the formation of Fe(ascorbate)$_2$**X**.

Hence given that the formation is exothermic, deduce the sign of the standard Gibbs free energy change. [4]

[Total: 20]

5 The use of the *Data Booklet* is relevant to this question.

(a) 2–methylbuta–1,3–diene, also known as isoprene, is produced by many plants and serves as a building block for monoterpenes when two isoprene units combine without any rearrangement of the carbon skeleton. Monoterpenes all have molecular formula of $C_{10}H_{16}$.



isoprene

Compounds **A** and **B** are geometric isomers of a monoterpene commonly used in perfumes for their sweet herbal scent. Compounds **A** and **B** react with cold dilute alkaline potassium manganate(VII) to produce stereoisomers of $C_{10}H_{22}O_6$.

Compounds **A** and **B** react with hot concentrated acidified potassium manganate(VII) to produce compounds **C**, $C_3H_4O_3$, **D**, $C_3H_4O_4$, **E**, C_3H_6O and a gas **F**. Both **C** and **E** give a yellow precipitate with aqueous alkaline iodine. A 1.04 g sample of **D** reacted with excess sodium metal to produce 240 cm^3 of gas.

Use the information to suggest, with explanation, identities of **A** to **F**. [9]

(b) Fehling's solution is often used as a distinguishing test in the qualitative analyses of organic compounds. It is prepared by mixing two separate solutions, known as Fehling's A and Fehling's B. Fehling's A is aqueous copper(II) sulfate while Fehling's B is an aqueous solution of potassium sodium tartrate made in sodium hydroxide.

Tartaric acid, H_4T, can exist as a tetraanion, T^{4-}, in a strongly alkaline medium. In Fehling's B, it exists as the H_2T^{2-} anion.

The standard electrode potentials, $E^\ominus$, of several species are shown in the table below.

	Electrode reaction	$E^\ominus$ **/V**
1	$Cu_2O + H_2O + 2e^- \rightleftharpoons 2Cu + 2OH^-$	–0.36
2	$2Cu^{2+} + H_2O + 2e^- \rightleftharpoons Cu_2O + 2H^+$	+0.20
3	$[Cu(HT)_2]^{4-} + 2H_2O + 2e^- \rightleftharpoons Cu + 2H_2T^{2-} + 2OH^-$	+0.25
4	$HCO_2H + 2H^+ + 2e^- \rightleftharpoons HCHO + H_2O$	–0.03
5	$CO_2 + 4H^+ + 4e^- \rightleftharpoons HCHO + H_2O$	–0.07
6	$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	–0.11

Adding Fehling's solution to methanal causes a reaction to take place.

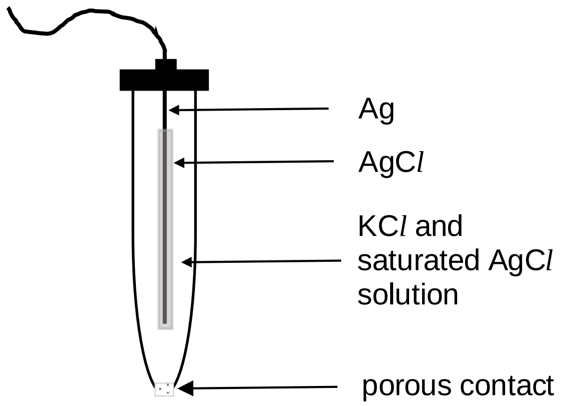
(i) By selecting appropriate electrode reactions from the *Data Booklet* or the table above, construct a balanced equation for this reaction. [1]

(ii) Use your answer in part **(i)** to calculate the $E^\ominus_{cell}$ for this reaction. [1]

(iii) Describe the observations for this reaction. [1]

(c) Electrode potential values are often quoted with reference to the standard hydrogen electrode (SHE). It is however, seldom used because it is difficult to regulate the pressure of hydrogen gas at 1 atm.

One of the more commonly used reference electrodes in electrochemistry is the silver/silver chloride electrode (SSCE). It is made of a silver wire that is coated with a thin layer of silver(I) chloride, immersed in a potassium chloride solution saturated with silver(I) chloride.



schematic of a silver/silver chloride electrode

One of the advantages of using the SSCE is that it can be directly immersed into the other half-cell, thereby negating the use of a salt bridge.

(i) Suggest the purpose of having the porous contact. [1]

The solution in the SSCE is colourless in spite of the presence of a d–block element.

(ii) Explain how the colour in transition metal compounds arise. [2]

(iii) Write the full electronic configuration of Ag^+ and hence explain why it is **not** coloured. [2]

(d) Adding a reagent that selectively brings one of the ions out of a solution as a precipitate while leaving the other ion in the solution is a technique known as selective precipitation.

Data about the solubilities in water and solubility products of silver(I) hydroxide and copper(II) hydroxide at 298 K are given below. Only the numerical values of the solubility products are given.

hydroxide	solubility/ mol dm^{-3}	solubility product
AgOH	1.23×10^{-4}	1.52×10^{-8}
$Cu(OH)_2$	1.77×10^{-7}	2.20×10^{-20}

As a general standard, two ions are selectively separated when a maximum 0.01% of the precipitated compound still remains as the aqueous ions.

Determine if selective precipitation can be performed on a solution containing 0.200 mol dm^{-3} Ag^+ and 0.200 mol dm^{-3} Cu^{2+} with the addition of solid potassium hydroxide. [3]

[Total: 20]

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CHEMISTRY Preliminary Examination

CHEMISTRY
Higher 2

9647/03

Paper 3

23 August 2016
2 hours

Additional Materials: Writing Paper
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Answer any **four** questions. Start each question on a new sheet of writing paper.
A Data Booklet is provided.
The use of an approved calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

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

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

9647/03/
Prelim/16

[Turn over

1 Besides reducing carbon dioxide emission, CO_2 levels in the atmosphere can be lowered through a process known as carbon capture and sequestration (CCS). One form of naturally occurring CCS is the conversion of CO_2 into plant biomass during photosynthesis.

Scientists have also devised chemical methods of CCS. The processes for isolating carbon dioxide and for storing it has been the focus of some research.

(a) Amine gas treating has been studied as a reaction for the first part of the CCS process. This method uses aqueous solutions of various alkylamines to capture carbon dioxide from the waste gases of industrial productions.

(i) Monoethanolamine (MEA) and dimethylethanolamine (DMEA) are two alkylamines that are commonly used in amine gas treating.

base	pK_b
$HOCH_2CH_2N(CH_3)_2$ (DMEA)	3.73
$HOCH_2CH_2NH_2$ (MEA)	4.52
$C_6H_5NH_2$	9.13

Explain the difference in pK_b values in the table. [3]

Basic strength:
$C_6H_5NH_2 < HOCH_2CH_2NH_2$ (MEA) $< HOCH_2CH_2N(CH_3)_2$ (DMEA)

$C_6H_5NH_2$ is the weakest base as the lone pair of electron on the N atom is delocalised into the phenyl group. This makes the lone pair less available to accept H^+.

DMEA is a stronger base than MEA because it has two additional electron donating methyl groups which increases the electron density on the N atom and improves is ability to accept proton.

(ii) The aqueous solution containing 32% MEA by weight can neutralise up to 0.5 mol CO_2 per mole of the amine. Assume that density of the solution is 1 kg dm^{-3}.

Calculate the pH of 32% MEA solution. [3]

n(MEA) in 1 dm^3 of 32% solution
= 320 ÷ [16.0 + 14.0 + 2(12.0) + 7(1.0)]
= 5.246 mol
Concentration MEA solution = 5.246 mol dm^{-3}

$K_b = 10^{-4.52} = 3.162 \times 10^{-5}$ mol dm^{-3}

Let $[OH^-]$ be y mol dm^{-3}
$K_b = \frac{[HOCH2CH2NH3+][OH-]}{[HOCH2CH2NH2]}$
$3.162 \times 10^{-5} = \frac{y^2}{5.246}$
y = 0.01288 mol dm^{-3}

pOH = 1.89
pH = 12.1

(b) **(i)** Another alkylamine, dimethylpiperazine (DMP), has the molecular formula $C_6H_{14}N_2$.

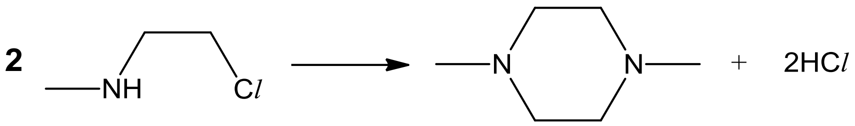
1 mole of DMP can be formed from 2 moles of N-methyl-2-chloroethylamine under suitable conditions.

1. State the conditions needed for this reaction.
2. Write the balance equation for the conversion of N-methyl-2-chloroethylamine into DMP, showing the structural formulae of N-methyl-2-chloroethylamine and DMP.

[2]

1. Ethanol, heat under pressure / in a sealed tube

2.

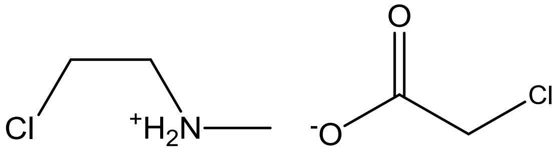


(ii) Under room conditions, N-methyl-2-chloroethylamine reacts with

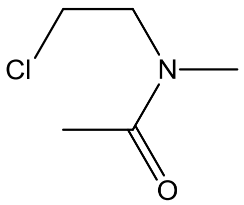
1. $ClCH_2CO_2H$ and
2. CH_3COCl

Name the type of reaction that occur and suggest the structure of the compound formed in each reaction.
[3]

1. Acid-base reaction



2. Condensation reaction / Nucleophilic substitution



(c) CO_2 that is captured from amine gas treating needs to be sequestered so that it does not return into the atmosphere.

Carbon sequestration has been attempted using mineral carbonation. In this method, liquid CO_2 is buried under a volcanic rock known as basalt. Over a period of time, CO_2 reacts with metal oxides in the rock to form $MgCO_3$ and $CaCO_3$. This method allows a large amount of CO_2 in the atmosphere to be trapped as solid thus reducing its effect as a greenhouse gas.

(i) In volcanic areas, underground temperatures rises with increasing depth. Two types of carbonates found in these areas are rhodochrosite $MnCO_3$ and calcite $CaCO_3$.

By quoting suitable data from the Data Booklet, explain whether $MnCO_3$ or $CaCO_3$ decomposes more readily in the presence of geothermal heat. [3]

Ion	Radii / nm
Ca^{2+}	0.099
Mn^{2+}	0.080

$MnCO_3$ is expected to decompose more readily than $CaCO_3$.

This is because Mn^{2+} has smaller ionic radius than Ca^{2+}. This causes the charge density and polarising power of Mn^{2+} to be greater than that of Ca^{2+} thus polarising the C-O bond / distorting the electron cloud in the C–O bond of the anion in $MnCO_3$ to a greater extent.

(ii) Magnesite, $MgCO_3$, forms an equilibrium with CO_2 when it is trapped underground in high temperature.

Reaction 1 $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$ $\Delta H_r = +117 \text{ kJ mol}^{-1}$

Suggest how mineral carbonation can be maintained despite high temperature and justify your answer. [2]

High partial pressure of CO_2 must be maintained so that the backward reaction is favoured to lower the number of moles of gaseous particles.

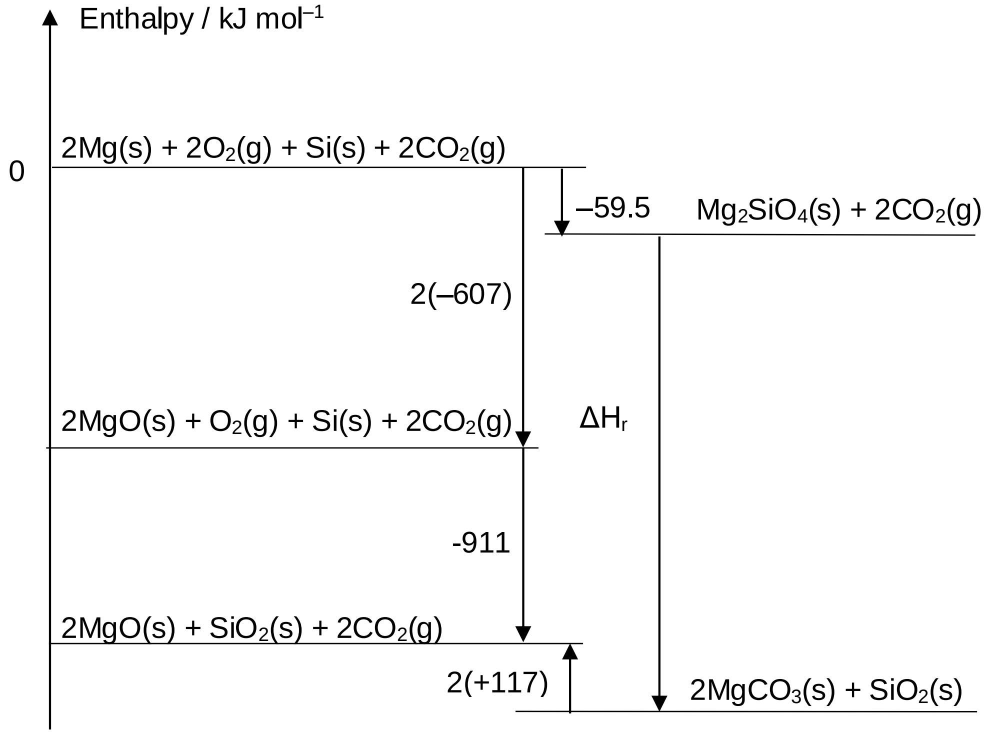
(iii) Fosterite, Mg_2SiO_4, is a component of basalt that reacts with CO_2 in the following reaction.

Reaction 2 $Mg_2SiO_4(s) + 2CO_2(g) \longrightarrow 2MgCO_3(s) + SiO_2(s)$ $\Delta H_r < 0$

enthalpy change of combustion of Mg(s) = –607 kJ mol^{-1}
enthalpy change of formation of $Mg_2SiO_4(s)$ = –59.5 kJ mol^{-1}
enthalpy change of formation of $SiO_2(s)$ = –911 kJ mol^{-1}

Using the information above and relevant data from the *Data Booklet*, draw an energy level diagram and hence calculate the enthalpy change of **reaction 2**.

[4]



$\Delta H_r = 2(–117) + 2(–607) + 59.5 – 911$
$\Delta H_r = –2299.5$
$\Delta H_r = –2300$ kJ mol^{-1} (correct to 3 s.f.)

[Total: 20]

2 **(a)** The primary fermentation of grape juice produces wine and carbon dioxide. Sometimes, a secondary fermentation takes place a few months after the primary fermentation is finished and the wine has been bottled. This secondary fermentation converts 2-hydroxybutanedioic acid (malic acid) in the wine into 2-hydroxypropanoic acid (lactic acid). There are two benefits: the carbon dioxide produced can be used to make the wine sparkling; the conversion of the malic acid into lactic acid decreases the acidity of the wine.

$$HOOCCH_2CH(OH)COOH \longrightarrow CH_3CH(OH)COOH + CO_2$$

A typical concentration of malic acid in wine is 0.05 mol dm^{-3}.

(i) Calculate the volume of carbon dioxide produced at room temperature and pressure conditions when 1.0 dm^3 of wine undergoes secondary fermentation.

[1]

Amount of CO_2 = amount of malic acid = 0.05 x 1.0 = 0.05 mol

Volume of carbon dioxide produced = 0.05 x 24 = $\underline{1.20 \text{ dm}^3}$ (correct to 3 s.f.)

(ii) A typical wine bottle has a capacity of 1.5 dm^3. Using the ideal gas equation, calculate the pressure the carbon dioxide produced would exert inside the air gap of the bottle containing 1.3 dm^3 of wine at room temperature.

[1]

PV = nRT

P = (0.065)(8.31)(298)/(0.2x10^{-3}) = $\underline{8.05 \times 10^5 \text{ Pa}}$ (correct to 3 s.f.)

(iii) In fact, the pressure inside the bottle is much less under these conditions. Explain why this differs from the pressure you calculated in **(a)(ii)**.

[1]

This is due to the fact that CO_2 is not an ideal gas and as such, it will not obey the ideal gas equation. CO_2 is a relatively massive non-polar molecule, thus its molecular volume is not considered to be negligible as compared to the total volume of the gas at such a high pressure.

OR

Intermolecular interactions between CO_2 molecules are not negligible at such a high pressure too. Thus, CO_2 deviate more from ideality.

OR

Carbon dioxide can dissolve in aqueous solution. Thus less CO_2 will occupy in the empty space.

(b) Another way by which the acidity in wine can be decreased is by acid-catalysed ester formation:

$$\text{ethanol} + \text{acid} \rightleftharpoons \text{ester} + \text{water}$$

Wine consists of ethanol and water. A 1.0 dm^3 of wine typically contains 10% of ethanol by mass and a 0.10 mol dm^{-3} concentration organic acid, assuming density of wine is 1 g cm^{-3}.

(i) Calculate the value for the equilibrium constant K_c for the ester formation, given that 17.4% of acid is converted to ester. [3]

	ethanol	+	acid	⇌	ester	+	water
I/mol	100/46		0.1		0		
C	-0.0174		-0.0174		+0.0174		
E/mol	2.1565		0.0826		0.0174		

$K_c = 0.0977$

(ii) Maturation is the process where the wine evolves to a state of readiness for bottling or drinking. Before the wine is ready to be kept in a dark and cool environment at an ambient temperature below 20 °C in barrels for storage, they will equilibrate to form ester. Suggest two reasons why wine needs several months to mature before this reaction takes place significantly. [2]

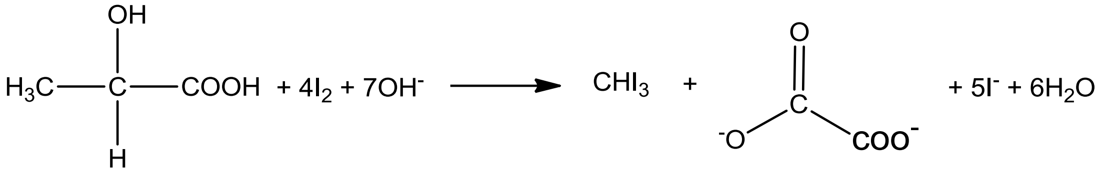
The reaction is slow due to low temperature.

Concentration of acid is low thus leading to slow rate of reaction.

(c) Describe a laboratory test to distinguish between 2-hydroxybutanedioic acid (malic acid) and 2-hydroxypropanoic acid (lactic acid). State the reagents and conditions you would use and any observations that you would make for each compound. Write equation for any reaction that occurs. [3]

Reagents & Conditions: aqueous I_2, NaOH (aq), warm to 60 °C
Observations: 2-hydroxypropanoic acid will give yellow ppt. while 2-hydroxybutanedoic acid will not.

Equation:

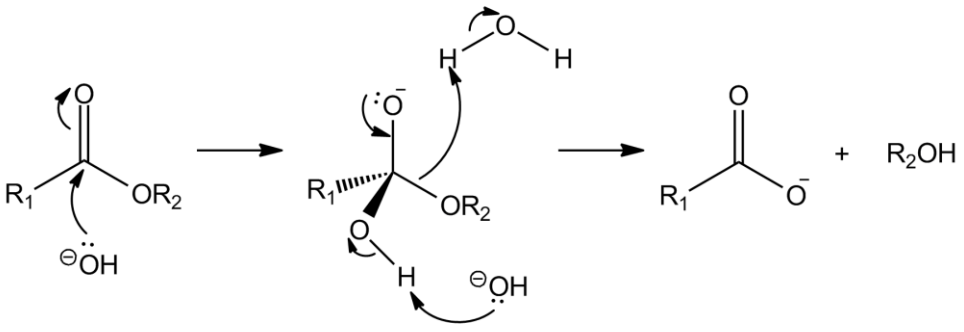


$$CH_3CH(OH)COOH + 4I_2 + 7OH^- \longrightarrow CHI_3 + {}^-OC(=O)COO^- + 5I^- + 6H_2O$$

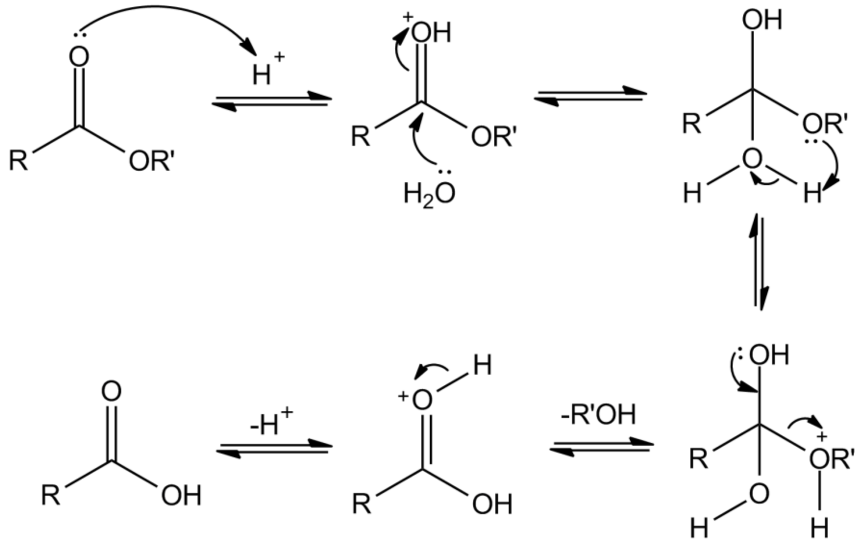
[1]

(d) Typically, esters can be hydrolysed in dilute acid or alkali.

The mechanism of both hydrolysis methods are shown as follow:



alkaline hydrolysis



acidic hydrolysis

In alkaline hydrolysis, the hydroxide anion attacks the electron deficient carboxyl carbon.

In acid hydrolysis, the acid protonates the carboxyl oxygen to render the carboxyl carbon more electrophilic towards nucleophilic attack by water.

(i) What is the role of

1. OH^- in step 1 of alkaline hydrolysis
2. H^+ in acidic hydrolysis respectively? [2]

OH^- is acting as a nucleophile.
H^+ is acting as a catalyst.

(ii) What is the role of water in acid hydrolysis? [1]

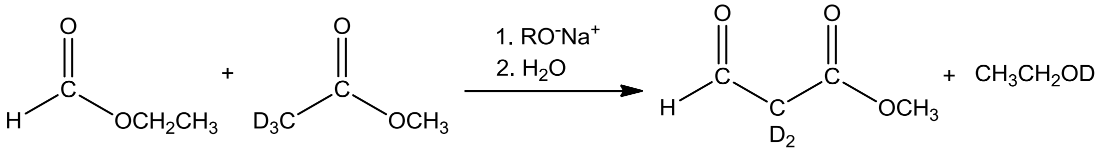
Water is acting as a nucleophile.

(iii) Outline the two advantages of alkaline hydrolysis. [2]

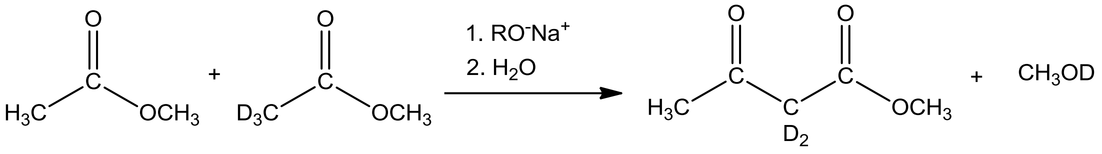
The reaction is irreversible or complete which means that there will be high yield.

The products are easier to separate as one of the products is ionic (aqueous layer) and will be found in a different phase from the organic reactants.

(e) Claisen condensation is a carbon–carbon bond forming reaction that can occur between two esters in the presence of a strong base, resulting in a β–keto ester. In the mixture of methyl ethanoate and ethyl methanoate, the following Claisen condensation products are formed.

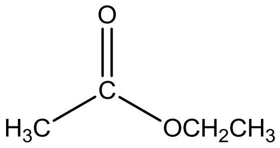


and

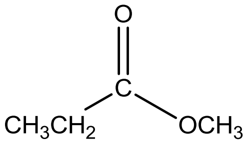


(Deuterium, $^{2}_{1}D$, is an isotope of hydrogen.)

Predict the structures of β–keto esters formed when ethyl ethanoate is mixed with methyl propanoate under suitable reaction conditions.

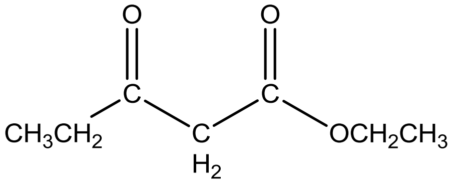


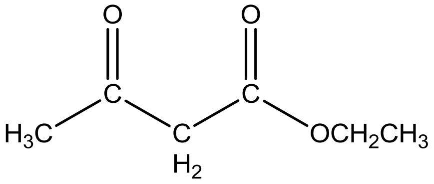
ethyl ethanoate

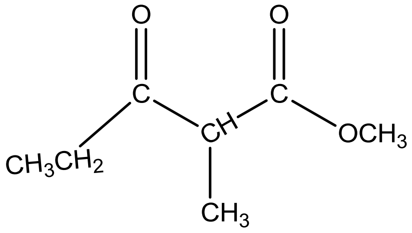


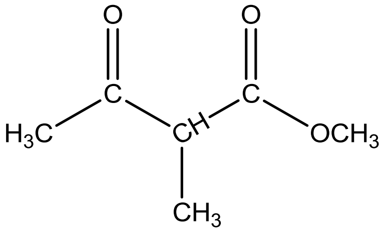
methyl propanoate

[4]









[Total:20]

3 **(a)** The characteristic properties of transition metals include coloured ions, complex formation, variable oxidation states and catalytic activity.

Transition metals are used extensively as heterogeneous catalysts in industrial processes. An example is the use of iron as a catalyst in the Haber process to manufacture ammonia.

(i) Explain what is meant by the term *heterogeneous*? [1]

Reactants and catalyst are in different phase.

(ii) State, in the correct order, three essential steps for the mechanism of heterogeneous catalysis. [2]

1) Surface adsorption/adsorption of reactant molecules on surface of catalyst
2) Reaction between reactant molecules Allow :bonds in reactants weakened
3) Products desorbed from the surface

(iii) The strength of the adsorption of reactants and products onto the surface of a transition metal helps to determine its efficiency as a heterogeneous catalyst.

Suggest a reason why transition metals which adsorb weakly are usually not good heterogeneous catalysts. [1]

Reactants not brought together or
No increase in reactant concentration on catalyst surface or
Reactants not held long enough for a reaction to occur or
Reactant bonds not weakened

(iv) A catalyst containing molybdenum(VI) was analysed for its molybdenum content by reducing a sample to the molybdenum(III) state.

When titrated with acidified potassium manganate(VII), the molybdenum(III) was oxidised back to molybdenum(VI).

A 0.330 g sample of the catalyst, after reduction, required 27.50 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) to convert the molybdenum(III) into molybdenum(VI).

Calculate the percentage by mass of molybdenum in the catalyst. [2]

1 mole of molybdenum(III) compound loses 3 moles of electrons on oxidation while 1 mole of manganate(VII) accept 5 moles of electrons in acidic medium.

Amount of MnO_4^- in 27.50 cm^3 = $27.5 \times 10^{-3} \times 0.02 = 5.50 \times 10^{-4}$ mol

Amount of Mo = $5/3 \times 5.50 \times 10^{-4} = 9.17 \times 10^{-4}$ mol

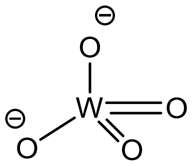
Mass of Mo = $95.9 \times 9.17 \times 10^{-4} = 8.80 \times 10^{-2}$ g

% Mo = $(8.80 \times 10^{-2}/0.330) \times 100 = 26.7$ %

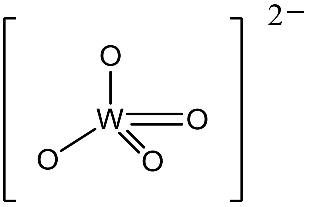
(b) **(i)** The chemistry of the transition metal, tungsten, has certain similarities to that of sulfur. Both elements reach their maximum +6 oxidation states when combined with the electronegative element, oxygen.

Most tungsten occurs naturally in the tungsten anion, WO_4^{2-}, analogous to the sulfate ion, SO_4^{2-}. A common mineral is Scheelite which is calcium tungstate, $CaWO_4$.

Draw the structure showing the bonding in the WO_4^{2-} ion and give the O–W–O bond angle. [2]



or



Bond angle:109.5°

(ii) Tungsten(VI) oxide, WO_3, is used in electrochromic windows which change colour when an electrical voltage is applied.

In electrochromic windows, a voltage is applied between a transparent layer of tungsten(VI) oxide and a source of ions such as a lithium salt, and the following reaction takes place during which some of the lithium ions are incorporated into the structure of the oxide:

$$WO_3 + xLi^+ + xe^- \longrightarrow Li_xWO_3$$

The product, Li_xWO_3, is known as a tungsten bronze and its colour depends on the value of x. The value of x can vary from 0 to 1; a typical value giving blue-black colour is when x = 0.3.

Calculate the average oxidation state of the tungsten when x = 0.3. [1]

Let oxidation state of the tungsten be m
$0.3 + m + (-2)3 = 0$
$m = \underline{+5.7}$

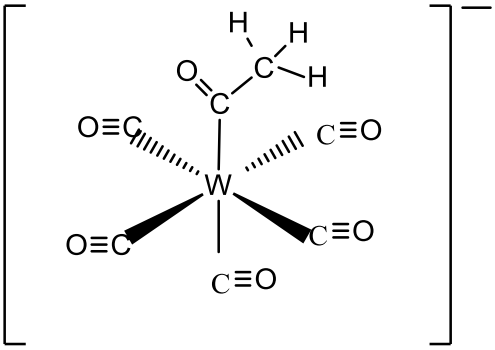
(iii) A complex of tungsten, $W(CO)_6$, has zero oxidation state for tungsten. It reacts with $CH_3^-Li^+$ as shown by the following equation:

$$CH_3^-Li^+ + W(CO)_6 \longrightarrow Li^+[W(CO)_5(COCH_3)]^-$$

The reaction is nucleophilic addition where CH_3^- is a nucleophile.

Illustrate the shape of $[W(CO)_5(COCH_3)]^-$ by drawing the displayed formula of the anionic complex.

[1]

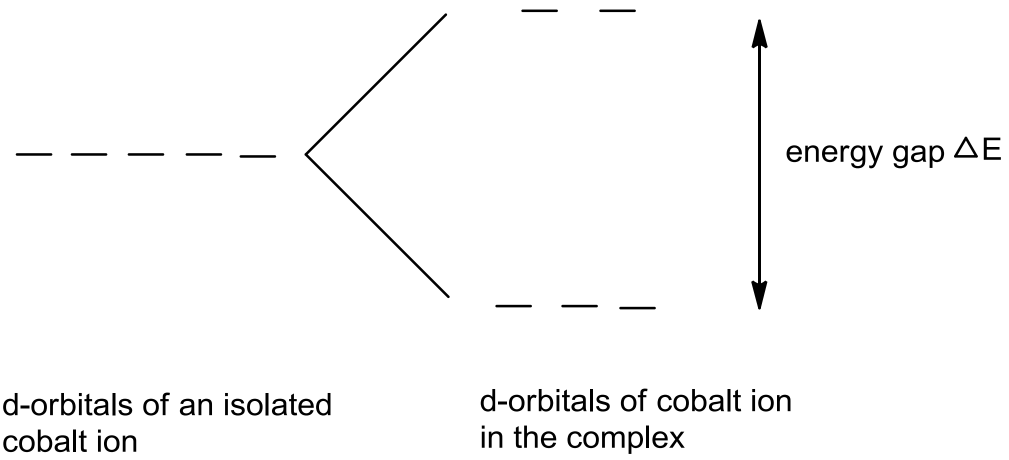


Note: all covalent bonds must be shown as it is a displayed formula.
Octahedral shape illustrated with wedge and dash bonds.

(c) CoF_6^{3-} and $Co(NH_3)_6^{3+}$ are two octahedral complexes which are blue and yellow in colour respectively.

The colours of the two complexes are different due to different ligands which cause splitting of the five 3d orbitals by different amount.

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

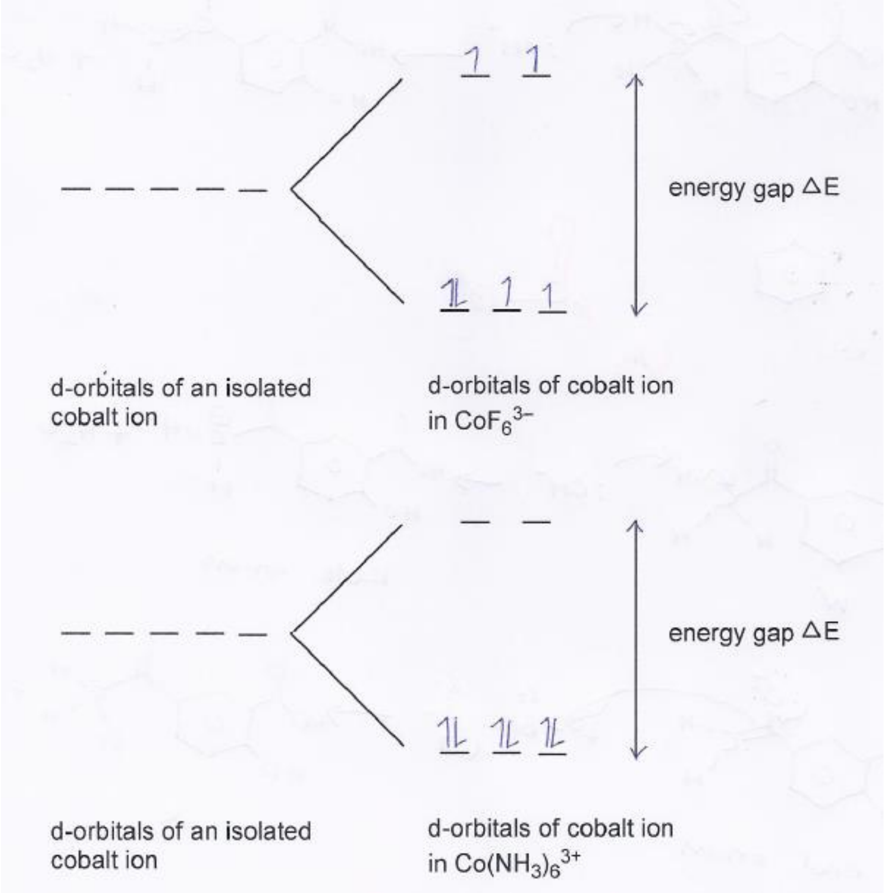


In the ‘high spin’ state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

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

CoF_6^{3-} is a ‘high spin’ complex while $Co(NH_3)_6^{3+}$ is a ‘low spin’ complex.

(i) Draw two diagrams like the one above to show the electronic configurations of cobalt ions in CoF_6^{3-} and $Co(NH_3)_6^{3+}$ respectively. [2]



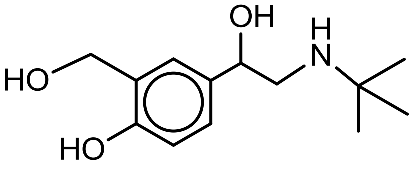
(ii) Hence, explain which of the two complexes will have a larger energy gap, ΔE. [1]

$Co(NH_3)_6^{3+}$ since ΔE is large so pairing of electrons at lower level is preferred rather than promotion of electrons to a higher level.

(iii) Explain why electrons usually prefer to occupy orbitals singly, rather than in pairs. [1]

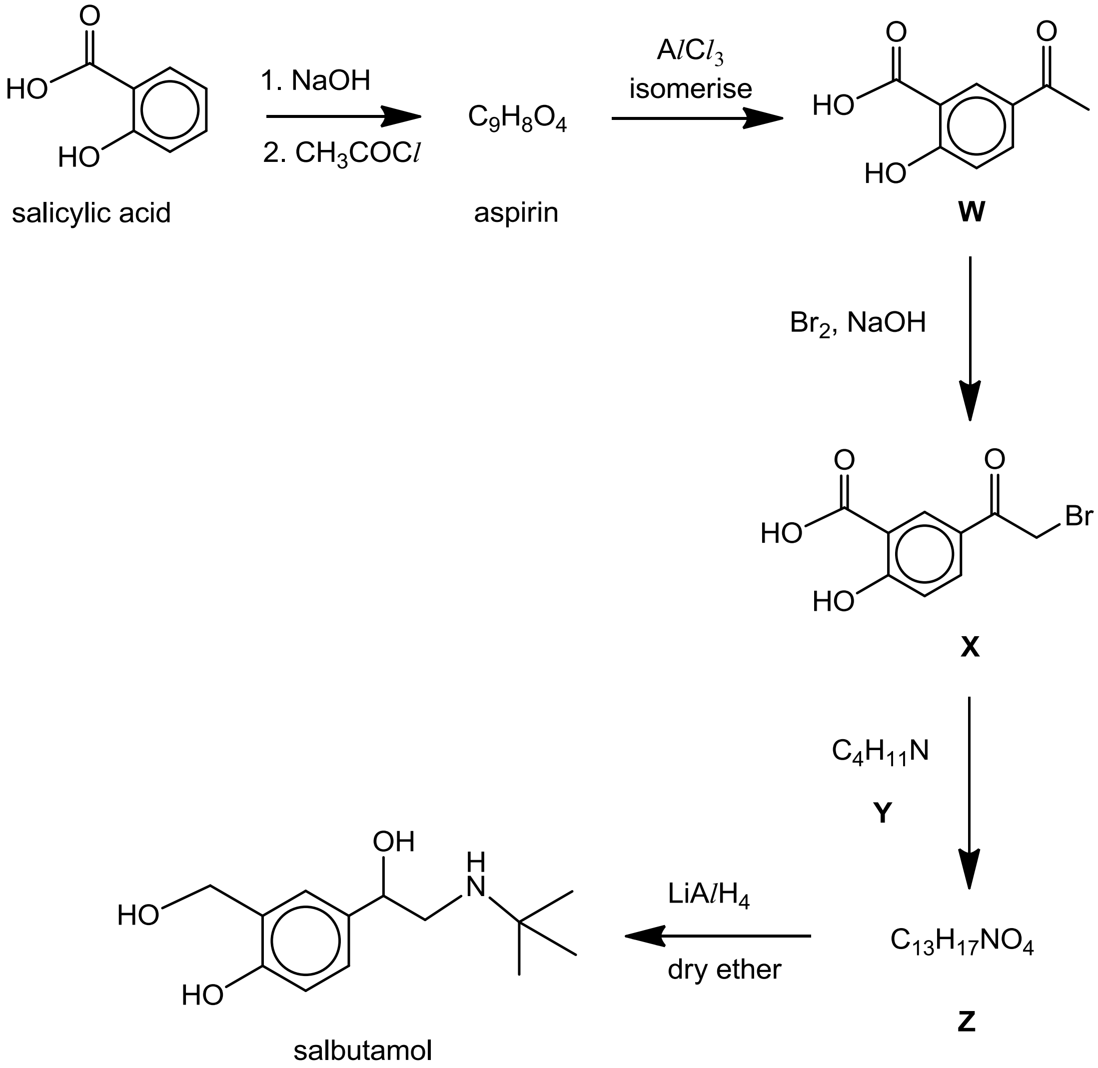
There will be electrostatic repulsion between electrons if they are paired up.

(d) Salbutamol is an anti-asthma drug which is prepared from aspirin, which in turn is prepared from salicylic acid.

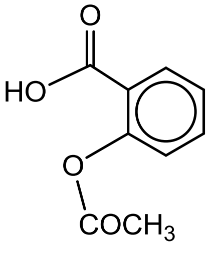


Salbutamol

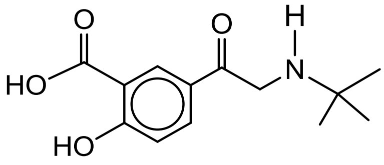
The following reaction scheme shows the synthesis of Salbutamol from salicylic acid.



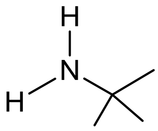
(i) Draw the structures of aspirin, product **Z** and reagent **Y.** [3]



aspirin

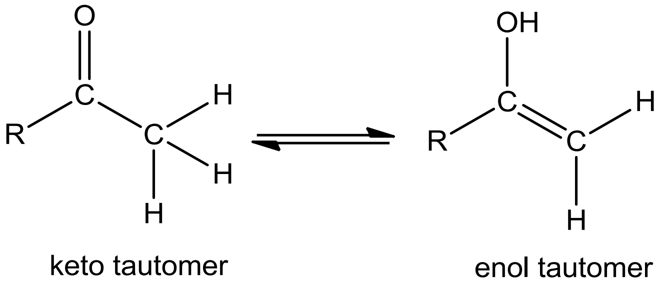


product Z



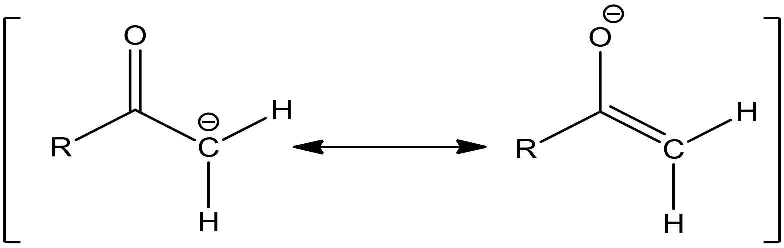
reagent Y

(ii) A carbonyl compound with a hydrogen atom on its α carbon rapidly equilibrates with its corresponding enol form as shown.



This rapid inter-conversion between the keto and enol form is a special kind of isomerism known as tautomerism.

In the presence of strong bases, the hydrogen atom on its α–carbon is abstracted to form a resonance-stabilised enolate anion as shown below:



two resonance structures of the enolate anion

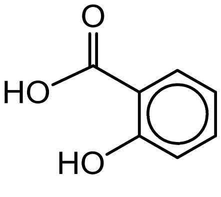
Resonance structures differ only in the position of their electrons.

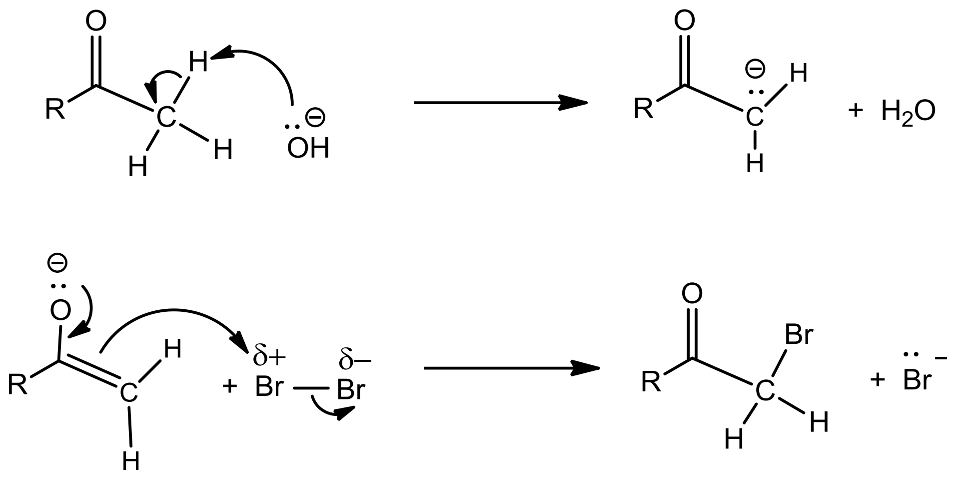
The mechanism for the reaction from product **W** to form product **X** using Br_2 and NaOH involves the intermediate, enolate anion. The two steps are:

- The first step involves an acid-base reaction between the hydroxide ion and the methyl group to give the enolate anion.
- Using its resonance structure with the C=C bond, the enolate anion undergoes electrophilic attack by Br_2 to give product **X**.

Based on the information given, describe the mechanism for the reaction to form product **X** from product **W**. In your answer, show any relevant charges, lone pairs of electrons and arrows to show movement of electrons. [3]

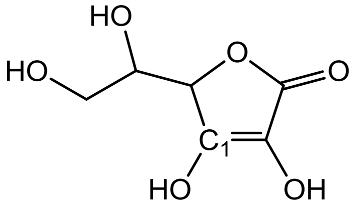
Let R be





[Total: 20]

4 This question concerns ascorbic acid (vitamin C, $C_6H_8O_6$) and its chemistry. The structure of ascorbic acid is provided below.



ascorbic acid

(a) Ascorbic acid can be used in the synthesis of other compounds, with the use of $Si(CH_3)_3Cl$ as a protecting group for the alcohol groups.

(i) In water, $Si(CH_3)_3Cl$ hydrolyses at a much faster rate than $C(CH_3)_3Cl$.

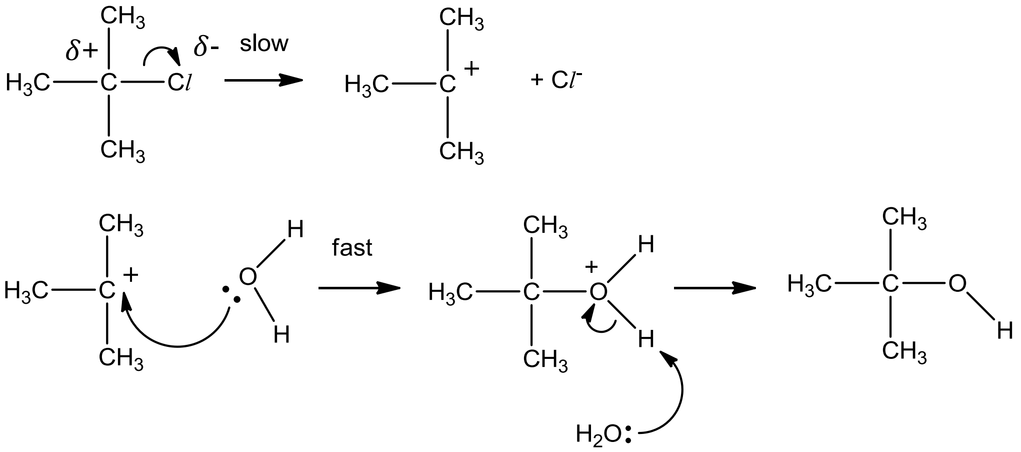
Explain the difference in the ease of hydrolysis. [2]

Si has empty 3d orbitals that can accept a lone pair of electrons from water while there are no empty orbitals available to accept lone pair for C, requiring the formation of a carbocation prior to nucleophilic attack by water.

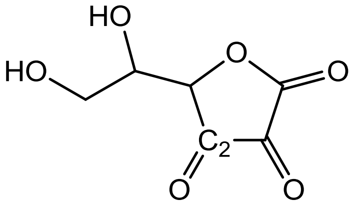
(ii) State and describe the mechanism for the hydrolysis of $C(CH_3)_3Cl$ in water. You should include in your answer:

- Dipoles of relevant covalent bonds
- Curly arrows
- Label for the slow step [3]

S_N1 / unimolecular nucleophilic substitution



(b) Dehydroascorbic acid (DHA), $C_6H_6O_6$, with its structure shown below, is the oxidised product of ascorbic acid.



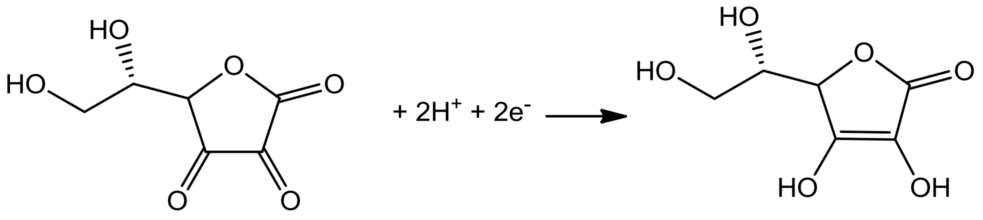
Dehydroascorbic acid

(i) State the oxidation number of:

- the carbon labelled C_1 in ascorbic acid.
- the carbon labelled C_2 in DHA. [2]

Ascorbic acid: +1
DHA: +2

(ii) Write a balanced half equation, showing their structural formulae, for the reduction of DHA to ascorbic acid. [1]



(iii) The electrode potential of ascorbic acid at pH 2 is +0.281 V. Explain how the electrode potential value changes as the pH increases. [2]

With an increase in pH, there is a decrease in the concentration of H^+. Thus the position of equilibrium for the reaction in (ii) shifts to the left, favouring the tendency for oxidation of ascorbic acid. Hence the electrode potential becomes less positive / more negative with a rise in pH.

(c) Electrolysis of an aqueous solution of $Fe(ascorbate)_2$ buffered at pH 2 was carried out, with 22.4 cm^3 of hydrogen gas obtained at room temperature and pressure, Ascorbate is the conjugate base of ascorbic acid.

(i) Using information from the *Data Booklet*, determine the minimum voltage required to run this electrolysis. [2]

Cathode
$Fe^{2+} + 2e^- \rightleftharpoons Fe$ −0.44V
$2H^+ + 2e^- \rightleftharpoons H_2$ +0.00V

Anode
$DHA + 2H^+ + 2e^- \rightleftharpoons$ ascorbic acid +0.281V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23V

E_{cell} is to be calculated correctly based on correctly selected electrode potentials

$E_{cell} = -0.00 - (+0.281) = -0.281V$

A minimum of 0.281V is required to run the electrolysis.

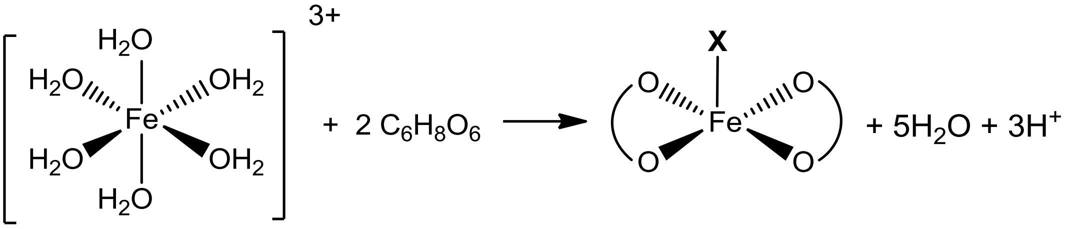
(ii) Calculate the mass of the product obtained at the anode. [2]

The oxidation of ascorbic acid is easier at the anode than water.
Identifies DHA as the product at the anode in words or working

Amount of $H_2 = \frac{22.4}{24000} = 9.333 \times 10^{-4}$ mol
$2H^+ \equiv H_2$
$DHA \equiv 2H^+$

Mass of DHA = $9.333 \times 10^{-4} \times 174 = 0.162$ g

(d) To 50 cm^3 of an aqueous solution of ascorbic acid, 200 cm^3 of ethanol was added. Some $FeCl_3$ was dissolved in this solution and the solid, $Fe(ascorbate)_2\mathbf{X}$ with an M_r of 422.8, was filtered off. The equation is as follows:



(i) Suggest the role of ethanol in the preparation of the precipitate. [1]

It serves to reduce the solubility of the compound in solution / encourages precipitation.

(ii) Determine the identity of the ion **X**. [1]

Either by inspection of the equation
OR
422.8 – 55.8 – 2(175) = 17

Hydroxide / OH^-

(iii) The formation of $Fe(ascorbate)_2\mathbf{X}$ from $Fe(H_2O)_6^{3+}$ involves a ligand substitution between H_2O and the ascorbate ion as shown above.

Explain the sign of the entropy change for the formation of $Fe(ascorbate)_2\mathbf{X}$.

Hence given that the formation is exothermic, deduce the sign of the standard Gibbs free energy change. [4]

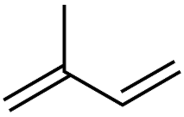
Being bidentate, each ascorbate ion replaces 2 water molecules coordinated to Fe^{3+} OR increase in the number of species/particles. There is an increase in the entropy during the formation of $Fe(ascorbate)_2X$. Hence $\Delta S > 0$.

As $\Delta G = \Delta H - T\Delta S$ and $\Delta H < 0$,
ΔG will have a negative sign.

[Total: 20]

5 The use of the *Data Booklet* is relevant to this question.

(a) 2–methylbuta–1,3–diene, also known as isoprene, is produced by many plants and serves as a building block for monoterpenes when two isoprene units combine without any rearrangement of the carbon skeleton. Monoterpenes all have molecular formula of $C_{10}H_{16}$.



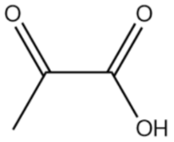
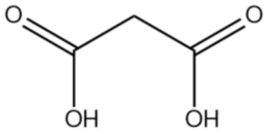
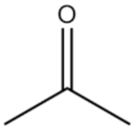
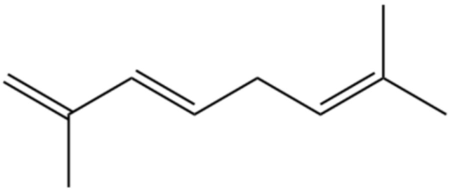
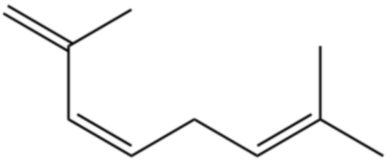
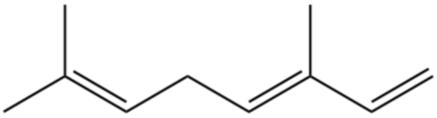
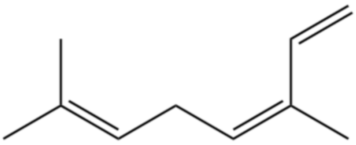
isoprene

Compounds **A** and **B** are geometric isomers of a monoterpene commonly used in perfumes for their sweet herbal scent. Compounds **A** and **B** react with cold dilute alkaline potassium manganate(VII) to produce stereoisomers of $C_{10}H_{22}O_6$.

Compounds **A** and **B** react with hot concentrated acidified potassium manganate(VII) to produce compounds **C**, $C_3H_4O_3$, **D**, $C_3H_4O_4$, **E**, C_3H_6O and a gas **F**. Both **C** and **E** give a yellow precipitate with aqueous alkaline iodine. A 1.04 g sample of **D** reacted with excess sodium metal to produce 240 cm^3 of gas.

Use the information to suggest, with explanation, identities of **A** to **F**. [9]

Statements	**Explanations/Inferences/Deductions**
1. A and **B** react with cold dil. $KMnO_4/OH^–$ to produce $C_{10}H_{22}O_6$.	**A** and **B** underwent mild oxidation. An increase of 6 –OH groups suggests 3 alkenes.
2. A and **B** react with hot conc. $KMnO_4/H^+$ to produce **C**, $C_3H_4O_3$, **D**, $C_3H_4O_4$, **E**, C_3H_6O and a gas **F**.	**A** and **B** underwent vigorous oxidation. **F** is CO_2. ⇒ a terminal alkene is present on **A** and **B**.
3a. **C** and **E** give yellow ppt. with $I_2(aq)OH^–$.	**C** and **E** contain $CH_3CO–$ group. (Do not accept $CH_3CH(OH)–$ since these are products of vigorous oxidation.) ∴ **C** is 2–oxopropanoic acid. ∴ **E** is propanone.
3b. 1.04 g of **D** produces 240 cm^3 of gas with Na.	η(**D**) = 1.04 ÷ 104 = 0.0100 mol Gas is H_2, η(H_2) = 240 ÷ 24000 = 0.0100 mol Since 1 **D** ≡ 1 H_2 ⇒ **D** has 2 acidic protons. i.e. 2 carboxylic acid groups. ∴ **D** is propane–1,3–dioic acid.
4. Alternative to	Since **C**, **D** and **E** are oxidised products of alkene

deducing C, D and E.	cleavage, they either possess ketone and/or carboxylic acid functional groups. Based on molecular formula of **C**, the 3 O atoms can be attributed to (1) 3 ketones OR (2) 1 carboxylic acid and 1 ketone. Since there are only 3 C atoms, option (1) is invalid. ∴ **C** is a ketoacid ⟹ 2–oxopropanoic acid. Based on molecular formula of **D**, the 4 O atoms can be attributed to (1) 2 carboxylic acid groups OR (2) 1 carboxylic acid group and 2 ketones OR (3) 4 ketones. Since there are only 3 C atoms, options (2) and (3) are invalid. ∴ **D** has to be a 3 C dicarboxylic acid. ⟹ propane–1,3–dioic acid. Based on molecular formula of **E**, the 1 O atom can only be a ketone functional group. ∴ **E** is propanone.	
C 	**D** 	**E** 
Therefore, acceptable structure for **A** and **B:**  &  OR  & 		

(b) Fehling's solution is often used as a distinguishing test in the qualitatively analyses of organic compounds. It is prepared by mixing two separate solutions, known as Fehling's A and Fehling's B. Fehling's A is aqueous copper(II) sulfate while Fehling's B is an aqueous solution of potassium sodium tartrate made in sodium hydroxide.

Tartaric acid, H_4T, can exist as a tetraanion, T^{4-}, in a strongly alkaline medium. In Fehling's B, it exists as the H_2T^{2-} anion.

The standard electrode potentials, $E^\ominus$, of several species are shown in the table below.

	Electrode reaction	**$E^\ominus$ /V**
1	$Cu_2O + H_2O + 2e^- \rightleftharpoons 2Cu + 2OH^-$	–0.36
2	$2Cu^{2+} + H_2O + 2e^- \rightleftharpoons Cu_2O + 2H^+$	+0.20
3	$[Cu(HT)_2]^{4-} + 2H_2O + 2e^- \rightleftharpoons Cu + 2H_2T^{2-} + 2OH^-$	+0.25
4	$HCO_2H + 2H^+ + 2e^- \rightleftharpoons HCHO + H_2O$	–0.03
5	$CO_2 + 4H^+ + 4e^- \rightleftharpoons HCHO + H_2O$	–0.07
6	$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCO_2H$	–0.11

Adding Fehling's solution to methanal causes a reaction to take place.

(i) By selecting appropriate electrode reactions from the *Data Booklet* or the table above, construct a balanced equation for this reaction. [1]

$2[Cu(HT)_2]^{4-} + HCHO + H_2O \longrightarrow 2Cu + 4H_2T^{2-} + CO_2$
OR
$2[Cu(HT)_2]^{4-} + HCHO + 2OH^- \longrightarrow 2Cu + 4H_2T^{2-} + CO_3^{2-}$

$[Cu(HT)_2]^{4-} + HCHO + H_2O \longrightarrow Cu + 2H_2T^{2-} + HCO_2H$
OR
$[Cu(HT)_2]^{4-} + HCHO + OH^- \longrightarrow Cu + 2H_2T^{2-} + HCO_2^-$

(ii) Use your answer in part **(i)** to calculate the $E^\ominus_{cell}$ for this reaction. [1]

$E^\ominus_{cell} = E^\ominus_{cat} - E^\ominus_{an}$
$= +0.25 - (-0.07)$
$= \underline{+0.32\text{ V}}$

OR

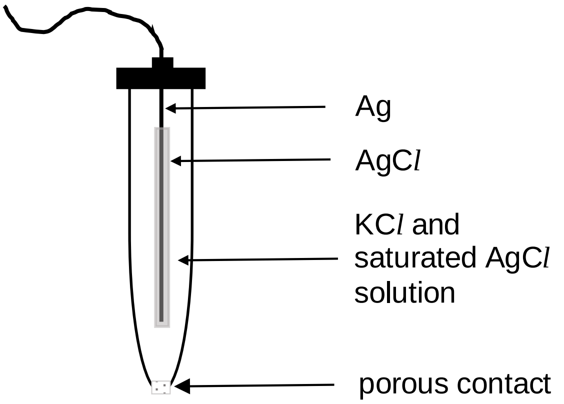
$E^\ominus_{cell} = E^\ominus_{cat} - E^\ominus_{an}$
$= +0.25 - (-0.03)$
$= \underline{+0.28\text{ V}}$

(iii) Describe the observations for this reaction. [1]

Blue coloured solution decolourises with the formation of a reddish–brown/ pink colouredmirror/solid/precipitate.

(c) Electrode potential values are often quoted with reference to the standard hydrogen electrode (SHE). It is however, seldom used because it is difficult to regulate the pressure of hydrogen gas at 1 atm.

One of the more commonly used reference electrodes in electrochemistry is the silver/silver chloride electrode (SSCE). It is made of a silver wire that is coated with a thin layer of silver(I) chloride, immersed in a potassium chloride solution saturated with silver(I) chloride.



schematic of a silver/silver chloride electrode

One of the advantages of using the SSCE is that it can be directly immersed into the other half-cell, thereby negating the use of a salt bridge.

(i) Suggest the purpose of having the porous contact. [1]

The porous contact allows for the exchange of ions between the two half–cells.

The solution in the SSCE is colourless in spite of the presence of a d–block element.

(ii) Explain how the colour in transition metal compounds arise. [2]

When ligands approach transition metal atom/ion, the degenerate d orbitals split into two non–degenerate energy levels (accept comparison of similar vs different energy; i.e. no need "degenerate" if student can explain). d–d* transition occurs when an electron from the lower energy level absorbs certain wavelength of visible light and gets promoted to the higher energy level. Colour seen is complementary to the wavelengths of light absorbed.

(iii) Write the full electronic configuration of Ag^+ and hence explain why it is not coloured. [2]

Ag^+: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$

As Ag^+ has a full d subshell, d–d* transition is not possible from the lower energy level to the higher energy level OR no wavelengths in visible light are absorbed and all are transmitted, making Ag^+ colourless.

(d) Adding a reagent that selectively brings one of the ions out of a solution as a precipitate while leaving the other ion in the solution is a technique known as selective precipitation.

Data about the solubilities in water and solubility products of silver(I) hydroxide and copper(II) hydroxide at 298 K are given below. Only the numerical values of the solubility products are given.

hydroxide	solubility/mol dm^{-3}	solubility product
AgOH	1.23×10^{-4}	1.52×10^{-8}
$Cu(OH)_2$	1.77×10^{-7}	2.20×10^{-20}

As a general standard, two ions are selectively separated when a maximum 0.01% of the precipitated compound still remains as the aqueous ions.

Determine if selective precipitation can be performed on a solution containing 0.200 mol dm^{-3} Ag^+ and 0.200 mol dm^{-3} Cu^{2+} with the addition of solid potassium hydroxide. [3]

Since solubility of $Cu(OH)_2$ is lower than AgOH, it will be precipitated first.

To maximally precipitate $Cu(OH)_2$, AgOH has to be saturated.

$[OH^-]$ when AgOH is sat. = $\dfrac{1.52 \times 10^{-8}}{0.200}$ = 7.60×10^{-8} mol dm^{-3}

$[Cu^{2+}]$ when AgOH is sat. = $\dfrac{2.20 \times 10^{-20}}{\left(7.60 \times 10^{-8}\right)^2}$ = 3.81×10^{-6} mol dm^{-3}

$\%[Cu^{2+}]$ remaining = $\dfrac{3.81 \times 10^{-6}}{0.200} \times 100\% = 0.001905\% \approx 0.00191\% < 0.01\%$

Therefore Cu^{2+} can be selectively precipitated from Ag^+.