2016 DHS H2 CHEMISTRY YEAR 6 PRELIMS
Paper 1 MCQ – Answers

1	2	3	4	5	6	7	8	9	10
D	**B**	**B**	**D**	**C**	**D**	**C**	**C**	**D**	**C**

11	12	13	14	15	16	17	18	19	20
A	**A**	**D**	**D**	**C**	**C**	**B**	**D**	**A**	**B**

21	22	23	24	25	26	27	28	29	30
D	**C**	**D**	**A**	**C**	**B**	**C**	**A**	**B**	**A**

31	32	33	34	35	36	37	38	39	40
B	**C**	**B**	**B**	**A**	**B**	**A**	**A**	**A**	**D**

Name:		**Index Number:**		**Class:**	

Preliminary Examinations
2016 Year 6

H2 CHEMISTRY

9647/01

Paper 1 Multiple Choice

27 September 2016

1 hour

Additional Materials: Optical Mark Sheet
Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name** and **class** on this question paper.

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

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

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

4 Any rough working should be done in this booklet.

5 You may use a calculator.

Section A

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

1 Ferrous sulfate ($FeSO_4$) tablets are commonly prescribed by doctors as 350 mg tablets and serve as a dietary supplement for pregnant women. However, it was found that these tablets may cause poisoning in young children if accidentally consumed. The lethal dosage for a 12.0 kg child is 590 mg of Fe^{2+}.

What is the minimum number of tablets that would constitute a lethal dose to a 12.0 kg child?

A 1

B 2

C 4

D 5

2 25.0 cm^3 of a solution of 0.0518 mol dm^{-3} hydroxylammonium chloride, $NH_3OH^+Cl^-$ was added to a solution containing an excess of acidified Fe^{3+} ions and the mixture boiled. The Fe^{2+} ions in the resultant solution was titrated with 25.90 cm^3 of 0.02 mol dm^{-3} potassium manganate (VII) solution.

Given the mole ratio $MnO_4^- \equiv 5Fe^{2+}$, which of the following nitrogen–containing species is formed in the reaction?

A NH_4^+

B N_2O

C NO_2

D NO_3^-

3 Two elements, **Y** and **Z**, have the following properties.

Property 1: **Y** and **Z** form ionic compounds Na_3**Y** and Na_3**Z** respectively.
Property 2: Element **Z** forms **Z**Cl_5 molecule whereas **Y** is unable to form **Y**Cl_5.

Which pair of electronic configurations of **Y** and **Z** is correct?

	Y	**Z**
A	[He] $2s^2\ 2p^2$	[Ne] $3s^2\ 3p^3$
B	[He] $2s^2\ 2p^3$	[Ne] $3s^2\ 3p^3$
C	[He] $2s^2\ 2p^2$	[He] $2s^2\ 2p^3$
D	[Ne] $3s^2\ 3p^2$	[Ne] $3s^2\ 3p^3$

4 For one mole of an ideal gas, which plot produces a straight line graph passing through the origin?

	Y–axis	**X–axis**	
A	PV	P	at constant T (K)
B	P	V	at constant T (K)
C	P/ρ	T (°C)	at constant V
D	P	1/V	at constant T (K)

5 Use of *Data Booklet* is relevant to this question.
Which substance is considered to have the largest covalent character?

A AlF_3 **B** Al_2O_3 **C** Be_3N_2 **D** BeO

6 Which substance does **not** contain an atom that has an unpaired electron?

A ClO_2 **B** NO **C** NO_2 **D** N_2O

7 Ammonia is made via the Haber Process. The reactants are nitrogen and hydrogen.

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

What will increase the rate of the forward reaction?

A Adding argon to the mixture but keeping the total volume constant.

B Decreasing the temperature.

C Increasing the total pressure by reducing the total volume at constant temperature.

D Removing nitrogen from the mixture but keeping the total volume of the mixture the same.

8 How much water must be added to a 10 cm^3 solution of 0.05 mol dm^{-3} sulfuric acid in order to increase its pH to 2.0?

A 10 cm^3

B 50 cm^3

C 90 cm^3

D 100 cm^3

9 Given that the K_{sp} for magnesium hydroxide, $Mg(OH)_2$, is 1.80×10^{-11} $mol^3\ dm^{-9}$ at 298 K, calculate the pH of a saturated solution of $Mg(OH)_2$.

A 3.48

B 3.78

C 10.2

D 10.5

10 The reaction of nitrogen monoxide and hydrogen gas

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

is hypothesised to involve the following steps:

I $NO + NO \rightleftharpoons N_2O_2$ (fast)
II $N_2O_2 + H_2 \rightarrow H_2O + N_2O$ (slow)
III $N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

Which of the following is true about the reaction?

A H_2 acts as a catalyst in this reaction.

B The overall order of the reaction is 2.

C There are 2 intermediates present in the reaction mechanism.

D Increasing the concentration of NO will increase the rate constant.

11 The radius and charge of each of the six ions are shown in the table.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

Which of the following pair shows the first compound having a smaller magnitude of lattice energy than the second?

A JX, MZ

B JX, LX

C JY, LX

D MZ, LY

12 The common rubber band has very interesting thermodynamic properties due to its randomly coiled long polymeric molecular structure. When the rubber band is stretched, a slight warming effect is felt.

What are the correct signs of ΔS, ΔH and ΔG if the stretched rubber band is released quickly?

	ΔS	ΔH	ΔG
A	+	+	–
B	+	–	+
C	–	–	+
D	–	+	–

13 The nickel–cadmium cell is a rechargeable battery which contains an alkaline electrolyte such as aqueous KOH.

During the discharging process, Cd is oxidised to solid $Cd(OH)_2$ while NiO(OH) is reduced to solid $Ni(OH)_2$.

Which statement is true about this rechargeable battery?

A Water is produced in the discharging process.

B The mass of cadmium remains unchanged.

C The alkaline electrolyte can be replaced by an acid.

D The concentration of the alkaline electrolyte remains unchanged in the discharging process.

14 Which statement regarding the oxides across Period 3 is true?

A The covalent character decreases from Na to S.

B The oxides of the elements changes from basic to neutral then to acidic from Na to S.

C The oxides formed are increasing soluble in water from Na to S.

D The standard entropy change of formation of the oxides becomes more negative from Na to A*l*.

15 The following information is about a Period 3 element **L**.

The oxide of **L** is a solid at room temperature.
The oxide of **L**, when added to water, gives a non-acidic solution.
The aqueous chloride of **L** gives a white precipitate with aqueous sodium hydroxide.

In which Group of the Periodic Table could **L** be found?

A V only

B I and III only

C II and III only

D II, III and IV only

16 Which property shows an increasing trend down Group II from Mg to Ba?

A Polarising power of metal cation

B Second ionisation energy

C Reducing strength

D Melting point

17 Which statement regarding the halogens or their hydrides is correct?

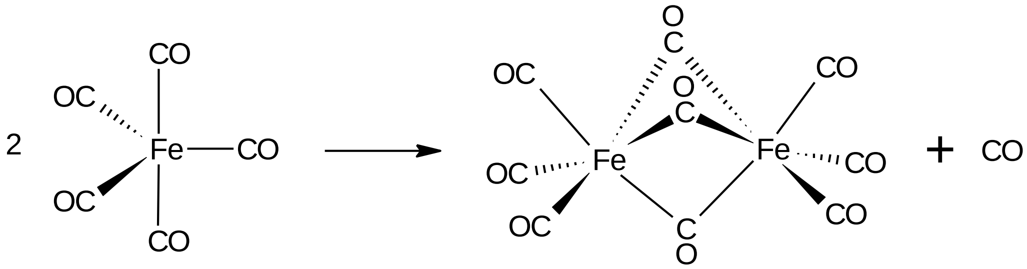
A HCl has a higher melting point than HF due to its larger electron cloud.

B Iodine, when dissolved in hexane, gives a colour that is similar to its vapour.

C The halogens become less volatile from fluorine to iodine due to the weaker covalent bonds.

D HF is less thermally stable than HI because of the larger electronegativity difference between the H and F atoms.

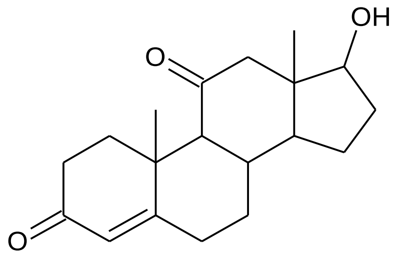
18 Photolysis of a solution of $Fe(CO)_5$ in ethanoic acid produces $Fe_2(CO)_9$ according to the following equation.



What is the oxidation state of Fe in $Fe(CO)_5$ and the coordination number of Fe in $Fe_2(CO)_9$?

	oxidation state of Fe in $Fe(CO)_5$	coordination number of Fe in $Fe_2(CO)_9$
A	+5	9
B	+5	6
C	0	9
D	0	6

19 The structure of 11-ketotestosterone, a sex hormone in fish, is shown below.



Which statement about 11-ketotestosterone is correct?

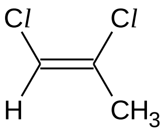
A Its molecular formula is $C_{19}H_{26}O_3$.

B It has a total of 2^7 stereoisomers.

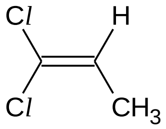
C It has six sp^2-hybridised carbon atoms.

D It has a tertiary alcohol functional group.

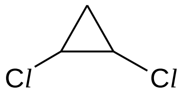
20 The following compounds have the same molecular formula.



X



Y



Z

Which of the following best describes the isomeric relationships between the compounds?

	X and **Y**	**Y** and **Z**
A	chain	optical
B	positional	functional group
C	cis–trans	positional
D	positional	chain

21 Which of the following is a **non**-greenhouse gas that could be released from the catalytic converter of a car exhaust?

A CO_2

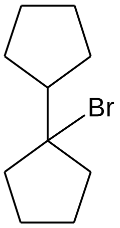
B H_2O

C CH_4

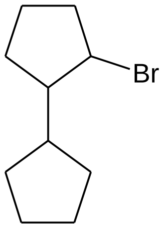
D N_2

22 Which compound is **not** possibly formed when cyclopentane is reacted with excess bromine gas in the presence of ultraviolet light?

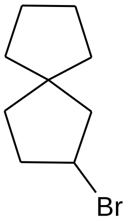
A



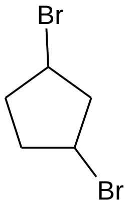
B



C



D



23 Carbonyl groups in aldehydes and ketones, C=O, undergo nucleophilic addition while alkene groups, C=C, undergo electrophilic addition.

Which statement explains the above reactions?

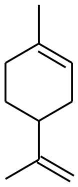
A Oxygen is more reactive than carbon.

B The different lengths of the double bonds.

C The different strengths of the double bonds.

D The electronegativity difference between the carbon and oxygen atoms in the carbonyl group.

24 The citrus flavour of lemons is due to the compound limonene, present in both the peel and the juice.



limonene

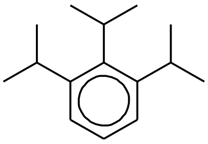
Limonene is separately treated with

- cold, dilute acidified $KMnO_4$,
- hot, concentrated acidified $KMnO_4$.

What is the change in the **number** of chiral carbon atoms in the molecule during each reaction?

	cold, dilute acidified $KMnO_4$	hot, concentrated acidified $KMnO_4$
A	+3	0
B	+3	–1
C	+4	0
D	+4	–1

25 The diagram shows the structure of a derivative of propofol.



When reacted with a dilute solution of Cl_2, a chlorine atom may substitute a hydrogen atom on the benzene ring but **not** for a hydrogen atom on the alkyl branches.

Given that any number of the benzene hydrogen atoms may be substituted, how many possible products of the reaction are there?

A 3

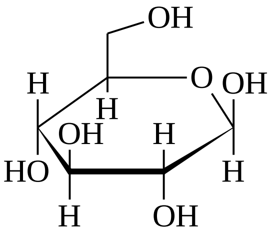
B 4

C 5

D 6

26 In the body, cellular respiration produces energy from the oxidation of glucose.

The diagram shows the structure of glucose.



A new artificial sweetener has been produced by replacing all of the hydroxyl groups attached directly to the ring carbon atoms in glucose with chlorine atoms.

What is the empirical formula of this chlorinated glucose?

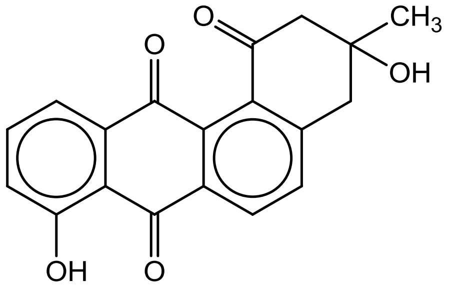
A CH_2Cl

B $C_3H_4Cl_2O$

C $C_6H_7Cl_5O$

D $C_6H_8Cl_4O_2$

27 *Tetrangomycin* is one of the first member of the class of antibiotics under the angucycline group. What is the maximum number of optical isomers that can be obtained when 1 mole of *tetrangomycin* fully reacts with $NaBH_4$?



Tetrangomycin

A 2

B 8

C 16

D 32

28 The small hive beetle, which invades colonies of the honeybee, identifies these colonies by detecting the bees' own alarm signal, the pheromone 3-methylbutyl ethanoate.

How may this ester be made in the laboratory?

A $CH_3COCl + (CH_3)_2CHCH_2CH_2OH \rightarrow$ ester + HCl

B $CH_3COCl + CH_3CH_2CH(CH_3)CH_2OH \rightarrow$ ester + HCl

C $(CH_3)_2CHCH_2CO_2H + CH_3CH_2OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$ ester + H_2O

D $(CH_3)_2CHCH_2CH_2CO_2H + CH_3CH_2OH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4}$ ester + H_2O

29 Why are amides, $RCONH_2$, less basic than amines, RNH_2?

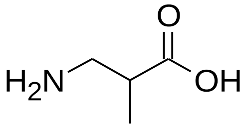
A Amides form a zwitterion in which the nitrogen atom carries a positive charge.

B Amides have a resonance structure involving the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

C Electrons on the nitrogen atom of amides move on the C-N bond giving it some double bond character so that it is more difficult to break.

D The amide carbonyl group withdraws electrons from the $-NH_2$ group to make the hydrogen atoms acidic.

30 3-aminoisobutyric acid was shown to prevent diet induced diabetes in mouse. It has the structure shown below.



Which statement about 3-aminoisobutyric acid is **not** true?

A It migrates to the cathode at pH 10.

B It exists predominately as a zwitterion at pH 7.

C It reacts with ethanoyl chloride to form an amide.

D It exists as a crystalline solid at room temperature.

Section B

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

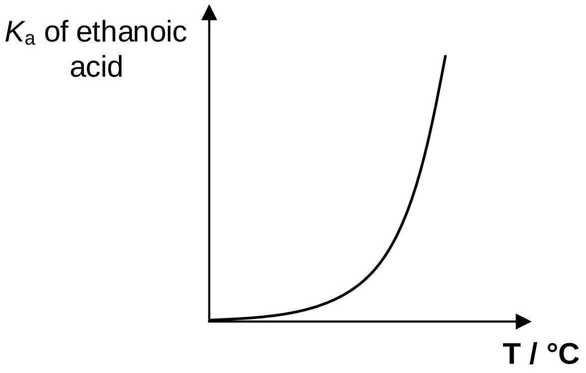
Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements which you consider to be correct).

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

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 Which statement about ethanoic acid can be deduced from the sketch below?



1 The ionic dissociation of ethanoic acid is an endothermic process.

2 The pH of the ethanoic acid decreases with increasing temperature.

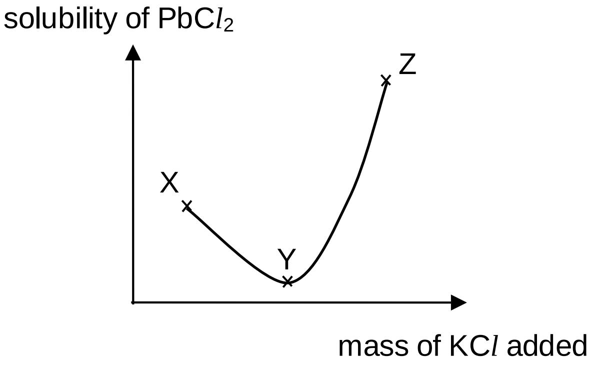
3 At T = 40 °C, pH of ethanoic acid = 14 – pOH

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.

32 The following graph represents how the solubility of a sparingly soluble salt lead(II) chloride, $PbCl_2$, changes upon addition of solid potassium chloride.



Which statement is correct?

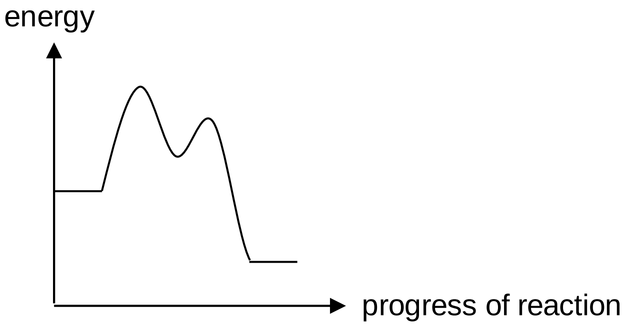
1 The K_{sp} value decreases along XY and then increases along YZ.

2 The change in solubility along XY is caused by common ion effect.

3 The change in solubility along YZ is caused by the formation of a complex between Pb^{2+} and Cl^{-} ions.

33 In a chemical reaction, **P** reacts with **Q** to form **R**. The rate equation is found to be rate = k [**P**] [**Q**].

The energy profile diagram for the reaction is as shown.



Which is the likely overall equation of the above reaction?

1 $2\mathbf{P} + \mathbf{Q} \rightarrow \mathbf{R}$

2 $\mathbf{P} + 2\mathbf{Q} \rightarrow \mathbf{R}$

3 $\mathbf{P} + \mathbf{Q} \rightarrow \mathbf{R}$

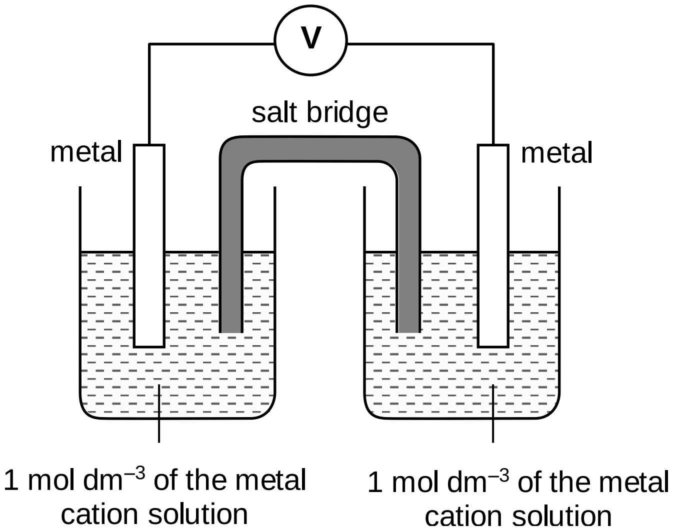
The responses **A** to **D** should be selected on the basis of

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.

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

The half-cells for four metals: Mg, **X**, **Y** and **Z** were in turn connected in pairs and the potential difference was recorded at room temperature.



The results obtained are as shown in the table below.

positive electrode	negative electrode	$E^\ominus$ / V
X	Mg	+2.10
Y	Mg	+2.72
Mg	**Z**	+0.33

Which of the following statements is true?

1 **Y** is likely to be copper metal.

2 **X** is stronger than **Y** in terms of reducing power.

3 Ease of oxidation of metals: **Z** < **X** < **Y**.

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 Solid **P** dissolves in aqueous chlorine to give a solution **Q** which gives precipitate **R** on adding excess aqueous sodium thiosulfate followed by aqueous lead(II) nitrate.

Which combination could agree with the procedure above?

	Identity of **P**	Colour of **Q**	Colour of **R**
1	NaI	brown	mixture of white and bright yellow
2	NaBr	orange	white only
3	NaC*l*	colourless	white only

36 Consider the two reactions of $Cu^{2+}(aq)$ below.

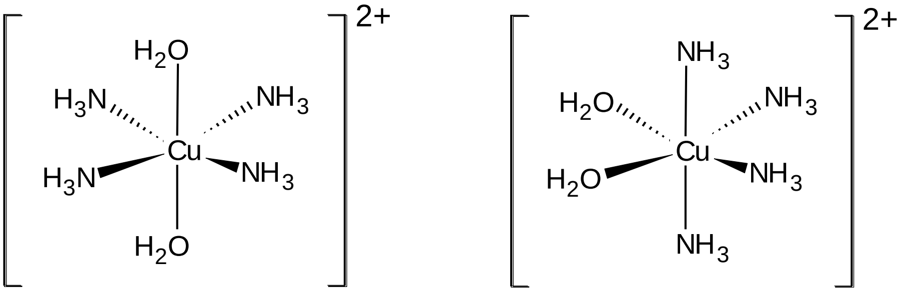
$$[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [Cu(EDTA)]^{2-} + 6H_2O \quad \text{(equilibrium 1)}$$

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O \quad \text{(equilibrium 2)}$$

What can you deduce from the equilibria above?

1 The entropy change of equilibrium 1 is more positive than that of equilibrium 2.

2 $[Cu(NH_3)_4(H_2O)_2]^{2+}$ in equilibrium 2 has two possible isomers:



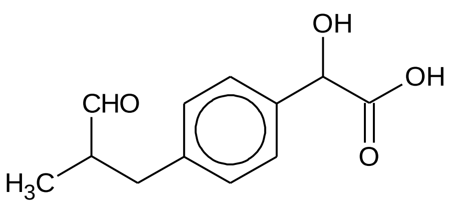
3 $EDTA^{4-}$ is a stronger ligand than NH_3.

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

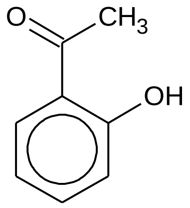
A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

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

37 Compounds **L** and **M** are precursors to the synthesis of some analgesic drugs.



L



M

Which statement is true?

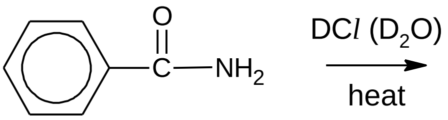
1 Only **L** reacts with KBr in concentrated H_2SO_4 to give a bromine-based compound under heat.

2 Both **L** and **M** react with HCN to form a product with at least one chiral carbon atom.

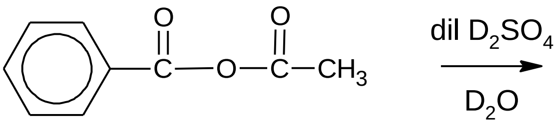
3 **L** is expected to be more acidic than **M**.

38 Which of the following will yield an organic compound containing deuterium? (D = ^{2}H)

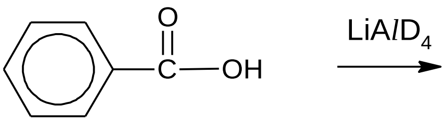
1



2



3

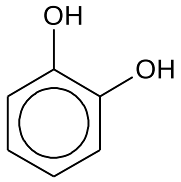


The responses **A** to **D** should be selected on the basis of

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 Which reagent can be used to distinguish catechol from benzene –1,2 – dicarboxylic acid?



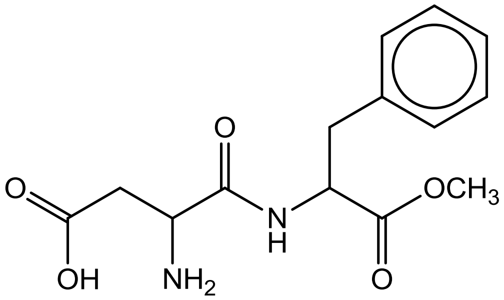
catechol

1 Sodium bicarbonate solution

2 Neutral iron(III) chloride solution

3 Aqueous bromine solution

40 Aspartame is an artificial sweetener used as a sugar substitute in some foods and beverages. The structure is shown below:



Which deduction about the reactions of aspartame can be made from this structure?

1 It undergoes hydrolysis to form two α-amino acids.

2 It reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate.

3 The solution remains orange when heated with acidified potassium dichromate(VI).

Name:		Index Number:		Class:	

Preliminary Examination
2016 Year 6

H2 CHEMISTRY

9647/02

Paper 2 Structured

16 September 2016
2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.
2 Answer ***all*** questions.
3 Write your answers in the spaces provided on the question paper.
4 A *Data Booklet* is provided.
5 The number of marks is given in brackets [ ] at the end of each question or part question.
6 You may use a calculator.

Question No.	1	2	3	4	5	Total	%
Marks	12	15	15	15	15	[72]	

Answer **all** questions in the spaces provided.

1 Planning (P)

The reaction between peroxodisulfate ions, $S_2O_8^{2-}$, and ethanedioate ions, $C_2O_4^{2-}$, is slow and can be catalysed by Cu^{2+} ions.

$$S_2O_8^{2-} + C_2O_4^{2-} \rightarrow 2SO_4^{2-} + 2CO_2$$

To determine the rate law of this reaction, it is necessary to selectively vary the concentrations of $S_2O_8^{2-}$ and $C_2O_4^{2-}$ ions and determine how the rate of reaction responds to these changes. The concentrations of the reactants are varied in such a way that one is in excess compared to the other in each experiment.

A suitable end point (the point at which the final time reading is made) for the experiments will be when the reaction produced the same volume of CO_2 gas. With the measured reaction time, relative rate of the reaction can be determined.

You are required to write a plan to determine the rate law of the reaction between $S_2O_8^{2-}$ and $C_2O_4^{2-}$ ions.

(a) Suggest an explanation why this reaction is slow when performed in the absence of a catalyst.

.... [1]

(b) You may assume that you are provided with

- 1.00 mol dm^{-3} peroxodisulfate ions
- 1.00 mol dm^{-3} ethanedioate ions
- 10 cm^3 aqueous copper (II) ions
- the equipment and materials normally found in a school laboratory.

It can be assumed that a reactant is in excess if its volume is at least **five** times the volume of the other reactant used.

Your plan should include the following:

- quantities of reactants and condition you would use in **four** different reaction mixtures
- the measurements you would take
- an outline of how **one** of the reaction mixtures is prepared
- brief, but specific details of how the results would then be used to determine the rate law of reaction

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[Turn over

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[8]

(c) Temperature can also affect the rate of reaction and the activation energy, E_a, of this reaction can be found by repeating the experiments at several different temperatures.

Using equation (1) and by means of a suitable graph, the activation energy of the reaction can be determined.

$$\ln\text{ (relative rate)} = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln\text{ (constant)} \quad \text{—— (1)}$$

Briefly describe, with specific experimental details, of how the activation energy, E_a, of the reaction could be determined.

[3]

[Total: 12]

2 **(a)** A lead–acid car battery is a reversible cell that consists of a lead anode and a grid of lead coated with lead (IV) oxide as the cathode. The electrolyte is a 30% solution of sulfuric acid. When the cell supplies electric current to power the car, the process is known as discharging. The reversible process is thus known as charging.

The overall reaction that takes place in the lead–acid car battery is as follows:

$$\mathrm{Pb(s)} + \mathrm{PbO_2(s)} + 2\mathrm{H_2SO_4(aq)} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2\mathrm{PbSO_4(s)} + 2\mathrm{H_2O}(l)$$

(i) Write the half–equations, with state symbols, for the reactions that take place at the anode and the cathode during the discharging process. Hence, state the polarity at the two electrodes.

	Half–equations	Polarity
Anode		
Cathode		

[3]

(ii) When the lead and lead (IV) oxide have been converted to lead (II) sulfate, the cell can no longer give a current and the battery becomes flat. As the car moves, the generator then charges the battery. When the lead–acid battery is fully charged, the sulfuric acid has a relative density of about 1.275.

Predict and explain what happens to the relative density of the sulfuric acid during the discharging process.

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.... [2]

(iii) Overcharging the lead–acid battery with high voltages causes hydrogen and one other gas to form. In addition, the electrolyte level is observed to have dropped.

Explain briefly what happens during overcharging and hence, suggest the identity of the other gas that is formed.

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.... [2]

(iv) A simple rechargeable cell similar to that of lead–acid car battery may be constructed by dipping two lead electrodes into aqueous lead (II) nitrate and passing a current for a few minutes. During the charging process, lead (IV) oxide is deposited on one of the electrodes. By reference to the *Data Booklet*, calculate the value of $E^\ominus$ when the cell discharges.

[2]

(v) The voltage of a typical lead–acid battery is 2.0 V. Explain the difference in the voltage and the $E^\ominus$ calculated in **(a)(iv)**, based on the concentration of ions.

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[2]

(b) **(i)** Pb^{2+} ions are often used in qualitative analysis to identify halide ions as they form insoluble precipitates. However, it is not an ideal test to distinguish between Cl^- and Br^- ions as both ions form white precipitate with Pb^{2+} ions.

Suggest another simple chemical test involving precipitation that could be used to distinguish between Cl^- and Br^- ions, stating clearly the steps and reagents involved and the expected observations.

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[2]

(ii) With reference to your answer in **(b)(i)**, explain the chemistry involved and writing equations where appropriate.

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.... [2]

[Total: 15]

3 Cobalt and vanadium are transition elements with more than one oxidation state and many of its compounds are coloured.

(a) When a few drops of aqueous ammonia is added to a test–tube containing Co^{3+}(aq), a brown precipitate, **X** is observed. The chemical formula of **X** does not contain water molecules. The precipitate then dissolves in excess aqueous ammonia to give a cation **Y** which has a co–ordination number of 6.

(i) Complete the electronic configuration of cobalt (III) ions.

Co^{3+}: $1s^2 2s^2 2p^6$ ....

[1]

(ii) Suggest the identities of **X** and **Y**.

X: ....

Y: ....

[2]

(iii) With the use of appropriate ionic equations, explain the formation of **X** and **Y**.

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.... [3]

(b) When concentrated hydrochloric acid is added to Co^{2+}(aq), the colour changes from pink to blue. When water is added to the blue solution, it returns to the pink colour.

The chemistry of Co^{2+}(aq) with concentrated hydrochloric acid closely resembles that of Cu^{2+}(aq).

Write a balanced ionic equation to account for the observations. In your answer, state the change in co–ordination number of cobalt ion in this reaction (if any).

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.... [2]

(c) Vanadium is also another commercially important transition element.

(i) Explain why V^{2+} is coloured.

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.... [2]

(ii) V_2O_5 is used as a catalyst to speed up the conversion of SO_2 into SO_3 in the contact process for making sulfuric acid.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197\ \text{kJ mol}^{-1}$$

For the reaction above, explain clearly how the catalyst works.

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[2]

(iii) When a 2:1 ratio of sulfur dioxide and oxygen is passed over V_2O_5, the catalyst in a fixed volume steel vessel at 430 °C, the percentage conversion of SO_2 to SO_3 is 95%.

Given that K_p is 7200 atm^{-1} at 430 °C, calculate the initial total pressure, in atm, in the steel vessel.

[2]

(iv) Comment on the effect on the rate of conversion if another unreactive but toxic gas was accidentally added to V_2O_5.

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[1]

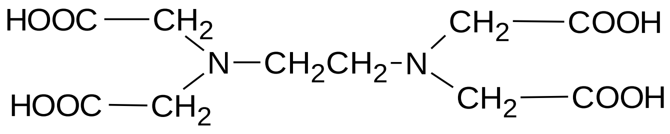
[Total: 15]

4 One of the factors that establishes the quality of a water supply is its degree of hardness. Water hardness is usually reported as parts per million (ppm) of calcium carbonate in the water sample.

$$\text{ppm CaCO}_3 = \frac{\text{mass of CaCO}_3}{\text{mass of water}} \times 10^6$$

Water Supply Classification	
calcium carbonate (ppm)	**Hardness Level**
0–43	soft
43–150	slightly hard
150–300	moderately hard
300–450	hard
>450	very hard

Water hardness can be determined by titrating Ca^{2+} ions with ethylenediaminetetraacetic acid (represented by H_4Y).



H_4Y

The titration is often carried out in a buffered basic medium, where H_4Y exists mainly as HY^{3-} (buffered solution).

$$Ca^{2+}(aq) + HY^{3-}(aq) \rightarrow CaY^{2-}(aq) + H^+(aq) \qquad \text{where } Y = C_{10}H_{12}N_2O_8$$

(a) A 50 g sample of hard water was titrated against the buffered solution of concentration 0.0149 mol dm^{-3}. The volume of the buffered solution required was 25.55 cm^3.

(i) Calculate the mass of $CaCO_3$ present in the water sample.

[1]

(ii) Hence calculate the ppm of $CaCO_3$ in the water sample and determine its hardness level.

[2]

There are two types of water hardness, temporary and permanent. The difference is due to the presence of different dissolved calcium compounds in the water.

Temporary hardness is caused by the presence of dissolved calcium hydrogencarbonate, $Ca(HCO_3)_2$. This type of hardness is called temporary hardness because the calcium ions can be removed from the water causing it to precipitate as $CaCO_3$.

$$Ca^{2+}(aq) + 2HCO_3^{-}(aq) \rightleftharpoons CaCO_3(s) + H_2O(l) + CO_2(aq) \qquad \Delta H = \text{positive}$$

(b) Using the given equilibrium, suggest and explain one way how the removal of Ca^{2+} from the water sample can be enhanced.

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[2]

A common detergent contains sodium dodecylbenzenesulfonate, $C_{18}H_{29}SO_3Na$. In hard water, it is ineffective as a detergent because it reacts with calcium ions to give a precipitate.

$$(C_{18}H_{29}SO_3)_2Ca(s) \rightleftharpoons Ca^{2+}(aq) + 2C_{18}H_{29}SO_3^{-}(aq) \qquad K_{sp} = 1.2 \times 10^{-17}\ mol^3\ dm^{-9}$$

A typical sample of hard water has a concentration of calcium ions of 2.5×10^{-4} mol dm^{-3}.

(c) **(i)** Calculate the maximum concentration of $C_{18}H_{29}SO_3^{-}$ in a solution of hard water.

[1]

The manufacturers claim that the detergent contains 17.4% by mass of $C_{18}H_{29}SO_3Na$ [M_r = 348]. In hard water, 1.0 g of the detergent should be used per dm^3 of hard water.

(ii) Calculate the number of moles of $C_{18}H_{29}SO_3Na$ added to 1 dm^3 of hard water.

[1]

(iii) Using your answer in **(c)(i) and (c)(ii)**, show that 99% of $C_{18}H_{29}SO_3Na$ in the detergent added will precipitate out of the hard water.

[2]

(d) In order for the detergent to be used in hard water, sodium tripolyphosphate, $Na_5P_3O_{10}$, is added as a water softening agent.

The sodium tripolyphosphate 'softens' water by complexing with calcium ions.

Equilibrium 1: $Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightleftharpoons CaP_3O_{10}^{3-}(aq)$

$K_c = 7.7 \times 10^8 \text{ mol}^{-1} \text{ dm}^3$

(i) Explain qualitatively why the addition of $Na_5P_3O_{10}$ will allow the detergent to be used in the hard water.

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[2]

(ii) What is the oxidation state of phosphorus in sodium tripolyphosphate?

.... [1]

(iii) Suggest a likely structure for the tripolyphosphate anion.

[1]

(iv) Magnesium ions can also cause water hardness. It forms a complex with tripolyphosphate ions as well.

State the effect, if any, of adding magnesium ions on the equilibrium position and value of K_c of **Equilibrium 1** at constant temperature. Explain your answer.

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.... [2]

[Total: 15]

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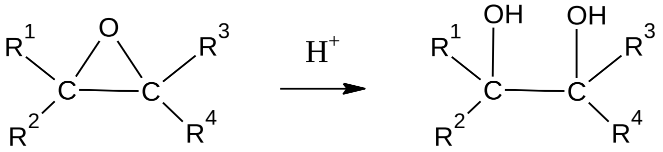
5 The male silk moth secretes ‘juvenile hormone’, $C_{16}H_{26}O_4$, which contains an unknown number of epoxide rings. Epoxide rings are readily hydrolysed by cold aqueous acid.



The reactions that ‘juvenile hormone’ and the resulting derivatives undergo are shown in the table below.

Reactant	Reagent	Result
‘Juvenile hormone’	hydrogen in the presence of a palladium catalyst	**S**, $C_{16}H_{28}O_4$, formed.
	cold dilute hydrochloric acid	**T**, $C_{16}H_{30}O_6$, containing four alcoholic groups and three chiral centres is formed.
T	warmed with aqueous sodium hydroxide and then acidified	Methanol and **U**, $C_{15}H_{28}O_6$ are formed.
U	Mild oxidation	**V**, $C_{15}H_{24}O_6$, which has two alcoholic groups, is formed.
V	hot concentrated acidified $KMnO_4$	Two moles of carbon dioxide and one mole of **W,** $C_{13}H_{22}O_5$ are formed.
W	2,4 – dinitrophenylhydrazine reagent	orange precipitate formed.
	alkaline aqueous iodine	yellow precipitate formed.

In addition, it is known that ‘juvenile hormone’ has a continuous 12–carbon long backbone. There are **three methyl substituents** on the skeletal backbone of ‘juvenile hormone’ and that **each** methyl substituent is five carbon atoms apart from the next methyl substituent.

(a) Give the products that will be formed when methylethyl ether, $CH_3OCH_2CH_3$ undergoes hydrolysis with aqueous acid.

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[1]

(b) State and explain the number of epoxide ring(s) in ‘juvenile hormone’.

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[2]

(c) State the type of reaction that **T** has undergone and the functional group that it contains other than the four alcoholic groups.

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.... [1]

(d) Classify the two alcoholic groups in **V** into either primary, secondary and tertiary alcohols. State the number of each alcohol and explain how you arrive at your conclusion.

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.... [2]

(e) **V** produced an intermediate upon reacting with hot concentrated acidified $KMnO_4$ which eventually produced carbon dioxide. Draw the displayed formula of this intermediate.

[1]

(f) State the type of reaction between **W** and 2,4 – dinitrophenylhydrazine reagent. State the deduction about **W** from the result of **W** reacting with aqueous alkaline iodine.

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.... [2]

(g) Suggest the structures for compounds **S** to **W** and for ‘juvenile hormone’.

Compound	**Structure**
‘Juvenile hormone’	
S	
T	
U	
V	
W	

[6]

[Total: 15]

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Answer **all** questions in the spaces provided.

1 (a)

Repulsion between two negatively charged ions causes the activation energy to be high.

[1]

(b)

Preparation of reaction mixture

1. Using a 50.0 cm^3 measuring cylinder, add 25.0 cm^3 of peroxodisulfate ions into a 250 cm^3 conical flask.
2. Using a 10.0 cm^3 measuring cylinder, add 2.0 cm^3 of aqueous copper (II) ions into the same conical flask.
3. Using a 50.0 cm^3 measuring cylinder, add 45.5 cm^3 of deionised water into the conical flask.
4. Using a 10.0 cm^3 measuring cylinder, measure out 2.5 cm^3 of ethanedioate ions.
5. Transfer the ethanedioate ions into the conical flask and insert a rubber bung into the conical flask. The rubber bung has a delivery tube connected to rubber tubing with the other end of the tubing inserted into an inverted burette filled with water.
6. Start the stopwatch immediately and gently swirl the conical flask continuously.
7. Monitor the water level in the burette and stop the stopwatch when 40.00 cm^3 of CO_2 is produced. Record the time taken.
8. Repeat step 1 to 7 using the following volumes of reactants, copper (II) ions and deionised water shown in experiment 2 to 4, at the same temperature.

Experiment	Volume of $S_2O_8^{2-}$ / cm^3	Volume of $C_2O_4^{2-}$ / cm^3	Volume of Cu^{2+} / cm^3	Volume of water / cm^3
1	25.0	2.5	2.0	45.5
2	25.0	5.0	2.0	43.0
3	2.5	25.0	2.0	45.5
4	5.0	25.0	2.0	43.0

Treatment of results

1. Relative rates (= 1/t) of expt 1 to 4 are calculated. Since total volume of mixture is constant in expt 1 to 4, concentration of reactant is proportional to its volume used.
2. Compare the relative rates of expt 1 to 2 and 3 to 4, to find the order of reaction with respect to (w.r.t) $C_2O_4^{2-}$ and $S_2O_8^{2-}$ respectively. If volume of $C_2O_4^{2-}$ doubles and rate remains the same, it is zero order w.r.t $C_2O_4^{2-}$. If volume of $C_2O_4^{2-}$ doubles, and rate remains doubles, it is first order w.r.t $C_2O_4^{2-}$. If volume of $C_2O_4^{2-}$ doubles and rate quadruples, it is second order w.r.t $C_2O_4^{2-}$. The same applies for $S_2O_8^{2-}$.
3. The rate law of reaction can then be found, rate = $k[S_2O_8^{2-}]^n[C_2O_4^{2-}]^m$, where n and m are the orders of reaction w.r.t to $S_2O_8^{2-}$ and $C_2O_4^{2-}$ respectively.

[8]

(c)

1. Repeat one of the experiments (e.g. expt 2) at two (at least) different temperatures, other than that for experiment 1 to 4 above. This can be done by immersing conical flasks in water bath maintained at different constant temperatures e.g. 40 °C and 60 °C.
2. Using the results in experiment 2 and that of the two further experiments, relative rate, followed by ln (relative rate) for each expt is calculated.
3. A graph of ln (relative rate) against $\frac{1}{T}$ is plotted. The gradient of the best fit line is then determined, where gradient = $-\frac{E_a}{R}$. E_a is given by $|\text{gradient} \times R|$.

[3]

[Total: 12]

2 **(a)** **(i)**

	Half–equations	Polarity
Anode	$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	–
Cathode	$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	+

[3]

(ii)

The relative density of the sulfuric acid will decrease.

During discharging, as sulfuric acid is used up to produce $PbSO_4$, the concentration of sulfuric acid will decrease, resulting in a decrease in density.

[2]

(iii)

Overcharging will result in electrolysis of water.
Identity of other gas: Oxygen

[2]

(iv)

$E^\ominus = 1.47 - (-0.13) = +1.60$ V

[2]

(v)

Lead–acid battery has a higher voltage as $PbSO_4$ formed is insoluble, which resulted in a lower concentration of Pb^{2+} in the electrolyte, thus driving the forward reaction.

[2]

(b) (i)

To 1 cm^3 of halide ions, add $AgNO_3(aq)$ dropwise. Then add aqueous NH_3 in excess.

Cl^- ions form white ppt with $AgNO_3$ which is soluble in excess $NH_3(aq)$.

Br^- ions form cream ppt with $AgNO_3$ which is insoluble in excess $NH_3(aq)$

[2]

(ii)

$Ag^+ (aq) + X^- (aq) \rightleftharpoons AgX (s)$, where X^- is Cl^- and Br^-

Both halide ions form insoluble ppt with Ag^+.

$Ag^+ (aq) + 2NH_3 (aq) \rightleftharpoons [Ag(NH_3)_2]^+ (aq)$

Ag^+ ions form soluble diammine complex which decreases the $[Ag^+]$, resulting in a corresponding decrease in ionic product (i.e. I.P = $[Ag^+][X^-]$) for both halide ions.
As K_{sp} value of AgC*l* is much larger than that of AgBr, the ionic product of AgC*l* will fall below its Ksp but not for AgBr.

[2]

[Total: 15]

3 (a) (i)

Co^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

[1]

(ii) Suggest the identities of X and Y.

X: $Co(OH)_3$

Y: $[Co(NH_3)_6]^{3+}$

[2]

(iii)

$[Co(H_2O)_6]^{3+} + 3OH^- \rightleftharpoons Co(OH)_3 + 6H_2O$ ——(1)

When aqueous ammonia is added in excess, a ligand exchange reaction occurs. The stronger NH_3 ligands replace weaker H_2O ligands in the $[Co(H_2O)_6]^{3+}$ ions to form $[Co(NH_3)_6]^{3+}$ complex.

$[Co(H_2O)_6]^{3+}(aq) + 6NH_3(aq) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq) + 6H_2O(l)$ ——(2)

This decreases the concentration of $[Co(H_2O)_6]^{3+}$ in solution. By Le Chatelier's Principle, equilibrium (1) shifts left to increase the concentration of $[Co(H_2O)_6]^{3+}(aq)$. Hence the brown precipitate of $Co(OH)_3$ dissolves [1].

[3]

(b)

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

There is a change of co–ordination number from 6 to 4.

[2]

(c) (i)

The partially–filled d orbitals of V^{2+} are split into two groups of different energy levels by H_2O ligands. When white light shines on the complex, a d electron undergoes d–d transition and is promoted to a higher energy d orbital. During the transition, the d electron absorbs light from the yellow region of the visible spectrum. The colour observed is the colour of transmitted light, which is a mixture of remaining wavelengths that have not been absorbed.

[2]

(ii)

The reactant molecules are physically adsorbed onto the catalyst surface. This allows for formation of weak bonds between reactants and the surface catalyst, thus weakening the intramolecular bonds in the reactants and helps to catalyse the reaction. After reaction, the reactant molecules desorb from the catalyst surface.

[2]

(iii)

	$2SO_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2SO_3(g)$
Initial pressure /atm	0.6667x	0.3333x	0
Change in pressure /atm	–0.6333x	–0.3167x	+0.6333x
Equilibrium pressure /atm	0.0334x	0.0166x	0.6333x

Let the initial total pressure be x atm.

$K_p = (0.6333x)^2 / (0.0166x)(0.0334x)^2 = 7200$

$\therefore\ x = (0.6333)^2 / 7200(0.0166)(0.0334)^2$

$= 3.01$ atm

[2]

(iv)

Rate of conversion will slow down/decrease due to poisoning of the catalyst.

[1]

[Total: 15]

4 (a) (i)

No. of moles of HY^{3-} required $= 0.0149 \times \frac{25.55}{1000}$

$= 0.00038070$ mol

No. of moles of Ca^{2+} present = 0.00038070 mol

No. of moles of $CaCO_3$ = 0.00038070 mol

Mass of $CaCO_3$ = 0.00038070 x [40.1 + 12 + 3(16)]

= 0.0381g (3 sf)

[1]

(ii)

ppm $CaCO_3 = \frac{0.038107}{50} \times 10^6 = 762$ (3 sf)
The water is very hard.

[2]

(b)

Ca^{2+} can be removed by heating the water sample.

By Le Chatelier's Principle, the position of equilibrium will shift right to remove the heat supplied causing a decrease in the concentration of Ca^{2+} ions.

OR

Ca^{2+} can be removed by heating the water sample.

Heating the water sample removes CO_2 (g) hence decreasing the concentration of CO_2 (aq).

By Le Chatelier's Principle, the position of equilibrium will shift right to increase the concentration of CO_2 (aq) causing a decrease in the concentration of Ca^{2+} ions.

[2]

(c) **(i)**

$[C_{18}H_{29}SO_3^-] = \sqrt{(1.2 \times 10^{-17} / 2.5 \times 10^{-4})}$
$= 2.1908 \times 10^{-7}$ mol dm^{-3}
$= 2.19 \times 10^{-7}$ mol dm^{-3}

[1]

(ii)

Mass of $C_{18}H_{29}SO_3Na$ added to 1.0 dm^{-3} = 0.174 g

No of moles of $C_{18}H_{29}SO_3Na$ added to 1.0 dm^3 = $\frac{0.174}{348} = 5.00 \times 10^{-4}$ mol

[1]

(iii)

Maximum moles of $C_{18}H_{29}SO_3^-$ dissolved in 1.0 dm^3 = 2.1908×10^{-7} mol

No of moles of $C_{18}H_{29}SO_3^-$ precipitated out = $5.00 \times 10^{-4} - 2.1908 \times 10^{-7}$
$= 4.9978 \times 10^{-4}$ mol

Percentage of $C_{18}H_{29}SO_3^-$ precipitated = $\frac{4.9978 \times 10^{-4}}{5.00 \times 10^{-4}} \times 100\%$

= 99% (shown)

[2]

(d) (i)

$Ca^{2+}(aq) + P_3O_{10}^{5-}(aq) \rightleftharpoons CaP_3O_{10}^{3-}(aq)$ — (1)

$Ca^{2+}(aq) + 2C_{18}H_{29}SO_3^-(aq) \rightleftharpoons (C_{18}H_{29}SO_3)_2Ca(s)$ — (2)

$P_3O_{10}^{5-}$ form complexes with Ca^{2+} causing a decrease in the concentration of Ca^{2+}.

By Le Chaterlier's Principle, the equilibrium position of (2) shifts left to increase the concentration of Ca^{2+}. Hence reducing the amount of $(C_{18}H_{29}SO_3)_2Ca$ formed.

Hence, preventing the formation of precipitate when detergent is added into hard water.

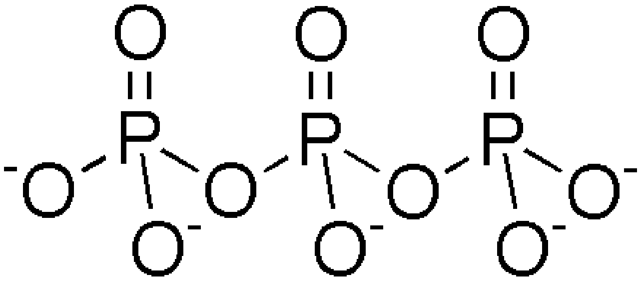
[2]

(ii)

+5

[1]

(iii)



[1]

(iv)

Concentration of $P_3O_{10}^{5-}$ decreases as it complexes with the added Mg^{2+} to form $MgP_3O_{10}^{3-}$.

By Le Chatelier's Principle, the equilibrium position of (1) will shift left to increase the concentration of $P_3O_{10}^{5-}$.

There is no change to the value of K_c as temperature is kept constant.

[2]

[Total: 15]

5 (a)

CH_3OH and CH_3CH_2OH.

[1]

(b)

Two epoxide rings.

Two alcoholic groups are produced for every epoxide ring that will be hydrolysed. Since there are four alcoholic groups formed after ‘juvenile hormone’ undergoes hydrolysis, this implies that there are two epoxide rings in ‘juvenile hormone’.

[2]

(c) State the type of reaction that T has undergone and the functional group that it contains other than the four alcoholic groups.

T undergoes basic hydrolysis to give methanol and U. T is likely to contain an ester.

[1]

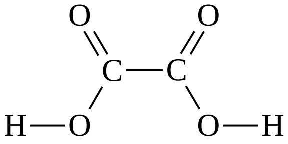
(d)

Two tertiary alcohol groups.

T has four alcohol groups which were retained in U even after basic hydrolysis. Since V has only two alcohol groups left after mild oxidation, this implies that the two alcohol group must be tertiary in order to resist oxidation.

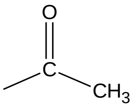
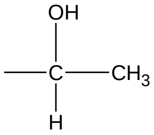
[2]

(e)



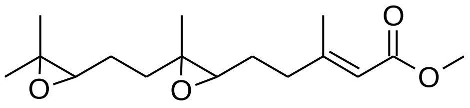
[1]

(f)

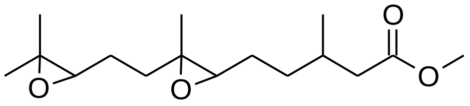
Condensation. W contains either  or 

[2]

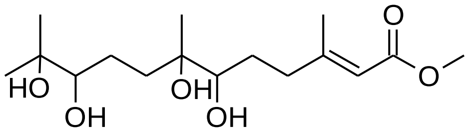
(g)



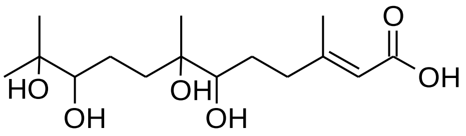
Juvenile hormone



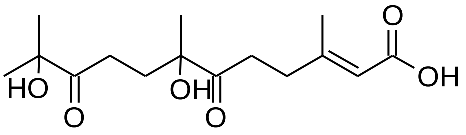
S



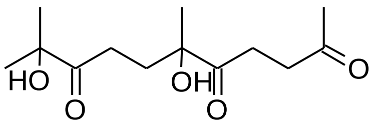
T



U



V



W

[6]
[Total: 15]

Name:		**Index Number:**		**Class:**	

Preliminary Examination
2016 Year 6

H2 CHEMISTRY

9647/03

Paper 3 Free Response

20 September 2016
2 hours

Additional Materials: Data Booklet
Writing Papers
Graph Paper

INSTRUCTIONS TO CANDIDATES

Write your **name**, **index number** and **class** on this question paper and on the Cover Sheet provided.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

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

Answer any **four** questions.

Start each question on a fresh sheet of paper.

A Data Booklet is provided.

You are reminded of the need for good English and clear presentation in your answers.

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

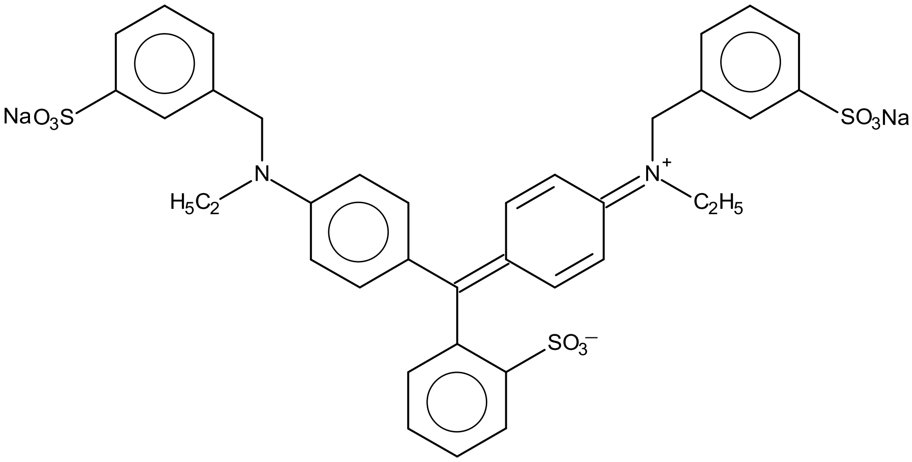
At the end of the examination:

- Fasten all work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

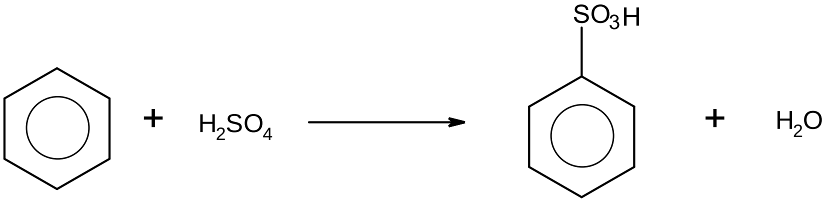
The total marks for this paper is 80 marks.

Answer *any* **four** questions.

1 Blue #1 ($Na_2C_{37}H_{34}N_2S_3O_9$) is a synthetic food colouring often found in ice cream.



(a) One of the main compounds used to produce Blue #1 is benzenesulfonic acid, which is produced by heating benzene under reflux with concentrated sulfuric acid for several hours.

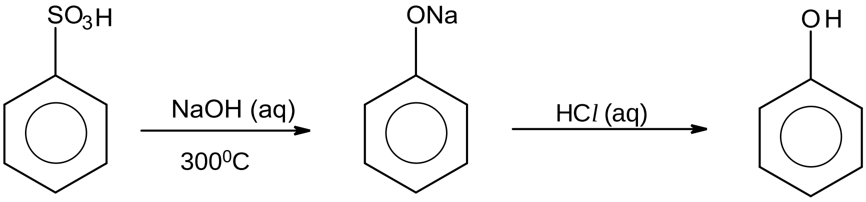


(i) The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

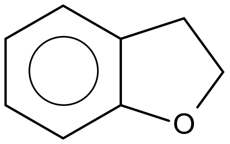
Name the type of reaction and describe the mechanism. In your answer, show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons.

[4]

(ii) Benzenesulfonic acid is a useful starting material as it can be easily converted to phenol by heating with NaOH(aq) at 300°C followed by acidification. It also has similar chemical reactivity as nitrobenzene.



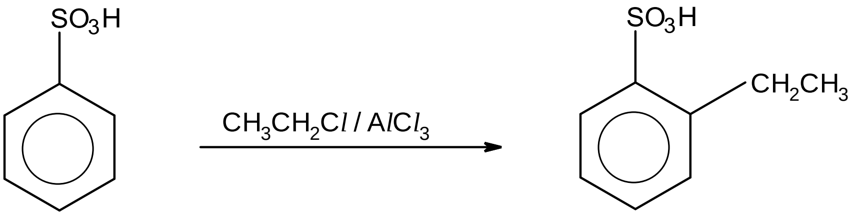
Compound **A** can be synthesised from either benzenesulfonic acid or ethylbenzene in not more than 4 steps.



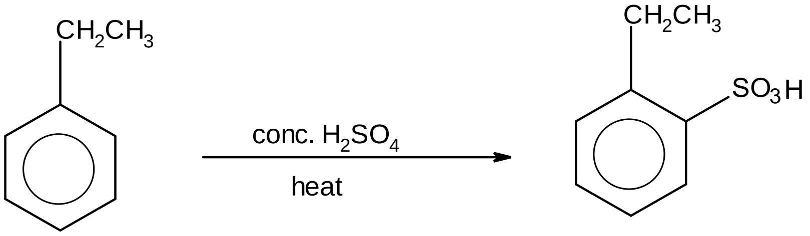
A

The first step of the synthesis using either benzenesulfonic acid or ethyl benzene is as shown below in Scheme 1 and 2 respectively:

Scheme 1:



Scheme 2:



Identify the correct scheme that will give compound **A** and copy the synthetic scheme in your answer.

Using information in **(a)(ii)**, suggest the next three steps to synthesise compound **A**. Show all intermediates, reagents and conditions clearly in your synthetic route.

[4]

(b) Blue #1 can be oxidised by household bleach to form colourless products, as represented by the equation below.

$$\underset{\textit{blue}}{Na_2C_{37}H_{34}N_2S_3O_9} \quad + \quad \underset{\textit{colourless}}{\text{bleach}} \quad \rightarrow \quad \underset{\textit{colourless}}{\text{products}}$$

To study the kinetics of the reaction, a student used an UV spectrophotometer to study the absorbance of Blue #1 over time during the bleaching process.

In experiment 1, the student mixes 3.0 cm^3 of 0.1 mol dm^{-3} Blue #1, 1.0 cm^3 of water and 0.5 cm^3 of 3.5 mol dm^{-3} bleach together. The results of experiment 1 are as shown below.

Time (s)	15	30	45	60	75	90	105	120	135
Absorbance	0.495	0.424	0.371	0.328	0.285	0.251	0.218	0.191	0.170

(i) Explain why bleach is used in large excess as compared to that of Blue #1. [1]

(ii) Given that absorbance measured varies linearly with the concentration of Blue #1, use a suitable graphical method to determine the order of reaction with respect to the blue food colouring, Blue #1. [3]

(iii) The student subsequently conducted a few more experiments using other volumes of Blue #1 and bleach. The table below shows the results obtained.

Experiment	**Volume of Blue #1 / cm^3**	**Volume of distilled water / cm^3**	**Volume of bleach / cm^3**	**Rate constant**
1	3.0	1.0	0.5	
2	4.0	0.0	0.5	0.00882
3	3.0	0.5	1.0	0.01698

Using results from **(b)(ii)**, determine the rate constant for experiment 1. Hence, deduce the overall order of reaction, showing your reasoning clearly. [3]

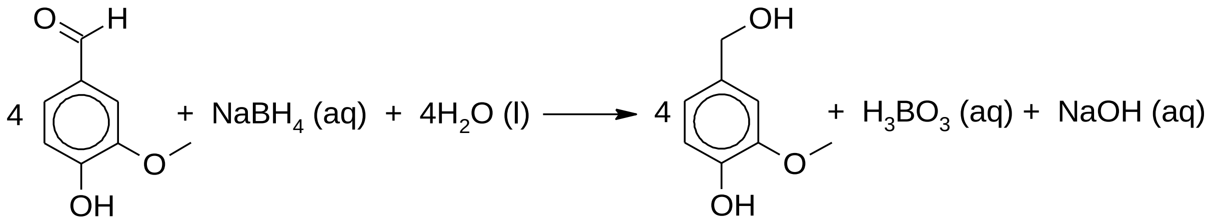
(c) **(i)** Household bleach is also often known as "chlorine water". The active chemical responsible for the bleaching action in household bleach is the anion, OCl^-, which is easily formed by the disproportionation of chlorine in water.

Write a balanced equation between chlorine and water, and hence, suggest the identity of the other compound formed. [1]

(ii) Chlorine reacts with Period 3 elements, Mg and Si, to give chlorides. The two chlorides differ in their reaction with water. Describe their differences, and explain them in terms of the different structures and types of chemical bonding. Write an equation for the reaction, if any. [4]

[Total: 20]

2 Vanillin and vanillyl alcohol (derived from vanillin) are both used as flavouring, usually in sweet foods such as chocolate. Vanillyl alcohol is commonly synthesised via the reduction of vanillin using sodium borohydride, as shown below.



vanillin

vanillyl alcohol

(a) **(i)** Draw a 'dot–and–cross' diagram to show the bonding in sodium borohydride.

[1]

(ii) Suggest why sodium borohydride is used in this reduction instead of lithium aluminium hydride.

[1]

(iii) Given that the melting points of vanillin and vanillyl alcohol are 355 K and 388 K respectively, predict and explain the sign of the entropy change of reaction at 360 K.

[1]

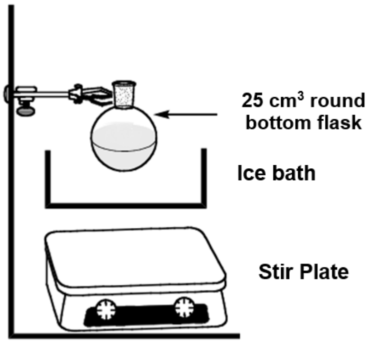
(iv) A higher temperature leads to a faster rate of reaction. However, thermodynamic factors must also be taken into consideration when considering appropriate conditions for a reaction.

Explain how higher temperatures will affect the thermodynamic outcome.

[2]

(b) The procedure for the reduction of vanillin to vanillyl alcohol is as follows:

1. Place 2 g of vanillin in a 25 cm^3 round bottom flask followed by 4 cm^3 ethanol. Add a magnetic stirrer, clamp the flask above a stir plate and commence stirring at room temperature to dissolve vanillin.
2. After the vanillin dissolves, add an ice bath under the flask to cool the solution.



3. In a separate reaction vial, dissolve 0.5 g of $NaBH_4$ in 3.8 cm^3 of 1 mol dm^{-3} NaOH solution.
4. Using a glass pipette, slowly add the $NaBH_4$ solution dropwise to the vanillin solution over a period of 10 minutes.
5. Only after the addition is complete, remove the ice bath. This is because $NaBH_4$ decomposes at high temperatures.
6. Stir the resulting mixture for 10 minutes at room temperature.
7. Add 6 mol dm^{-3} HC*l* dropwise until the evolution of hydrogen gas stops.
8. Stir to allow the product to precipitate from solution.

(i) State a reason why sodium borohydride must be added dropwise to the reaction mixture (in Step 4).

[1]

(ii) In Step 7, hydrochloric acid was added to react with excess sodium borohydride present in the reaction mixture. Write an equation for this reaction, given that boric acid (H_3BO_3) is one of the products formed.

[1]

(iii) State one way you could modify the procedure to increase the isolated yield.

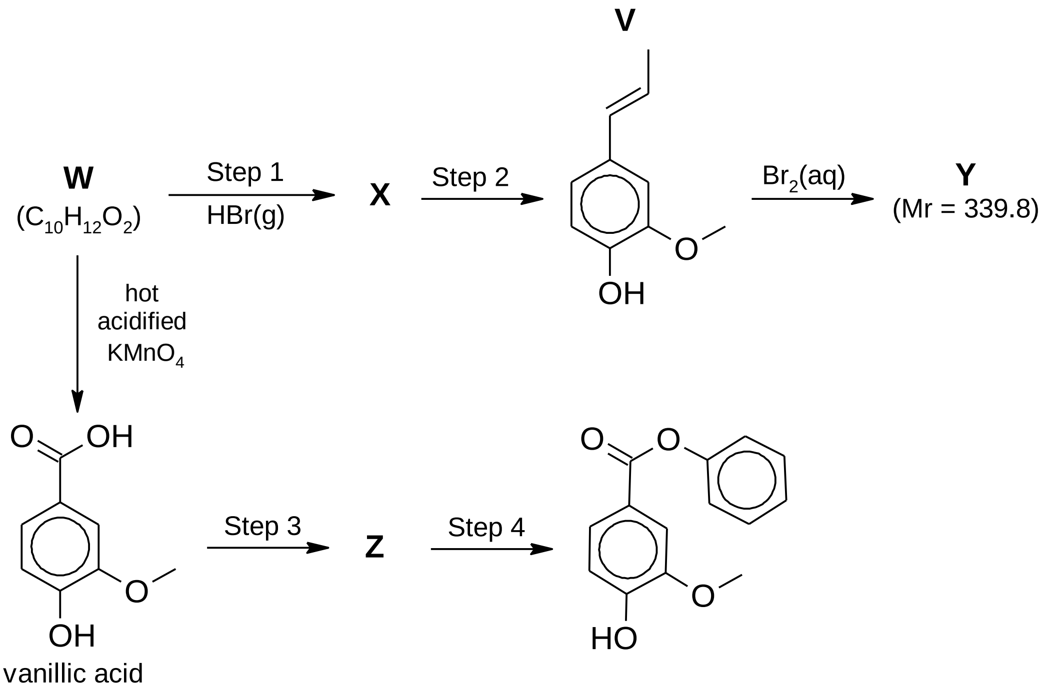
[1]

(iv) A preliminary way to determine whether the reaction has gone to completion is to draw out aliquots of the reaction mixture and test for the presence of vanillin in it.

Describe a simple chemical test to test for the presence of vanillin. Give the expected observations and write a balanced equation for the reaction with vanillin.

[2]

(c) Compound **W**, an isomer of **V**, can also be used as a starting reagent to synthesise vanillic acid and other organic compounds shown in the reaction scheme below.



(i) Draw the structures of compounds **W**, **X** and **Y**, and state the reagents and conditions for Steps 2 and 4.

[4]

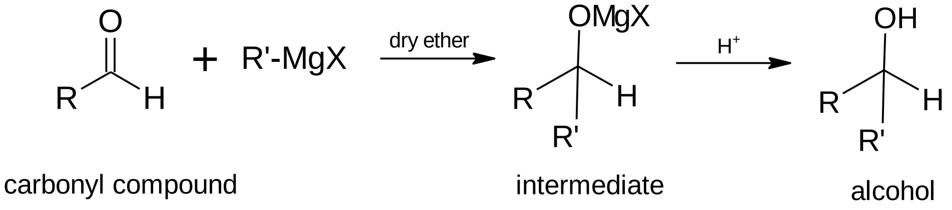
(ii) Vanillic acid (4–hydroxy–3–methoxybenzoic acid) has an isomer, 2–hydroxy–3–methoxybenzoic acid.

State which of the two isomers has a higher boiling point. Explain your answer.

[2]

(d) Organometallic compounds, usually a metal attached to an R group, can be used to convert carbonyl compounds to alcohols.

A common type of organometallic compound are Grignard reagents. They have the formula RMgX, where X is a halogen and R is an alkyl or aryl group.



Draw the structure of the intermediate formed when vanillin reacts with ethylmagnesium bromide.

[1]

(e) The chemistry of lithium and its compounds differs significantly from the rest of the Group I metals. In fact, lithium shows many similarities to magnesium exemplifying the so–called “diagonal relationship” because of their positions in the periodic table.

In an experiment, a sample of solid magnesium amide, $Mg(NH_2)_2$ and lithium amide, $LiNH_2$ are heated separately.

Magnesium amide decomposes when heated to give magnesium nitride, Mg_3N_2 and ammonia gas.

(i) Write a balanced chemical equation for the decomposition of lithium amide.

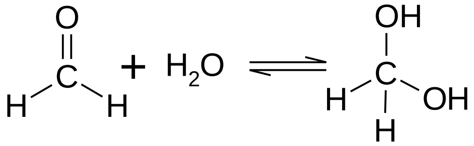
[1]

(ii) With reference to *Data Booklet*, predict the decomposition temperature of $LiNH_2$ when compared to $Mg(NH_2)_2$, given that the ionic radius of Li^+ is 0.060 nm. Explain your answer.

[2]

[Total: 20]

3 **(a)** Methanal undergoes reaction with water to yield 1,1–diol. The reaction is reversible and the 1,1–diol can eliminate water to regenerate methanal.



(i) State the type of reaction for the above reaction.

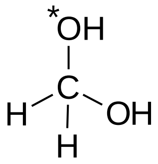
[1]

(ii) The reaction is slow but the rate is increased by the addition of a small amount of NaOH as catalyst. Suggest why NaOH is needed to initiate the reaction in the mechanism.

[1]

The oxygen in water is primarily 99.8% ^{16}O but water enriched with the heavy isotope, ^{18}O, is also available. When methanal is dissolved in ^{18}O–enriched water, the isotopic label becomes incorporated into the 1,1–diol which regenerates methanal.

(iii) Using your answer to **(a)(ii)**, suggest how ^{18}O is incorporated into the 1,1–diol.



where *O = ^{18}O

^{18}O-enriched 1,1-diol

[1]

(iv) The addition of water to aldehydes proceeds more rapidly than it does to ketones. Suggest a reason why.

[1]

(b) Methanal also reacts with HCN to form 2–hydroxyacetonitrile, HCH(OH)CN. The 2–hydroxyacetonitrile formed can be further converted to 2–hydroxyethanoic acid, as shown below.

$$HCH(OH)CN \rightarrow HCH(OH)COOH$$

(i) Explain whether 2–hydroxyethanoic acid has a larger or smaller K_a than ethanoic acid.

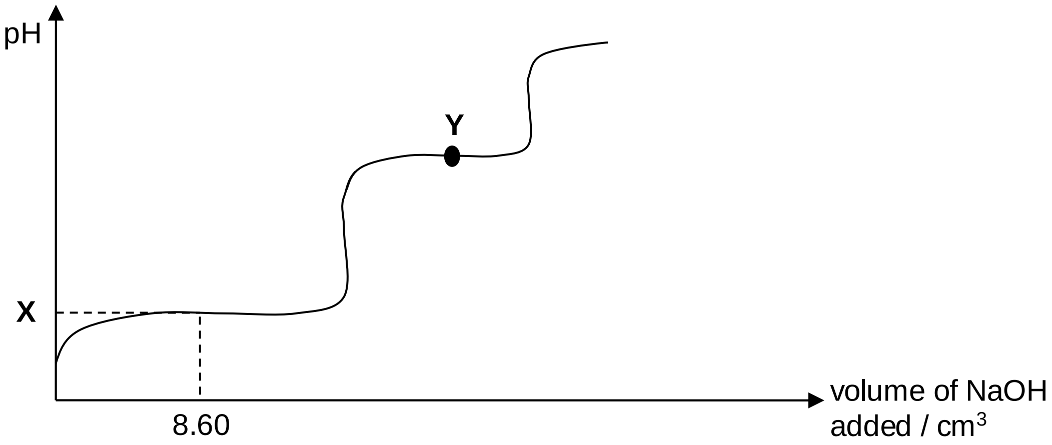
[2]

Phenol and 2–hydroxyethanoic acid are weak Brønsted acids with pK_a values of 9.80 and 3.86 respectively.

A mixture of 20.0 cm^3 of phenol and 2–hydroxyethanoic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein and bromothymol blue indicators are used in this titration.

It was found that the first colour change occurs at 17.20 cm^3 and the second colour change occurs at 26.80 cm^3 of sodium hydroxide used.

A sketch (not drawn to scale) of the pH titration curve is shown below.



(ii) Both phenolphthalein and bromothymol blue are weak acids. State the effect on the volume of sodium hydroxide used for titration, if both indicators are added in larger amount.

[1]

(iii) State the value of point **X**.

[1]

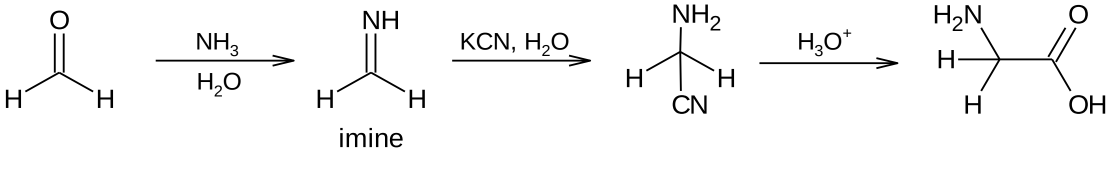
(iv) Write an equation to illustrate how the species found in point **Y** can maintain the pH of a solution when a small amount of $H^+(aq)$ is added.

[1]

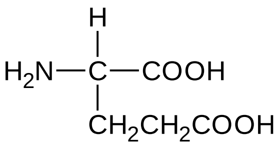
(v) Calculate the concentration of phenol and 2–hydroxyethanoic acid in the original mixture.

[2]

(c) The Strecker synthesis is a route to preparing amino acids. Methanal can be used to synthesise glycine, 2–aminoethanoic acid, in this way.



The amino acid shown below is glutamic acid.



$$H_2N-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_2CH_2COOH}{|}}{C}}-COOH$$

(i) Identify the aldehyde–containing compound and the imine intermediate which are needed to synthesise glutamic acid via the Strecker synthesis.

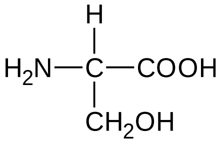
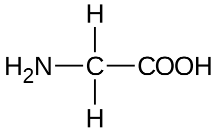
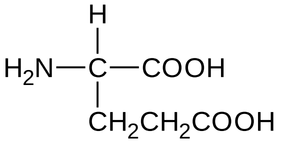
[2]

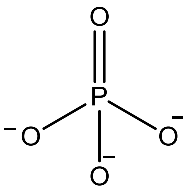
(ii) Suggest, with a reason, if there is any difference in the optical activity of a sample of glutamic acid synthesised by Strecker's method and that of natural occurring glutamic acid.

[1]

(d) Glycine and glutamic acid are among the many amino acids which constitute the long amino acid sequence of *protein kinase*. *Protein kinase* is an enzyme which plays a major role in protein regulation. It modifies other proteins by chemically adding phosphate groups to them. This process is called phosphorylation.

(i) In phosphorylation, a phosphate group (PO_4^{3-}) from adenosine triphosphate (ATP) is transferred to and replaces a free hydroxyl group of amino acid. Shown below are the structures of three amino acids and phosphate group.

serine (ser)	**glycine (gly)**	**glutamic acid (glu)**
 $H_2N-\overset{H}{\underset{CH_2OH}{C}}-COOH$	 $H_2N-\overset{H}{\underset{H}{C}}-COOH$	 $H_2N-\overset{H}{\underset{CH_2CH_2COOH}{C}}-COOH$



phosphate group (PO_4^{3-}):

Draw the structure of the tripeptide, ser–gly–glu, after phosphorylation.

[2]

(ii) The secondary structure of *protein kinase* consists of segments of α-helix. Describe the bonding which holds the α-helix in place.

[2]

(iii) The *protein kinase* is destroyed during the process of denaturation. Explain how this can occur by heating.

[2]

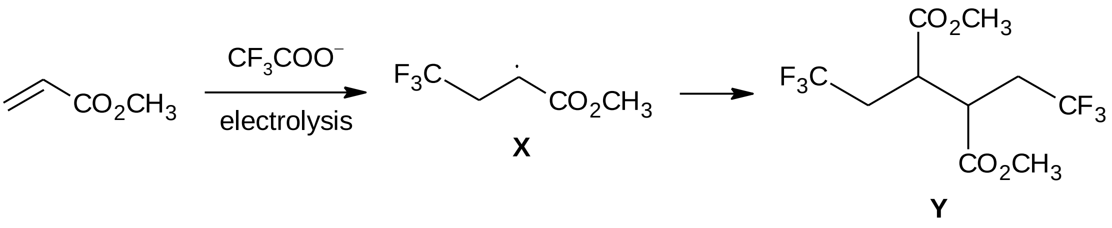
[Total: 20]

4 In 1849, the German chemist Adolf Kolbe reported his investigations into the electrolysis of aqueous solutions of some carboxylate anions, using inert platinum electrodes. The Kolbe electrolysis of trifluoroacetate ($CF_3CO_2^-$), for example, is known to produce trifluoromethyl radical ($\bullet CF_3$, $M_r = 69$) and a gas at the anode.

(a) Suggest the identity of the gas and hence construct a half-equation for the reaction at the anode.

[2]

When the Kolbe electrolysis of trifluoroacetate was carried out in the presence of alkenes such as $CH_2{=}CHCO_2CH_3$, the radical intermediate **X** was formed which further dimerised to yield product **Y** shown below.



(b) State the oxidation number of the carbonyl carbon atom in $CH_2{=}CHCO_2CH_3$.

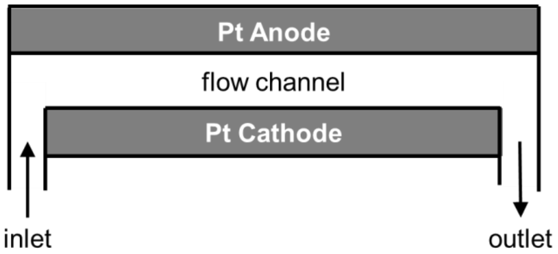
[1]

(c) Suggest a two-step mechanism for the reaction above to form **Y**, starting from the reaction between trifluoromethyl radical ($\bullet CF_3$) and the alkene. Use curly arrows to indicate the movement of single electrons and indicate any unpaired electrons by a dot ($\bullet$).

[3]

The Kolbe electrolysis in **(c)** was performed by continuous introduction of a water/CH_3CN solution containing trifluoroacetate and the alkene into an electrochemical microreactor at constant current and room temperature.

The electrochemical microreactor has a flow channel sandwiched between two platinum electrodes as shown in the figure below.



(d) **(i)** Given that the flow channel has a volume of 23 µL and reaction mixture was injected at a rate of 20 µL min^{-1}, calculate the time (in seconds) in which the current was passed through the solution.
(1 µL = 10^{-3} cm^3)

[1]

(ii) The purified product **Y** (M_r = 310) was obtained as a colourless solid weighing 0.401 g. Using your answers from **(a)** and **(d)(i)**, calculate the current (in ampere) that would have been applied to the microreactor.

[2]

(e) **(i)** How many stereoisomers does **Y** have?

[1]

(ii) Draw the isomer of **Y** that is **not** optically active, showing clearly the stereochemistry of the molecule using wedged ◀ and dashed bonds ⁞ .

[1]

(f) When the Kolbe electrolysis of trifluoroacetate was carried out in the presence of another alkene, $CH_2{=}CHCONH_2$ (M_r = 71), a non-dimer product (M_r = 209) was formed instead. Suggest the structure of the product obtained.

[1]

(g) The trifluoromethyl ($–CF_3$) group is regarded as an important structural feature in many pharmaceutically relevant molecules because it is known to enhance chemical inertness. Suggest an explanation for its property.

[1]

(h) **(i)** Deduce the structure of the radical intermediate formed when Kolbe electrolysis of difluoroacetate, $CHF_2CO_2^-$, was carried out in the presence of the alkene, $CH_2{=}C(CH_3)CO_2CH_3$.

[1]

(ii) The yield of the dimer product for this electrolysis was much poorer than that for trifluoroacetate and $CH_2{=}CHCO_2CH_3$. Use your answer in **(h)(i)** to suggest a reason for the difference in yield.

[2]

Some carboxylate anions, L^-, are also known to form 1:1 complexes with divalent metal ions, M^{2+}, according to the following equilibrium.

$$M^{2+} + L^- \rightleftharpoons ML^+$$

(i) The table below gives the values of log K for some 1:1 metal-carboxylate complexes.

metal ion	acetate (CH_3COO^-)	chloroacetate (CH_2ClCOO^-)
Cd^{2+}	1.30	0.99
Cu^{2+}	1.76	1.07
Ni^{2+}	0.72	0.23

Using relevant data from the table, deduce

I the relative stabilities of the metal complexes formed with the acetate ligand.

[1]

II the relative magnitude of the log K values of 1:1 Cu^{2+}-CH_3COO^- and Cu^{2+}-$HCOO^-$ complexes and suggest a reason for your answer.

[3]

[Total: 20]

5 This question is about Period 3 elements and the uses of its compounds.

(a) A sample of magnesium oxide is suspected to be contaminated with a substantial amount of aluminium oxide. Describe a simple gravimetric method to prove that the contamination has taken place. Include equation(s) for the chemical reaction(s) involved, if any.

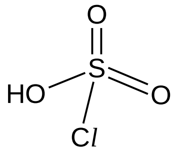
[3]

(b) Another Period 3 oxide, sulfur trioxide dissolves in water to form sulfuric acid, H_2SO_4 which can be converted into peroxodisulfuric acid, $H_2S_2O_8$ via the two-step process below, with chlorosulfonic acid, HSO_3Cl, as an intermediate:

$$H_2SO_4 + HCl \rightarrow HSO_3Cl + H_2O$$

$$H_2O_2 + 2HSO_3Cl \rightarrow H_2S_2O_8 + 2HCl$$

(i) The structure of HSO_3Cl is given below.



The boiling point of H_2SO_4 is 290 °C whereas that of HSO_3Cl is 152 °C. By making reference to the structures of the two compounds, explain the difference in the boiling points.

[2]

(ii) Draw the structure of a $H_2S_2O_8$ molecule, showing the spatial arrangement and estimated bond angle around any one sulfur atom. The $H_2S_2O_8$ molecule contains a O–O bond.

[2]

(c) Chlorine forms an oxide, Cl_2O_7, with the structure $O_3ClOClO_3$ and a boiling point of 82 °C. Its standard enthalpy change of formation is -546 kJ mol^{-1}.

(i) Write the equation which corresponds to the standard enthalpy change of formation of Cl_2O_7.

[1]

(ii) Given that the bond energy of Cl–O bond is 269 kJ mol^{-1} and using relevant data from the *Data Booklet*, estimate the average bond energy of the Cl=O bond.

[2]

(iii) The bond energy calculated in **(c)(ii)** could have been more accurate if the value of an additional enthalpy change is known. State what process this enthalpy change corresponds to.

[1]

(iv) Given that the value of the enthalpy change in **(c)(iii)** is +45 kJ mol^{-1}, construct an energy level diagram to calculate the enthalpy change of formation of gaseous Cl_2O_7.

[3]

(d) Aluminium oxide is used extensively in organic synthesis as a dehydrating agent.

An organic compound **A**, $C_{12}H_{18}O$, contains a benzene ring with 2 substituents on the 1– and 4– positions on the ring. **A** is optically active. When it is treated with Al_2O_3, compound **B** is formed. **B** can be converted into another optically active compound **C** by reacting with dry gaseous HCl. When **C** is heated under reflux with acidified $KMnO_4$, compound **D**, $C_{11}H_{14}O_2$, is produced. Treatment of **D** with PCl_5 produces compound **E**. When **E** is heated with gaseous NH_3, a neutral compound **F** is formed.

Identify the six compounds **A** – **F**.

[6]

[Total: 20]

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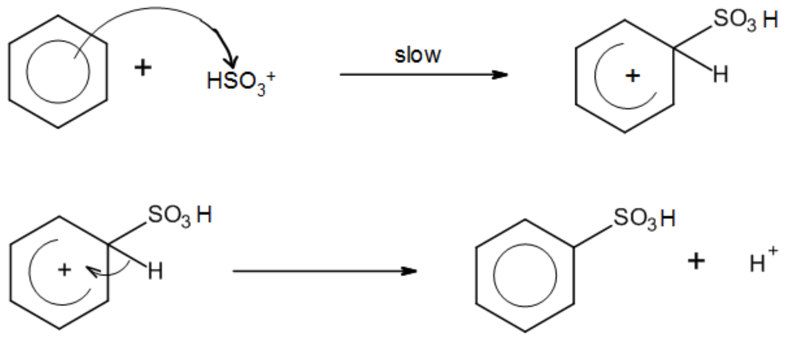
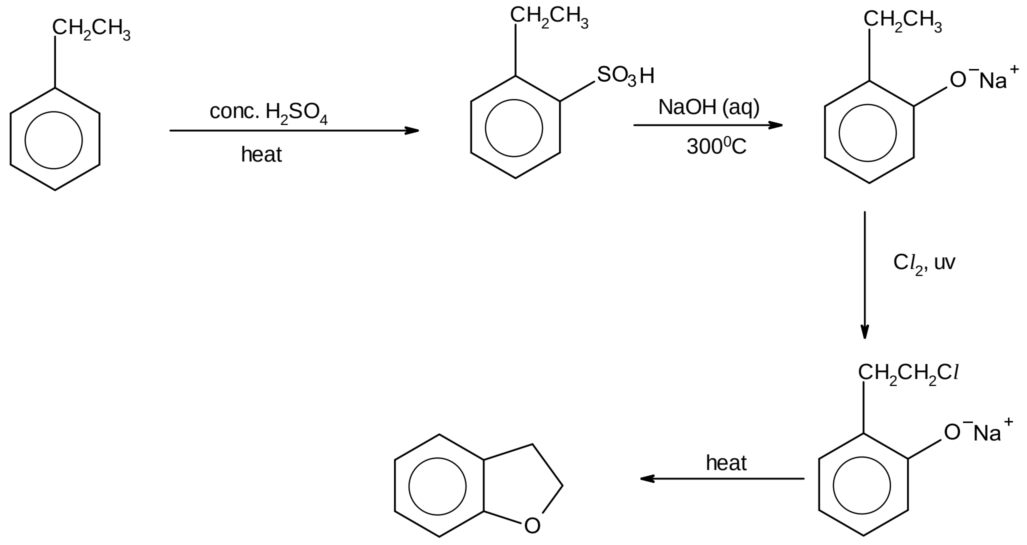
2016 Y6 H2 Chemistry Preliminary Examination Paper 3
(Answer Scheme)

1 **(a)** **(i)** Electrophilic substitution

$$H_2SO_4 + H_2SO_4 \longrightarrow HSO_3^+ + H_2O + HSO_4^-$$



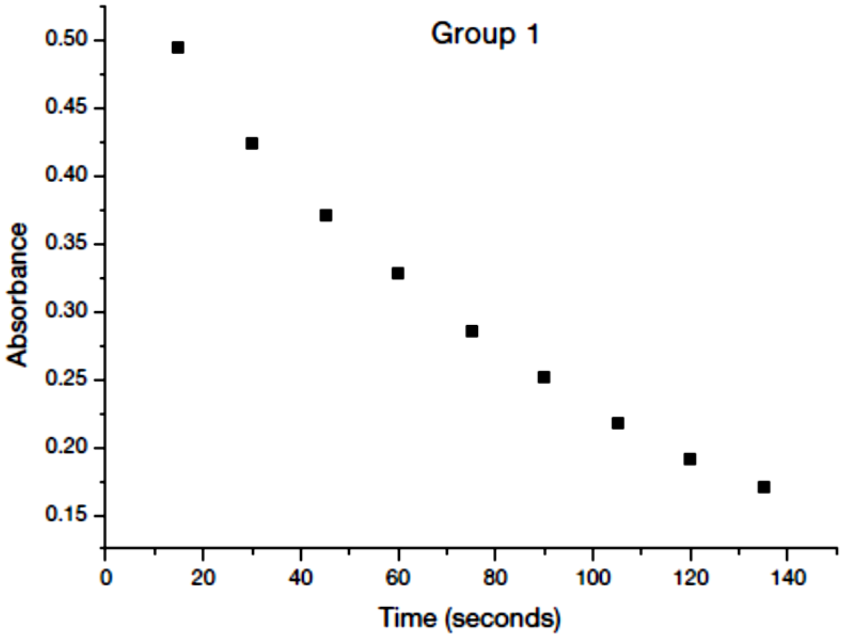
(ii) Choose scheme 2



A

(b) **(i)** To ensure that [bleach] remains almost constant throughout the reaction so that the rate can be measured with respect to Blue #1 in a pseudo-order reaction.

(ii)



From graph hand-plotted,
when absorbance decreases from 0.40 to 0.20, $t_{½} \approx$ 78s
when absorbance decreases from 0.50 to 0.25, $t_{½} \approx$ 76s
Since almost constant $t_{½} \approx$ 77s is observed, the order of reaction wrt to [Blue#1] is 1.
OR
Reaction is first order with respect to [Blue#1].

(iii) Using $t_{½} = {}^{\ln 2}/_{k}$, find value of k for experiment 1.

$k = {}^{ln2}/_{77} = 0.00900\ \text{s}^{-1}$

Compare experiment 1 and 3, when the volume of bleach doubles, rate constant almost doubles (i.e. ${}^{0.01498}/_{0.00900} = 1.67 \approx 2$).

The reaction is first order with respect to [bleach].

Hence, overall order of reaction is 2.

(c) **(i)** $Cl_2 + H_2O \rightarrow HCl + HOCl$

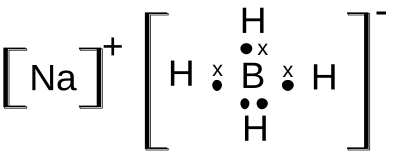
(ii) $MgCl_2$ is an ionic compound which ionises in water to form hydrated Mg^{2+} and Cl^- ions.
As Mg^{2+} has a high charge and small ionic radius / has a high charge density, it hydrolyses slightly in water to form a weakly acidic solution of pH 6.5

$$[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5OH]^{+} + H_3O^{+}$$

$SiCl_4$ is a covalent compound which hydrolyses in water to form an acidic solution of pH 2.

$$SiCl_4 + H_2O \rightarrow Si(OH)_4 + 4HCl$$

2(a) **(i)**



(ii) Sodium borohydride is a milder reducing agent and hence is less reactive and will not react as violently with water present.

OR

Lithium aluminium hydride is a very strong reducing agent and hence is highly reactive and will react violently with water present.

(iii)

- At 360 K, vanillin is a liquid while vanillyl alcohol is a solid. There is a decrease in the degree of disorderliness, hence the entropy change of reaction at 360 K is negative.

(iv)

- $\Delta H^\ominus$ and $\Delta S^\ominus$ will change as temperature increases.
- $\Delta G^\ominus$ may become more/less negative as temperature increases.

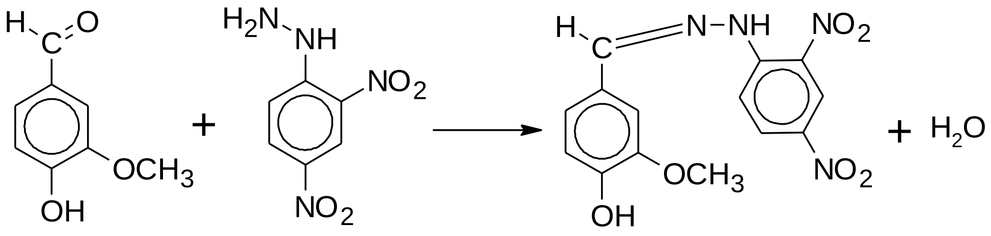
(b) **(i)** The reaction is exothermic / large amounts of heat will be produced. If it was added all at once and this may cause $NaBH_4$ to decompose.

(ii) $NaBH_4 + 3H_2O + HCl \rightarrow NaCl + H_3BO_3 + 4H_2$

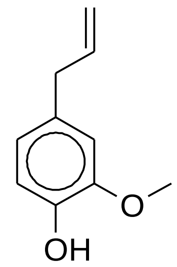
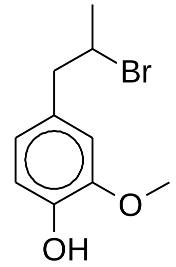
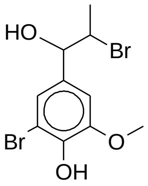
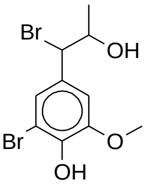
(iii) Use excess $NaBH_4$ as it may decompose at high temperatures.
Allow reactants to stir for a longer period.

(iv) To the aliquot drawn out, add a small amount of 2,4–DNPH.

An orange precipitate will be seen if vanillin is present.



(c) **(i)**

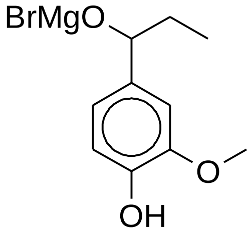
W	X	Y
		 or 

Step 2: alcoholic KOH, heat under reflux
Step 4: phenol, room temperature

(ii)

- Vanillic acid has a higher boiling point.
- Due to proximity of –OH and –COOH groups, 2–hydroxy–3–methoxybenzoic acid is capable of forming intramolecular hydrogen bonding, thus reduces the extent of intermolecular hydrogen bonding formed.
- More energy is needed to overcome the more extensive intermolecular hydrogen bonds in vanillic acid.

(d)



(e) **(i)** $3LiNH_2 \rightarrow Li_3N + 2NH_3$

(ii)

- Charge density: $Li^+ \left(\frac{1}{0.06}\right) << Mg^{2+} \left(\frac{2}{0.065}\right)$
- Polarising power: $Li^+ << Mg^{2+}$ OR
  Distortion of electron cloud of NH_2^- by both cations: $Li^+ << Mg^{2+}$
- Therefore $LiNH_2$ will have a higher decomposition temperature than $Mg(NH_2)_2$.

3 **(a)** **(i)** Nucleophilic addition

(ii) NaOH provides the ^{-}OH ions which is a stronger nucleophile for the nucleophilic attack on the carbonyl carbon.

(iii) $^{-}OH + H_2O* \rightleftharpoons H_2O + *OH^{-}$

The OH^{-} will deprotonate the ^{18}O–enriched water to form the $*OH^{-}$. $*OH^{-}$ then attacks the methanal via nucleophilic addition reaction.

(iv) The carbonyl carbon in aldehyde is less sterically hindered than that in ketones, hence more easily attacked by the nucleophile.
OR
The carbonyl carbon in aldehyde is more electron deficient (δ+) than that of ketones as ketones have an additional electron donating alkyl group.

(b) **(i)** 2–hydroxyethanoic acid has a larger K_a as it is a stronger acid.

$$HCH(OH)COOH \rightleftharpoons HCH(OH)COO^{-} + H^{+} \quad — (1)$$

$$CH_3COOH \rightleftharpoons CH_3COO^{-} + H^{+} \quad — (2)$$

The electron–withdrawing –OH group disperses the negative charge on the conjugate base of 2–hydroxyethanoic acid / 2–hydroxyethanoate ion hence stabilising the conjugate base/ 2–hydroxyethanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^{+} ions, resulting in 2–hydroxyethanoic acid being a stronger acid.

OR

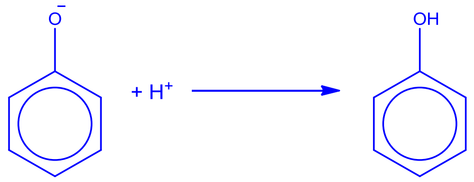
Intramolecular hydrogen bond can be formed in the 2–hydroxyethanoate ion between the carboxylate ion and the H of the alcohol group hence stabilising the conjugate base/ 2–hydroxyethanoate ion. The equilibrium position of reaction (1) lies more to the right, producing more H^{+} ions resulting in 2–hydroxyethanoic acid being a stronger acid.

(ii) If both indicators are used in larger amount, a larger volume of sodium hydroxide will be used to reach the end–point to deprotonate the indicators which are also weak acids.

(iii) X = 3.86

X corresponds to the pH of the buffer at maximum buffering capacity.
At maximum buffer capacity, pH = pK_a

(iv)



(v) First end–point corresponds to the neutralisation of 2–hydroxyethanoic acid.

Concentration of 2–hydroxyethanoic acid = $(\frac{17.20}{1000} \times 1) \div \frac{20}{1000}$

$= 0.860 \text{ mol dm}^3$

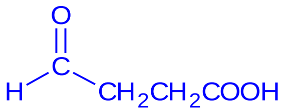
Second end–point corresponds to the neutralisation of phenol.

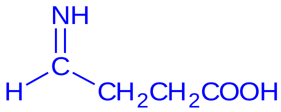
Volume of NaOH used for reaction with phenol = 26.80 – 17.20 = 9.60 cm^3

Concentration of phenol = $(\frac{9.60}{1000} \times 1) \div \frac{20}{1000}$

$= 0.480 \text{ mol dm}^3$

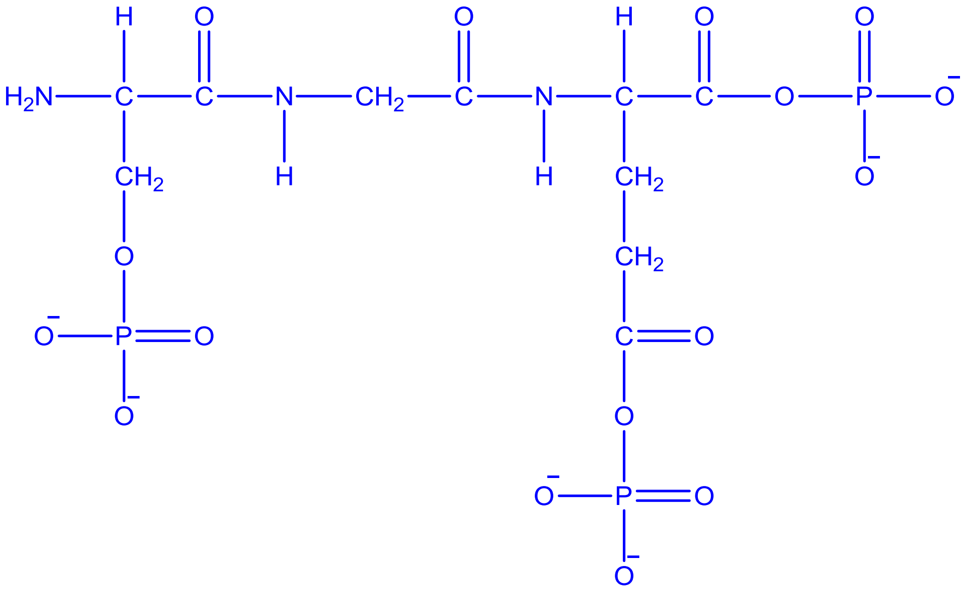
(c) **(i)**





(ii) Strecker's synthesis produces a racemic mixture and hence, do not display any optical activity while naturally occurring glutamic acid is present as one of the enantiomers and will rotate plane polarised light.

(d) **(i)**



(ii) The alpha helix is held in place due to hydrogen bonding.
Hydrogen bonding occurs between the peptide –C=O group of the nth amino acid and the peptide –NH group of the (n+4)th amino acid which is in the adjacent turn.

(iii) Heat increases thermal vibrations of the protein molecule, disrupting van der Waals' interactions formed between uncharged R–groups in the tertiary/quaternary structure.

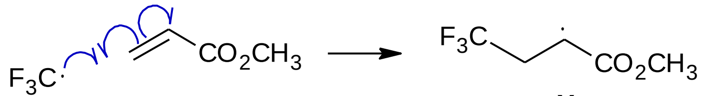
The hydrogen bonds between polar R groups in tertiary structure are also broken.

4 **(a)** CO_2

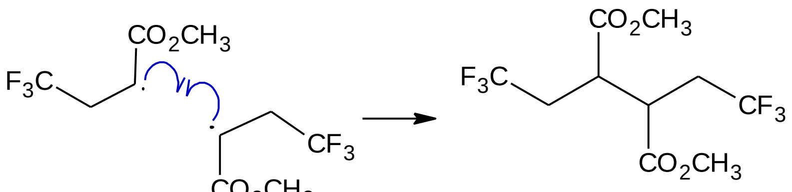
$CF_3CO_2^- \rightarrow \bullet CF_3 + CO_2 + e^-$

(b) +3

(c)



X



Y

(d) **(i)** time = 23/20 × 60 = 69 s

(ii) n(Y) = 0.401/310 = 0.0012935 mol

Since $2e^- \equiv 2\bullet CF_3 \equiv 2X \equiv Y$,

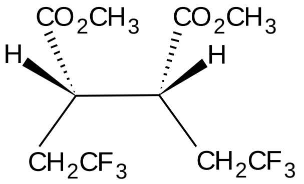
$n(e^-) = 0.0025870$ mol

Q = (0.0025870)(96500) = 249.65 C

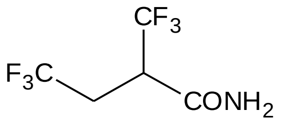
I = 249.65/69 = 3.62 A

(e) **(i)** 3

(ii)

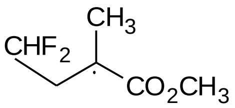


(f)



(g) The C–F bonds in the $-CF_3$ group are relatively strong and hence inert to chemical reactions.

(h) **(i)**



(ii) The presence of the methyl group at the C atom with the unpaired electron makes it more sterically hindered. It is more difficult for two bulkier radicals to collide effectively to form the dimer.

(i) **I** $CuL^+ > CdL^+ > NiL^+$

II $\log K\ (Cu^{2+}\text{-}CH_3COO^-) > \log K\ (Cu^{2+}\text{-}HCOO^-)$

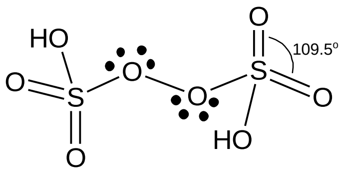
From the table, the stability of the complexes is in the same order as the availability of the lone pair of electrons on the negatively charged oxygen of the carboxylate anions for dative bonding with the metal ion. Since the lone pair of electrons on the negatively charged oxygen of CH_3COO^- is more available than that of $HCOO^-$ for dative bonding with Cu^{2+}, the Cu^{2+}-CH_3COO^- complex is expected to be more stable than the Cu^{2+}-$HCOO^-$ complex.

5 **(a)**

1. Weigh the original sample first.
2. Add aqueous sodium hydroxide in excess.
3. Only aluminum oxide will dissolve to form a soluble complex:
   $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$
4. The mixture is then filtered.
5. Dry the residue and re–weigh the sample again.
6. If there is contamination, then there should be a difference in mass.

(b) **(i)** The molecular formulae suggest that the structure of chlorosulfonic acid is derived from that of sulfuric acid, with –O atom being replaced by –C*l* atom. Hence the extent of hydrogen bonding is lesser between chlorosulfonic acid molecules and hence requires less energy to overcome, giving it a lower boiling point.

(ii)

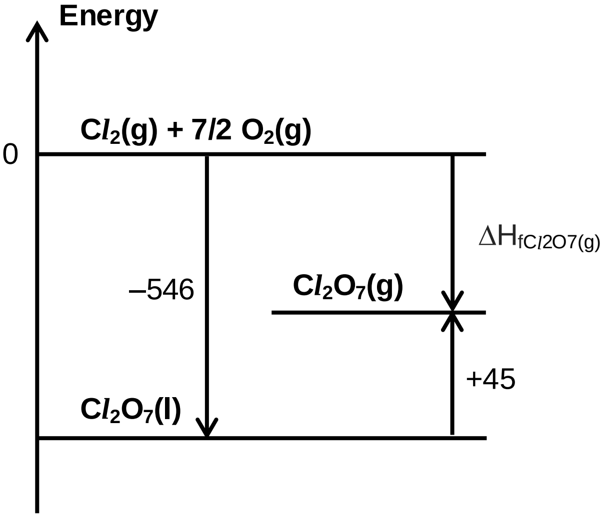


(c) **(i)** $Cl_2(g) + 7/2\ O_2(g) \rightarrow Cl_2O_7(l)$

(ii) Bond energy of C*l*–C*l* = 244 kJ mol^{-1}
Bond energy of O=O = 496 kJ mol^{-1}
$-546 = 244 + 7/2(496) - [2\times269 + 6(Cl{=}O)]$
Bond energy of C*l*=O = +331 kJ mol^{-1}

(iii) Vaporisation of $Cl_2O_7(l)$

(iv)



By Hess' Law,

$$\Delta H_{fCl_2O_7(g)} = +45 + (-546)$$
$$= -501 \text{ kJ mol}^{-1}$$

(d)