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DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY

9729/01

Paper 1 Multiple Choice

25 September 2017

1 hour

Additional Materials: Data Booklet
 Optical Mark Sheet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this question paper and the OTAS Mark Sheet.
- 2 There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate 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 The use of an approved scientific calculator is expected, where appropriate.
- 6 On the OTAS Mark Sheet, please shade the code as "Class/Index number".

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

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

Which sample of gas contains twice the number of atoms as 4 g of helium gas, He?

- A 22 g of carbon dioxide, CO₂
- B 8 g of methane, CH₄
- C 4 g of hydrogen, H₂
- D 12 g of steam, H₂O

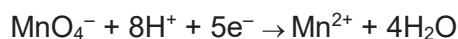
2 When 10 cm³ of a gaseous hydrocarbon was sparked with excess oxygen gas and cooled to room temperature, the gaseous mixture contracted by 30 cm³. When the residual gas was passed through aqueous potassium hydroxide, there was a further contraction of 40 cm³.

What is the hydrocarbon?

- A 2-methylpropene
- B propane
- C butadiene
- D butane

3 Ethanedioate ions, C₂O₄²⁻, are oxidised by acidified aqueous potassium manganate(VII) to give carbon dioxide. What volume of 0.020 mol dm⁻³ potassium manganate(VII) is required to completely oxidise 2.0 × 10⁻³ mol of the salt NaHC₂O₄·H₂C₂O₄?

The half equation for MnO₄⁻ is given below:



- A 20 cm³
- B 40 cm³
- C 80 cm³
- D 100 cm³

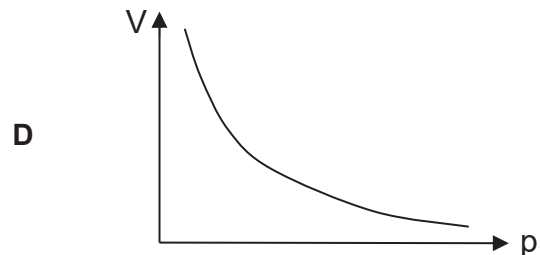
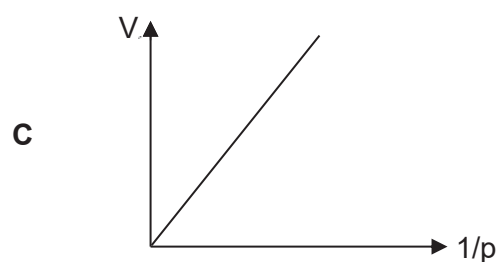
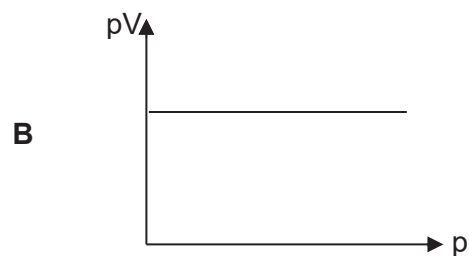
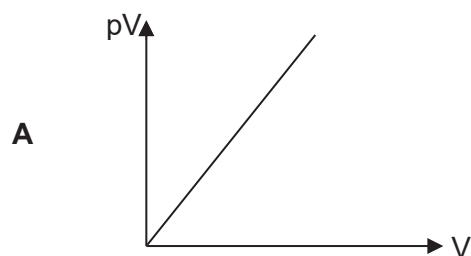
4 The successive ionisation energies, in kJ mol^{-1} , of elements **G** and **H** are given below.

G	580	1820	2740	11600	14800	18400	23300
H	940	2050	2970	4140	6590	7880	14900

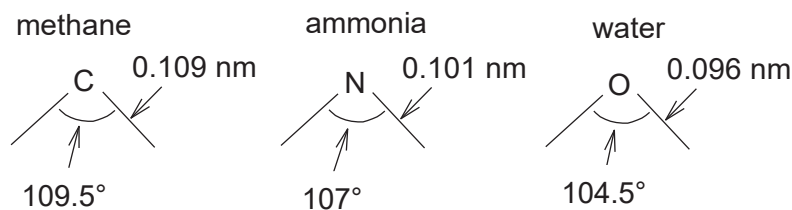
Which statements about elements **G** and **H** are true?

- 1 The first ionisation energy of **G** is lower than that of the element preceding it in the Periodic Table.
 - 2 **G** and **H** forms a compound with the formula G_3H_2 .
 - 3 **H** has an outer electronic configuration $ns^2 np^4$.
 - 4 When oxides of **G** and **H** are added separately to water containing Universal Indicator solution, the solution turns blue and red respectively.
- A 1 and 3 only
 B 3 and 4 only
 C 2, 3 and 4 only
 D 1, 2 and 4 only

5 Which graph does **not** describe the relationship between volume and pressure for a fixed mass of an ideal gas under constant temperature?



- 6 The bond lengths and bond angles in the molecules of methane, ammonia and water may be represented as follow:



What causes this trend in the bond angles shown?

- 1 Increasing repulsion between hydrogen atoms as the bond length decreases.
 - 2 Number of non-bonding electron pairs of the central atom in the molecule.
 - 3 Non-bonding electron pair-bonding electron pair repulsion is greater than bonding electron pair-bonding electron pair repulsion.
- A** 3 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3
- 7 Equimolar samples of gaseous NH_3 and HBr were injected into an evacuated flask maintained at a fixed temperature. Some white crystals of NH_4Br were observed in the flask.
- Which is the only piece of information you would need to calculate the value of K_p ?
- A** initial amount of HBr used
B mass of NH_4Br formed at equilibrium
C base dissociation constant, K_b , of NH_3
D total pressure of the system at equilibrium
- 8 *Use of the Data Booklet is relevant to this question.*

Nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, is an intermediate in the Mond process. It has a melting point of -17.2°C and a boiling point of 43°C .

A 40.3 g sample of nickel tetracarbonyl is placed in a 10 dm^3 vessel under an atmosphere of neon gas at 20°C and a pressure of 1.0 atm. When the vessel is warmed to 60°C and the contents are allowed to reach equilibrium, 10% of the nickel tetracarbonyl has dissociated into nickel metal and carbon monoxide.

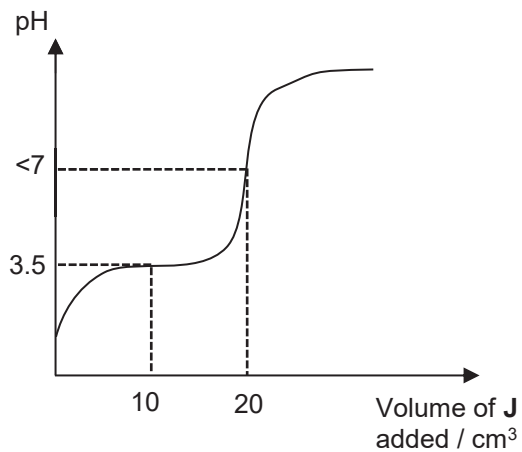
What is the total pressure of the gases in the vessel at 60°C ?
 [M_r of $\text{Ni}(\text{CO})_4 = 170.7$]

- A** 2.04 atm **B** 1.97 atm **C** 1.37 atm **D** 0.837 atm

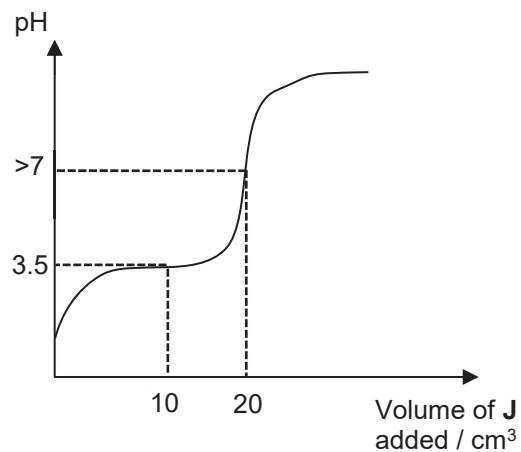
- 9 **J** is a monoacidic weak base with a pK_b of 3.5.

A total of 50 cm^3 of 0.1 mol dm^{-3} of **J** was added dropwise to 20 cm^3 of 0.1 mol dm^{-3} HNO_3 . Which pH curve correctly describes the changes in the pH of the resultant solution as **J** was added to HNO_3 ?

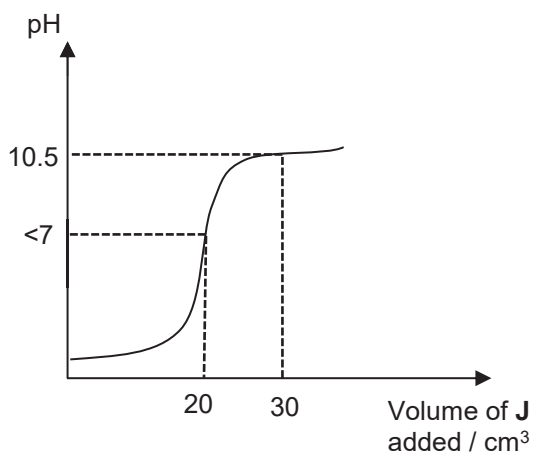
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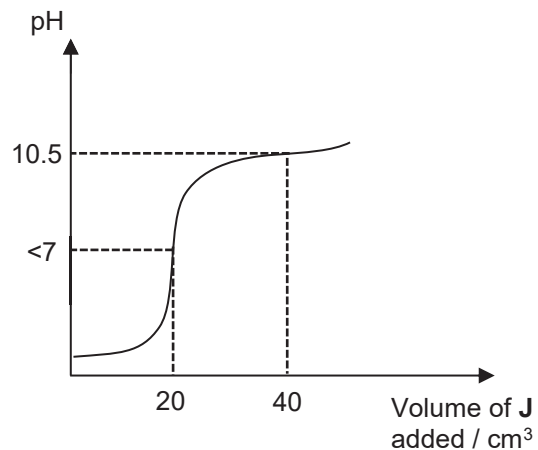
B



C



D



10 Consider the following solutions at 298K:

solutions	concentration / mol dm ⁻³
NH ₃ ($K_b = 1.8 \times 10^{-5}$ mol dm ⁻³)	0.010
CH ₃ COOH ($K_a = 1.8 \times 10^{-5}$ mol dm ⁻³)	0.010
NH ₄ Cl	0.10
CH ₃ COO ⁻ Na ⁺	0.10

Which sequence correctly ranks these solutions in increasing pH?

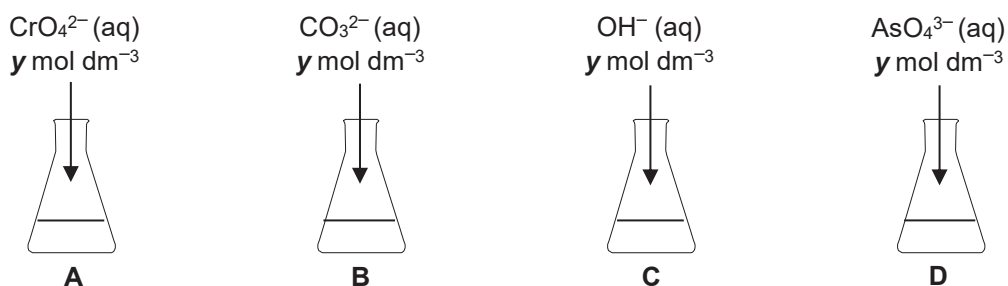
- A NH₄Cl < CH₃COO⁻Na⁺ < CH₃COOH < NH₃
 B NH₄Cl < CH₃COOH < NH₃ < CH₃COO⁻Na⁺
 C CH₃COOH < NH₄Cl < CH₃COO⁻Na⁺ < NH₃
 D CH₃COOH < NH₄Cl = CH₃COO⁻Na⁺ < NH₃

11 The table below lists the K_{sp} values of some lead containing salts.

salts	K_{sp} value
PbCrO ₄	2.8×10^{-13}
PbCO ₃	7.4×10^{-14}
Pb(OH) ₂	1.2×10^{-15}
Pb ₃ (AsO ₄) ₂	4.0×10^{-36}

A student prepared four solutions containing x mol dm⁻³ of Pb²⁺ ions. She then added solutions containing an anion drop-wise to one of these Pb²⁺ containing solutions, as shown below.

Which set-up will allow for the greatest volume of anion-containing solution to be added before a precipitate is formed?



- 14 Aqueous solutions **Y** and **Z** react according to the following equation:



The reaction rate of the above reaction is determined to follow the rate equation:

$$\text{rate} = k[\text{Y}][\text{Z}]$$

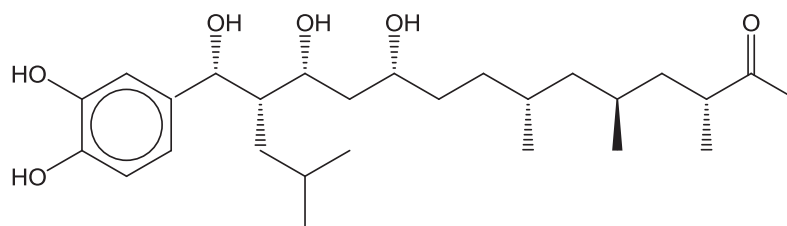
Which statements must be true regarding the above reaction?

- 1 The reaction mechanism has at least 2 steps.
 - 2 Adding water to the reaction will not affect the rate of reaction.
 - 3 When **Y** is present in large excess, the half-life of **Z** is independent of **[Z]**.
 - 4 The half-lives of **Y** and **Z** remain constant when an initial concentration of 1 mol dm^{-3} of each reactant is used.
- A** 1 and 3 only
B 1 and 4 only
C 2 and 3 only
D 1, 2 and 4 only

- 15 Which statement about Group 2 metals is correct?

- A** Melting point increases down the group.
B Reducing strength increases down the group.
C Each ground state atom contains 2 unpaired electrons in its valence shell.
D The second electron is lost more easily than the first electron, forming the M^{2+} cation with a noble gas configuration.

- 16 Baulamycin B is found to halt the growth of methicillin-resistant *Staphylococcus aureus* (MRSA) and anthrax.



Baulamycin B

What is true of its enantiomer?

- A It has 256 stereoisomers.
 B It is inactive against MRSA.
 C It reacts with 5 mol of sodium hydroxide.
 D It forms a violet colouration with neutral iron(II) chloride.
- 17 Halothane, CF_3CHBrCl is a common anaesthetic.

Which reaction is a termination step in the chain reaction between chlorine and halothane, in the presence of ultraviolet light?

- A $\dot{\text{C}}\text{F}_2\text{CHBrCl} + \dot{\text{C}}\text{l} \rightarrow \text{CF}_2\text{ClCHBrCl}$
 B $\text{CF}_3\dot{\text{C}}\text{HCl} + \dot{\text{H}} \rightarrow \text{CF}_3\text{CH}_2\text{Cl}$
 C $\text{CF}_3\dot{\text{C}}\text{BrCl} + \text{Cl}_2 \rightarrow \text{CF}_3\text{CBrCl}_2 + \dot{\text{C}}\text{l}$
 D $2 \text{CF}_3\dot{\text{C}}\text{HBr} \rightarrow (\text{CF}_3\text{CHBr})_2$

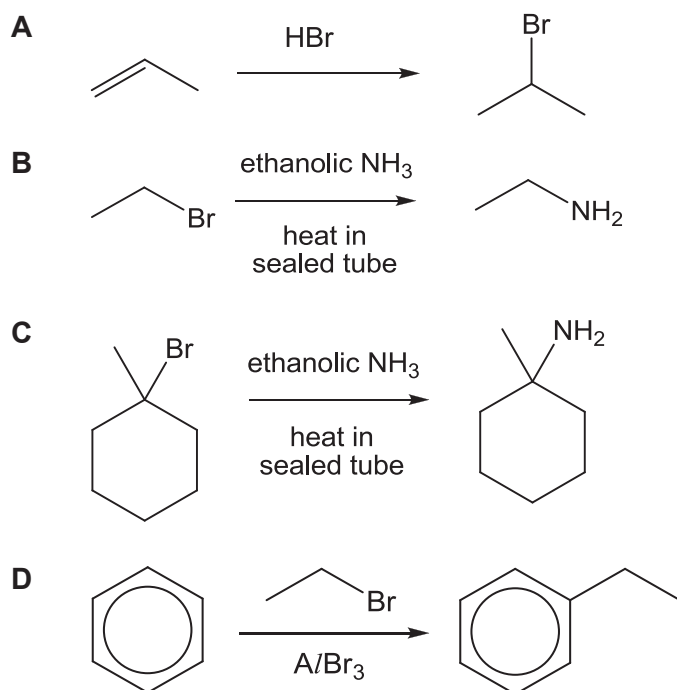
- 18 A comparison is made of the nitration reactions of some aromatic compounds.

How will the reaction temperatures required compare?

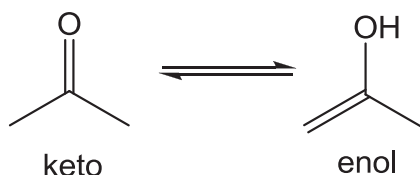
- | | lowest | —————> | highest |
|---|--------------|--------------|--------------|
| A | benzoic acid | benzene | phenylamine |
| B | phenylamine | benzene | ethylbenzene |
| C | phenylamine | ethylbenzene | benzaldehyde |
| D | benzoic acid | benzaldehyde | ethylbenzene |

- 19 As a reaction progresses, there is no change in the hybridisation state of a reactive carbon from the reactant to the **reaction intermediate**.

Which reaction does this statement apply to?



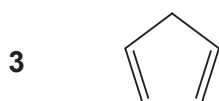
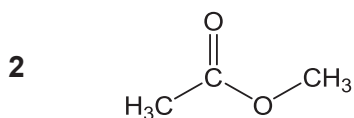
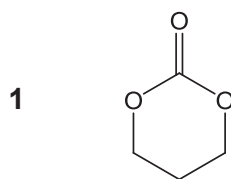
- 20 Carbonyl compounds exist as an equilibrium between its keto and enol forms. For propanone, the K_c of the tautomerism process is 3×10^{-7} .



Which statement explains the equilibrium position for the tautomerism of propanone?

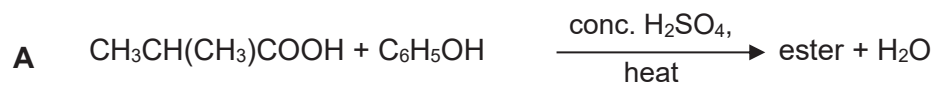
- A** The C=O bond is stronger than the C=C bond.
- B** The O–H bond is stronger than the C–H bond.
- C** The hydroxyl group exerts an electron-withdrawing effect.
- D** A lone pair of electrons on oxygen moves to the C–O bond in enol, resulting in partial double bond character.

- 21 Which compounds liberate carbon dioxide gas when heated with acidified potassium manganate(VII)?

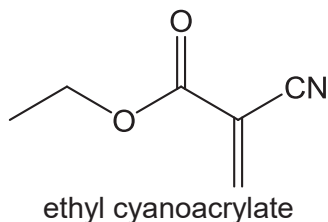


- A 3 only
 B 1 and 2 only
 C 2 and 3 only
 D 1, 2 and 3

- 22 How may the ester, phenyl 2-methylpropanoate, be made in the laboratory?



- 23 Ethyl cyanoacrylate, $C_6H_7O_2N$, is the major component of superglue.



Which statements about the molecule are true?

- 1 It contains 3 lone pairs of electrons.
 - 2 It reacts with H_2 in the presence of Ni catalyst to form $C_6H_{11}O_2N$.
 - 3 It contains 4 π bonds.
 - 4 It is hydrolysed by dilute H_2SO_4 to give a diacid and an alcohol.
- A** 1 and 2 only
B 3 and 4 only
C 1, 2 and 3 only
D 1, 2, 3 and 4

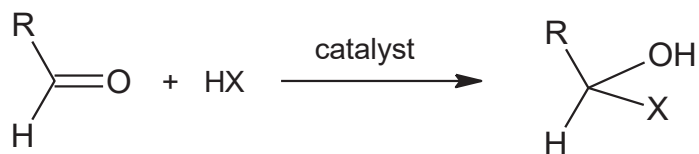
- 24 When a compound **O** is heated in a tube containing reagent **P**, a colour change is observed. The product formed is then heated with reagent **Q**, giving compound **R**. **R** can react with reagent **S** to give an observable change.

Which combination could be **O**, **P**, **Q** and **S**?

	O	P	Q	S
1	$CH_2=CH_2$	Br_2 in CCl_4	excess conc. NH_3	$Cu^{2+}(aq)$
2	$CH_2=CHCH_3$	acidified $KMnO_4(aq)$	methanolic $NaBH_4$	Tollens' reagent
3	$CH_2=CH_2$	$HBr(g)$	$NaOH(aq)$	hot alkaline $I_2(aq)$

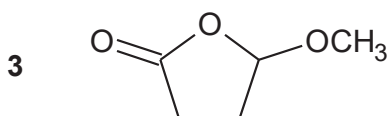
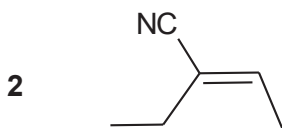
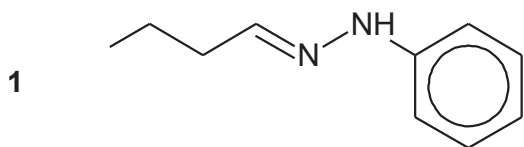
- A** 1 only
B 1 and 2 only
C 2 and 3 only
D 1, 2 and 3

- 25 There is a range of reactions of the aldehyde group which have the pattern



of which the formation of the cyanohydrin (where X = CN) is one.

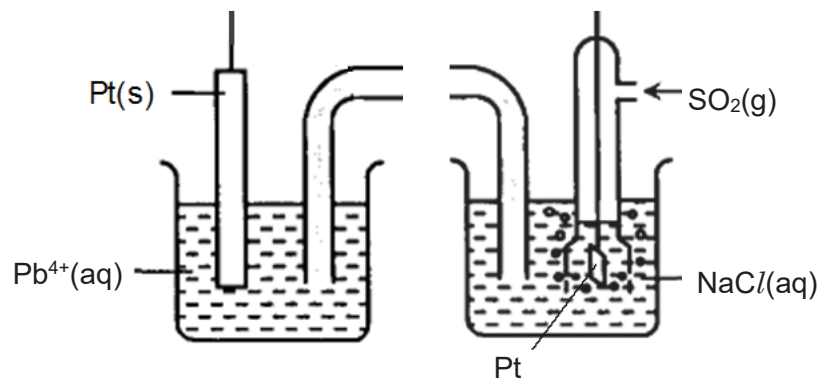
Which compounds could be obtained by such an addition to an aldehyde group, followed by dehydration?



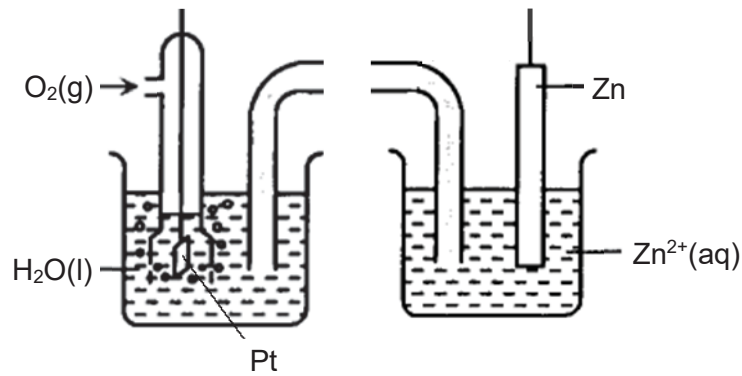
- | | | | |
|----------|---------------------|----------|---------------------|
| A | 1 and 2 only | B | 1 and 3 only |
| C | 2 and 3 only | D | 1 only |

26 Which pair of half-cells will form an electrochemical cell that generates electricity?

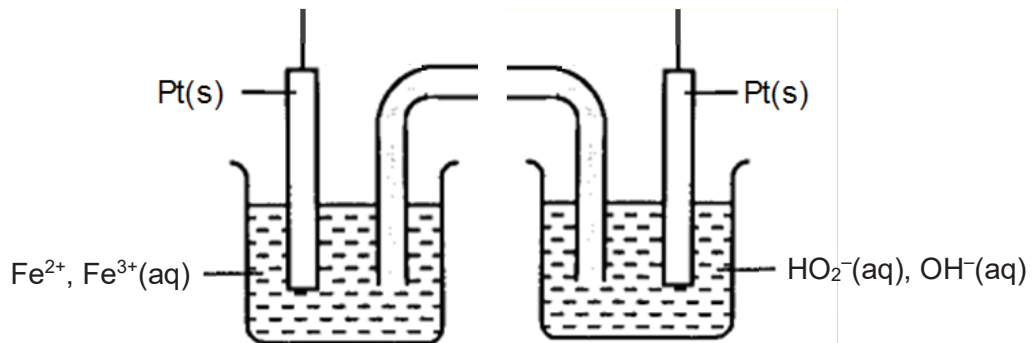
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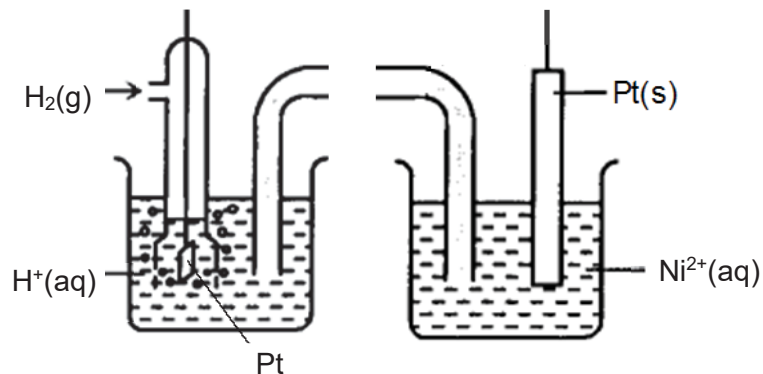
B



C

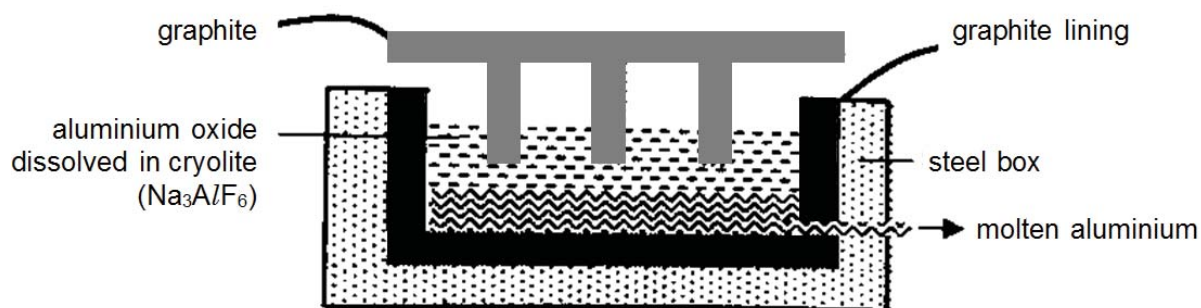


D



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

Aluminium ore is called bauxite. The bauxite can be purified to yield a white powder, aluminium oxide, from which aluminium can be extracted by electrical means. A current of 100 A is passed through the cell for 15 minutes. At the end of the extraction, one of the graphite electrodes has decreased in mass.

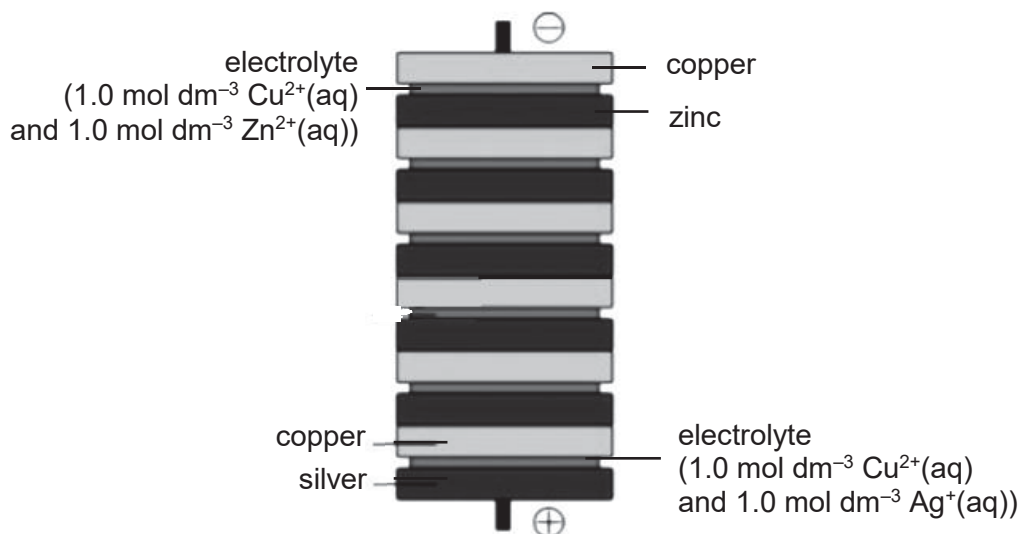


Which statement about the extraction is correct?

- A Cryolite should not be used as its sodium ions will be discharged in the process.
- B Molten aluminium is obtained at the cathode and oxygen is produced at the anode.
- C A maximum mass of 16.8 g of aluminium can be obtained from this extraction process.
- D The graphite cathode reacts with oxygen produced to give CO_2 , hence its mass decreases.

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

The voltaic pile was the first modern electric battery invented by Alessandro Volta in 1800. The pairs of alternating discs of copper, silver and zinc are separated by cardboard soaked in an aqueous electrolyte to increase the conductivity.

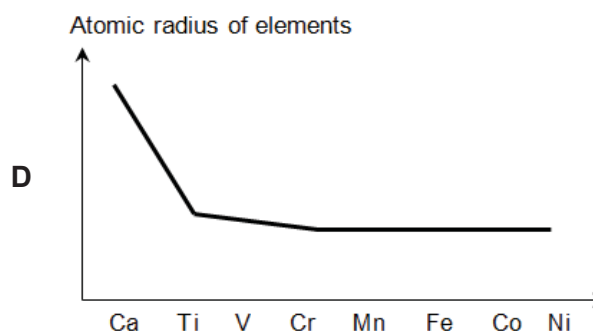
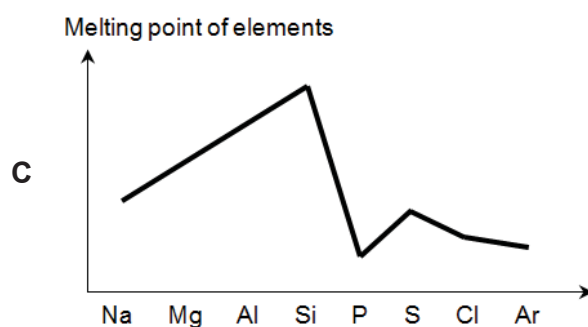
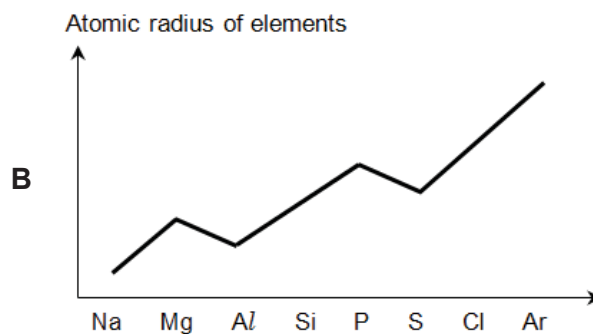
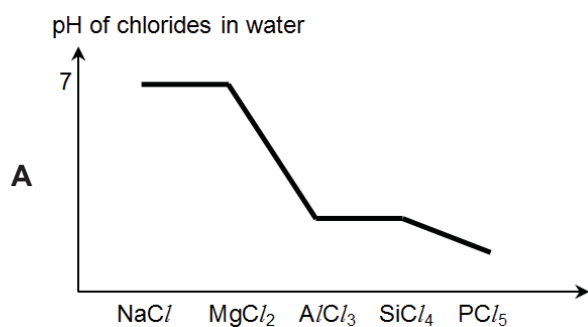


The voltaic pile above has four pairs of Cu and Ag discs and two pairs of Cu and Zn discs, which will be connected to a voltmeter. The voltage of the voltaic pile is the sum of the voltages of each component cell.

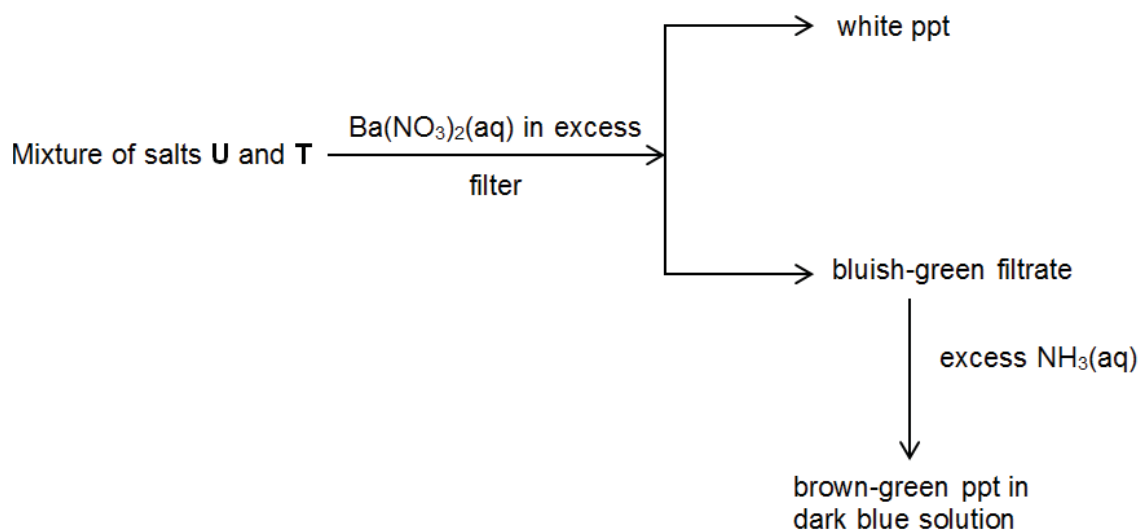
What is the reading on the voltmeter?

- | | | | |
|----------|--------|----------|--------|
| A | 1.00 V | B | 1.56 V |
| C | 4.04 V | D | 6.76 V |

29 Which sketch below is correct?



30 Below is a reaction scheme of salts **U** and **T**.



What are the identities of salts **U** and **T**?

- A chromium(III) chloride and copper(II) chloride
- B chromium(III) sulfate and copper(II) sulfate
- C copper(II) chloride and iron(II) chloride
- D copper(II) sulfate and iron(II) sulfate

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Name:		Index Number:		Class:	
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DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY

Paper 2 (Structured)

9729/02

11 Sep 2017

2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page.
- 2 Write in dark blue or black pen.
- 3 You may use an HB pencil for any diagrams or graphs.
- 4 Do not use staples, paper clips, glue or correction fluid.
- 5 Answer **all** questions in the spaces provided on the Question Paper.

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

You are advised to show all workings in calculations.

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

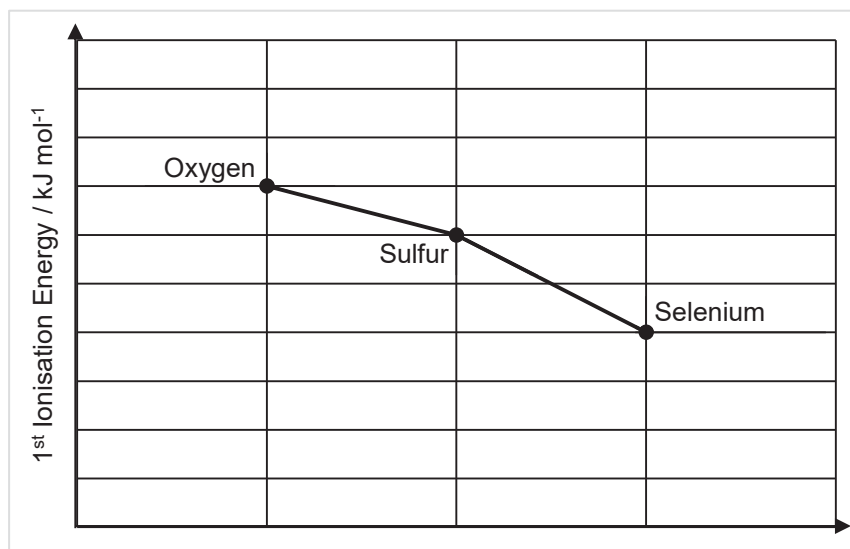
For Examiner's Use	
Question No.	Section A Marks
1	13
2	13
3	20
4	14
5	15
Total	75

This question paper consists of **21** printed pages and **1** blank page.

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

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

.....

.....

.....

.....

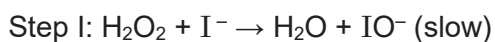
[2]

(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.

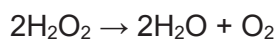
[1]

- (b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2 . Hydrogen peroxide readily decomposes at room temperature. However, this process is slow.

Iodide ions, I^- , catalyse this decomposition, as shown below:



The overall equation for the decomposition of hydrogen peroxide is shown below:



The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	-98
Entropy change / $\text{J K}^{-1} \text{mol}^{-1}$	+71

- (i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions.



[2]

- (ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm³ closed vessel at 120 °C. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel.

(Assume that H₂O and O₂ are ideal gases under the above reaction conditions)

[2]

- (c) Chalcogens are also very commonly found in organic compounds. Table 1 below shows some common oxygen or sulfur containing organic functional groups.

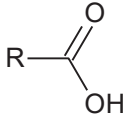
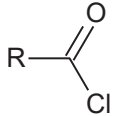
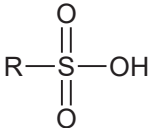
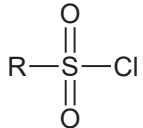
Oxygen-containing functional groups	Alcohols R-OH	Carboxylic acids 	Acyl chlorides 
Sulfur-containing functional groups	Thiols R-SH	Sulfonic acids 	Sulfonyl chlorides 

Table 1

- (i) Explain why carboxylic acids are generally more acidic than alcohols.

.....

.....

[1]

- (ii) Hence, suggest a reason why carboxylic acids are generally less acidic than their corresponding sulfonic acids.

.....

 [1]

- (iii) A reaction scheme for the synthesis of dimethyl sulfide (CH_3SCH_3) from methylsulfonyl chloride ($\text{CH}_3\text{SO}_2\text{Cl}$) is shown below:



Given that sulfur-containing functional groups undergo similar reactions as their corresponding oxygen-containing functional groups (Table 1), suggest:

- I. The reagent(s) and condition(s) required for Step I.

..... [1]

- II. The role of KI in Step II.

..... [1]

- III. The identity of Reagent X in Step III.

..... [1]

- IV. The structure of the product(s) formed when methylsulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) is reacted with ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) at room temperature.

[1]

[Total: 13]

- 2 The electrolysis of dilute sulfuric acid was carried out using two different currents at room temperature and pressure.

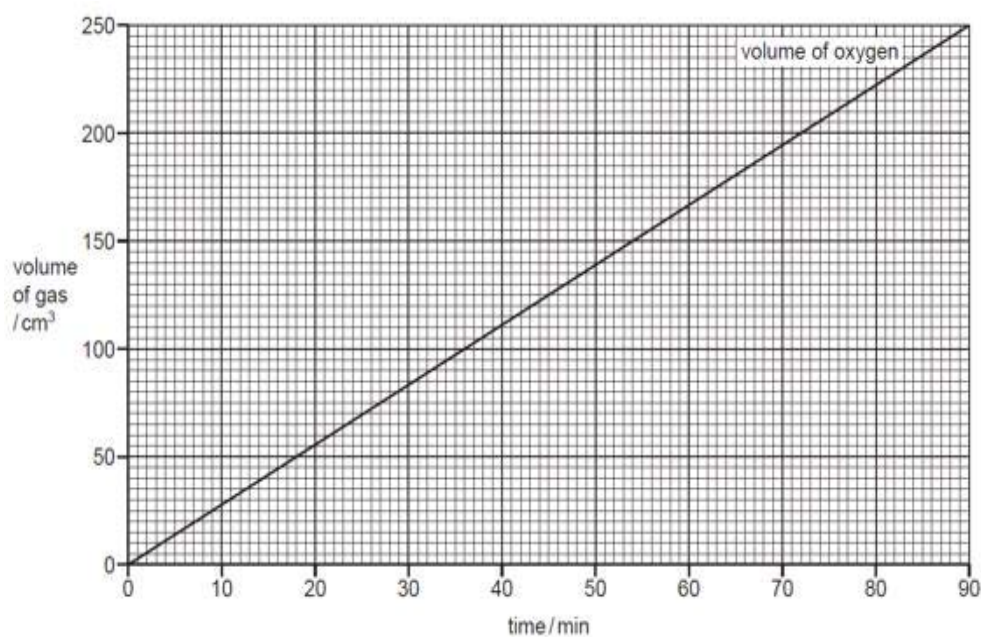
	Current / A	Duration / min
Experiment 1	0.75	90
Experiment 2	0.45	90

Oxygen gas is collected at one of the electrodes.

- (a) (i) Calculate the final volume of oxygen produced in experiment 2.

[2]

- (ii) The volume of oxygen collected for experiment 1 is shown below.



On the graph above, draw a line to show each of the following:

- I. the volume of H_2 gas that would be given off in experiment 1
(Label this line **1**)
- II. the volume of oxygen that would be produced in experiment 2
(Label this line **2**)

[2]

- (b) In another experiment, electrolysis of aqueous potassium butanedioate, $(\text{OOCCH}_2\text{CH}_2\text{COO})\text{K}_2$, was carried out. It was found that two gases, **Y** and **Z**, were liberated at the anode in a 2:1 ratio by volume.

Gas **Y** formed is absorbed by soda lime while gas **Z** is able to decolourise bromine water.

- (i) Suggest the identities of gases **Y** and **Z**.

Gas **Y** is Gas **Z** is [1]

- (ii) Construct the half-equation for the reaction that occurs at the anode and the cathode respectively.

Anode

Cathode [2]

- (iii) Predict the main organic product that would be obtained at the anode when a solution of potassium pentanedioate is electrolysed.

..... [1]

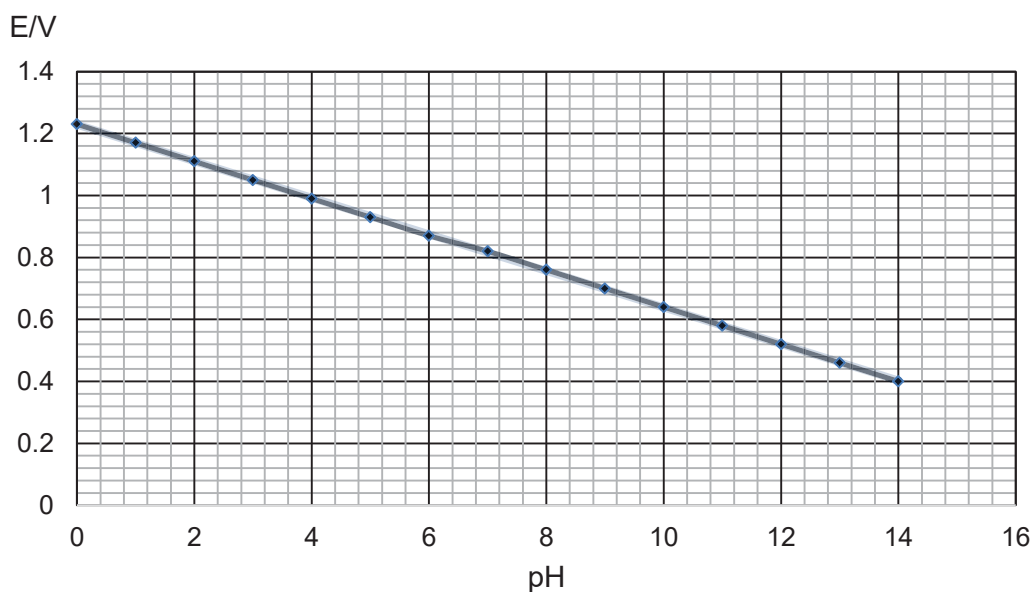
- (c) Nicotinamide adenine dinucleotide (NAD^+) is involved in redox chemistry throughout the respiratory system. Aerobic respiration is the process of producing cellular energy involving oxygen.

The electrode potential for the reduction of NAD^+ in a *biological* system, $E(\text{pH } 7)$, at 1 mol dm^{-3} , $25 \text{ }^\circ\text{C}$ and $\text{pH } 7$, is as shown.

Its oxidised and reduced forms are represented as NAD^+ and NADH respectively.



The reduction electrode potential of oxygen at different pH is given below.



- (i) With reference to the *Data Booklet* and the graph given above, calculate the value of E_{cell} for aerobic respiration. Write a balanced equation for this reaction.

[3]

- (ii) State how the E_{cell} will differ if the aerobic reaction is performed at a pH of 7.4.

.....
[1]

- (iii) Using your answer in (c)(i), calculate $\Delta G(\text{pH } 7)$ for the aerobic respiration process.

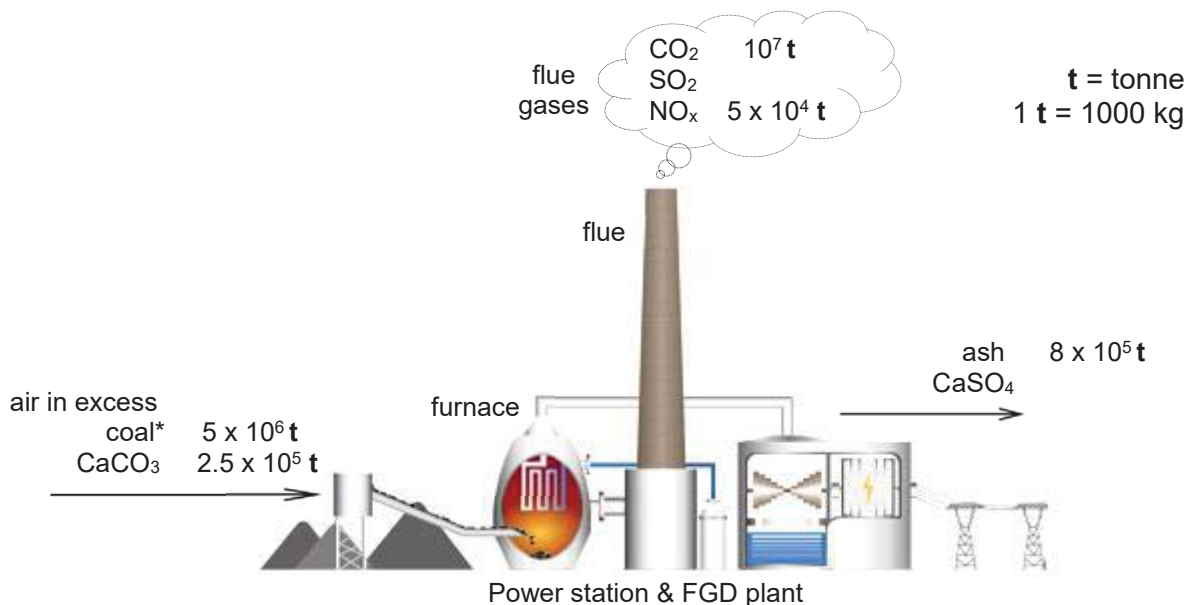
[1]

[Total: 13]

- 3 A coal-fired power station is fitted with a Flue Gas Desulfurisation (FGD) plant, which removes some of the sulfur dioxide from flue (waste) gases.

In the FGD plant, the flue gases are treated with powdered limestone, CaCO_3 , where sulfur dioxide is absorbed and reacted to produce calcium sulfite, CaSO_3 , which is oxidised by air to form solid calcium sulfate, CaSO_4 .

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in **one** year.



*coal is chiefly hydrocarbons

- (a) (i) State the process that produces the energy in the power station.

.....
[1]

- (ii) Identify a gas, not listed in the diagram, which will be a chief component of the flue gases.

.....
[1]

- (iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases.

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

(b) Write a balanced equation in each case to show how

- sulfur dioxide is removed from flue gases;

.....

- calcium sulfate is formed.

.....

[2]

(c) Using your answer in (b), determine the maximum mass of sulfur dioxide which could be removed in the FGD plant.

[1t = 1 tonne = 1000 kg]

[1]

(d) Given that your answer in (c) was only 90% of the sulfur dioxide removed from the flue gases, calculate the mass of sulfur dioxide which is released into the atmosphere in **five** years by this power station when the same mass of coal is burnt each year.

(e) Another method for removing sulfur dioxide from the flue gases is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, MgSO_3 .

(i) Explain why magnesium oxide can also be used to remove sulfur dioxide.

.....
.....

[1]

(ii) Magnesium sulfite decomposes readily to give magnesium oxide and sulfur dioxide. Magnesium oxide could be recycled, while sulfur dioxide could be used to make sulfuric acid.

Explain whether it would be easier to obtain magnesium oxide or calcium oxide from its respective sulfite.

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

[3]

- (f) When 1 mol of magnesium oxide, calcium oxide and other Group 2 metal oxides were separately dissolved in 1 dm³ of deionised water, the pH of the resulting solutions were obtained.

Some data regarding these Group 2 metal oxides, **MO**, and their resulting solutions are provided in the table below.

ion	ionic radius/ nm	$\Delta H_{\text{hydration}} / \text{kJ mol}^{-1}$	pH of MO in water	Electronegativity difference (ΔEN) in MO
O ²⁻	0.140			
Be ²⁺	0.031	-2370	7.0	1.87
Mg ²⁺	0.065	-2024	9.0	2.13
Ca ²⁺	0.099	-1680	9.5	2.44
Sr ²⁺	0.113	?	11	2.49
Ba ²⁺	0.135	-1314	12	2.55

- (i) Suggest why there is no value for $\Delta H_{\text{hydration}}$ of the oxide ion, O²⁻.

.....
[1]

- (ii) Using the data given, estimate $\Delta H_{\text{hydration}}$ of Sr²⁺.

enthalpy change of hydration of Sr²⁺ =
[1]

- (iii) State and explain the trend in $\Delta H_{\text{hydration}}$ in the table, in terms of the interaction between cations and water.

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

(iv) With reference to the relevant data given in (f), suggest explanations for the increasing pH of the resulting solution from BeO to BaO in terms of:

I. Lattice energy and enthalpy change of solution of **MO**

.....

.....

.....

.....

.....

.....

[3]

II. ΔEN and the nature of the bonding in **MO**

.....

.....

.....

.....

[2]

[Total: 20]

- 4 Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

- (a) Determine the molecular formula of ascorbic acid.

[2]

- (b) Ascorbic acid is a monobasic acid, HA , and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water.
- (i) Calculate the volume of $0.100 \text{ mol dm}^{-3}$ sodium hydroxide required for complete neutralisation.

[1]

(ii) Calculate the initial pH of the ascorbic acid solution.

[2]

(iii) Suggest a suitable indicator for the titration. Describe the expected colour change at the endpoint.

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

(iv) With the aid of a suitable equation, explain your choice of indicator in (iii).

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

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

[2]

The pH of blood is maintained at 7.35 by a $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ buffer.

- (ii) Using appropriate equations, explain how the buffer minimises changes in pH.

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

[2]

- (d) Organic acids like ascorbic acid react with amines in aqueous medium.

- (i) State the type of bond formed during the reaction.

.....

[1]

- (ii) Account for the increasing basicity of primary, secondary and tertiary amines in gas phase.

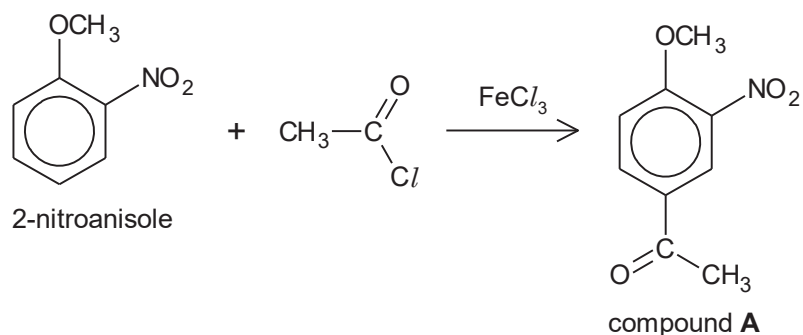
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.....
.....

[1]

[Total: 14]

- 5 (a) In Friedel-Crafts acylation, FeCl_3 is employed to attach an acyl group to an aromatic ring via electrophilic substitution.

For example, compound **A** can be prepared by the reaction of 2-nitroanisole with ethanoyl chloride in the presence of FeCl_3 .



- (i) Draw the displayed formula of the electrophile and write an equation to show how it is generated.

equation:

[2]

- (ii) Using your answer in (i), draw the mechanism of the acylation of 2-nitroanisole by ethanoyl chloride. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[2]

Empirical evidence shows that the electrophile generated in (i) is not exceptionally reactive. As such, the Friedel-Crafts acylation of nitrobenzene by ethanoyl chloride does not take place under any conditions.

- (iii) Explain why nitrobenzene does not undergo acylation but the presence of the $-\text{OCH}_3$ group in 2-nitroanisole permits acylation.

.....

.....

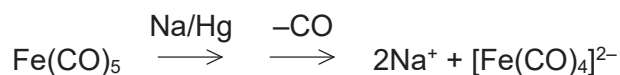
.....

.....

.....

[2]

- (b) Another iron compound, $\text{Na}_2[\text{Fe}(\text{CO})_4]$, is used in the reaction between alkyl halides and carbon monoxide to synthesise ketones. This iron-based reagent is made as follows.



- (i) Draw the structure of $\text{Fe}(\text{CO})_5$ to show its shape clearly.

[1]

- (ii) The oxidation state of Fe in $\text{Fe}(\text{CO})_5$ is 0 and the CO ligands are neutral. Suggest the oxidation state of Fe in the $[\text{Fe}(\text{CO})_4]^{2-}$ anion.

oxidation state of Fe in $[\text{Fe}(\text{CO})_4]^{2-}$:

[1]

- (iii) Besides the oxidation states exhibited in the above reaction, iron also exists in other oxidation states like +2 and +3.

State a property of iron that allows its compounds to behave in this manner and give a reason why this property arises in iron.

Property of iron:

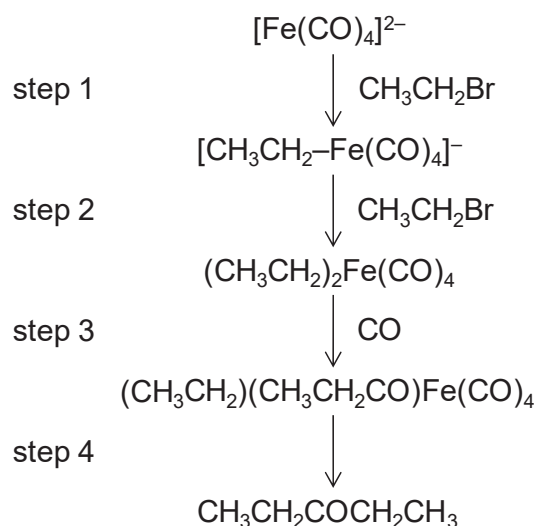
Reason:

.....

.....

[2]

The reaction between $[\text{Fe}(\text{CO})_4]^{2-}$ and bromoethane takes place under an applied pressure of carbon monoxide via the following steps.



- (iv) Explain what is meant by the term *coordination number* in the context of a metal complex.

State the coordination number of iron in $[\text{Fe}(\text{CO})_4]^{2-}$ and $(\text{CH}_3\text{CH}_2)(\text{CH}_3\text{CH}_2\text{CO})\text{Fe}(\text{CO})_4$.

.....

.....

Coordination number of iron in $[\text{Fe}(\text{CO})_4]^{2-}$:

Coordination number of iron in $(\text{CH}_3\text{CH}_2)(\text{CH}_3\text{CH}_2\text{CO})\text{Fe}(\text{CO})_4$:

[2]

- (v) Studies show that steps 1 and 2 proceed via nucleophilic substitution.

If bromoethane were replaced by bromobenzene, the above reaction with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ would not work. With reference to the bonding and structure of bromobenzene, give **two** reasons why both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ cannot occur.

.....

.....

.....

.....

.....

.....

.....

[3]

[Total: 15]

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DUNMAN HIGH SCHOOL
Preliminary Examination 2017
Year 6

H2 CHEMISTRY

9729/03

Paper 3 Section A and B (Free Response)

18 September 2017

2 hours

Additional Materials: Data Booklet
Writing Paper
Cover Sheet

INSTRUCTIONS TO CANDIDATES

- 1 Write your **name**, **index number** and **class** on this cover page and on the Cover Sheet provided.
- 2 Write your answers on the separate writing papers provided.
- 3 Write in dark blue or black pen.
- 4 You may use an HB pencil for any diagrams or graphs.
- 5 Start each question on a fresh sheet of paper.
- 6 At the end of the examination:
 - Fasten all your work securely together with the Cover Sheet on top.
- 7 Do not use staples, paper clips, glue or correction fluid.

Section A

- 8 Answer **all** questions in this section.

Section B

- 9 Answer **one** question from this section.

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

You are advised to show all workings in calculations.

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

This question paper consists of **14** printed pages and **0** blank page.

Section A

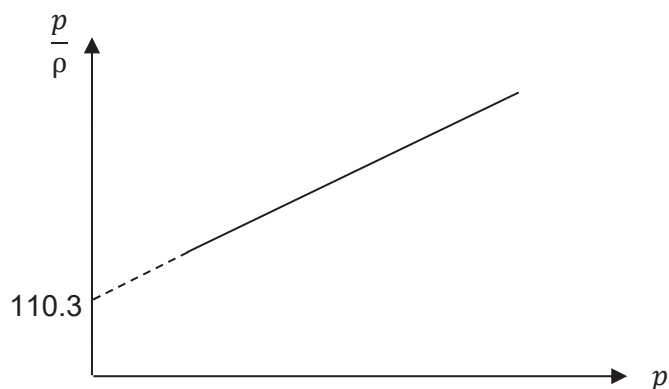
Answer **all** questions.

- 1 (a) Singapore has been affected by severe smoke haze due to forest fires in the region periodically. The National Environment Agency (NEA) is taking action to ensure that its population is better equipped to deal with haze.

During one of the sample analysis of air, the air sample was found to contain elevated amounts of NO_2 and gas **S**.

By careful measurements and extrapolation, the value of $\frac{p}{\rho}$ for gas **S** has been found to be approximately 110.3, at 100 °C and at very low pressure.

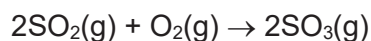
[p is the pressure of the gas in Pa and ρ is the density of the gas in g m^{-3}]



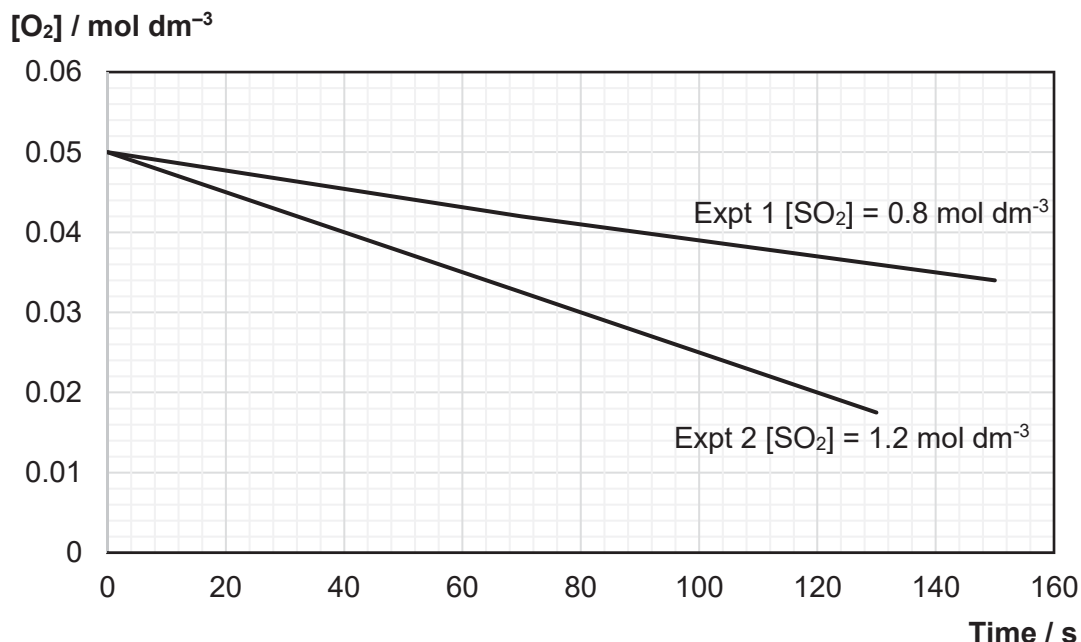
- (i) State two main assumptions of the kinetic theory, and use these to explain why you might expect the behaviour of nitrogen dioxide to be less ideal compared to that of hydrogen. [3]
- (ii) Calculate an approximate value for the relative molecular mass of **S**. [1]
- (iii) Hence, identify gas **S**, where **S** is a diatomic neutral pollutant. [1]
- (b) Atmospheric sulfur dioxide is a major air pollutant that forms acid rain. The pollution problem caused by sulfur dioxide is amplified in the presence of atmospheric oxides of nitrogen, which act as a homogeneous catalyst.

Explain, with the aid of equation(s), how atmospheric oxides of nitrogen act as a homogeneous catalyst to amplify the pollution problems of sulfur dioxide. [3]

- (c) The Contact Process is an important industrial process that occurs at 450 °C. The key stage in this process is the reaction between sulfur dioxide and oxygen.



Two laboratory experiments were conducted at 450 °C to investigate the kinetics of this reaction. The graph below shows the results obtained when concentrations of sulfur dioxide were varied.



- (i) Use the graphs above to deduce the order of reaction with respect to sulfur dioxide and oxygen. [3]
- (ii) Using one of the graphs above, calculate the value of rate constant, stating its units. [2]
- (iii) Using your answer in (i), sketch the graph of concentration of sulfur dioxide against time for this reaction, while keeping [O₂] constant. Use construction lines to label the first and second half-lives in your sketch. [1]
- (iv) Sketch and label clearly, on the same axes as in (iii), how the graph would look like if the experiment was conducted at 200 °C. [1]

[Total: 15]

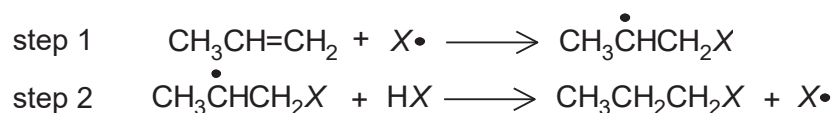
- 2 (a) Two 1.0 mol samples of hexane are mixed with separate 1.0 mol samples of cyclohexane and ethanol. The following results were obtained.

hexane mixed with	observations
cyclohexane	no heat is absorbed or given out
ethanol	1.0 kJ of heat is absorbed

For each mixture, consider interactions between molecules of the two liquids mixed and explain the observations. [4]

- (b) In the presence of peroxides, HX may be added to alkenes by a free radical mechanism. The addition is said to be *anti-Markovnikov*, that is, the H atom from HX attaches itself to the C atom in the carbon-carbon double bond with the least number of H atoms.

The propagation steps for propene are as follows.



The table below shows values of the enthalpy changes, ΔH , for the propagation steps 1, 2, and for the overall reaction for HX respectively.

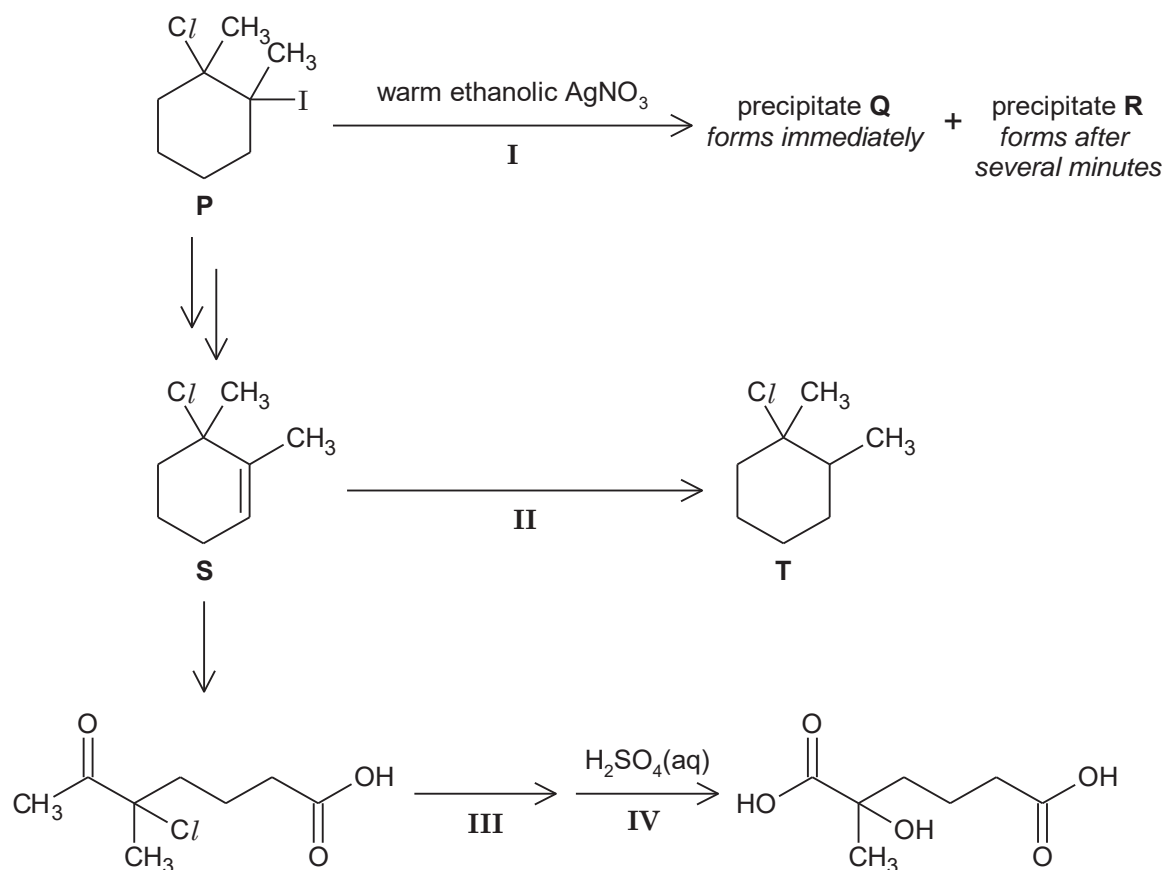
X	Cl	Br	I
$\Delta H_{\text{step 1}} / \text{kJ mol}^{-1}$	-80	-20	+20
$\Delta H_{\text{step 2}} / \text{kJ mol}^{-1}$	+21	-44	-111
$\Delta H_{\text{overall}} / \text{kJ mol}^{-1}$	-59	-64	-91

- (i) By selecting relevant data from the *Data Booklet*, show that $\Delta H_{\text{step 1}}$ for HI and $\Delta H_{\text{step 2}}$ for HCl are $+20 \text{ kJ mol}^{-1}$ and $+21 \text{ kJ mol}^{-1}$ respectively. [2]
- (ii) Experiments show that only HBr adds across an alkene via free radical mechanism.

With reference to the ΔH values given above, explain why HBr is most likely to do so and why the other two HX does **not** undergo the same mechanism. [2]

- (iii) Hence suggest the structure of the major product formed when HI that is contaminated with small amount of peroxides is added to propene. [1]

- (c) The following scheme shows the reactions of **P**, a dihalogen derivative of 1,2-dimethylcyclohexane.



- (i) Identify precipitates **Q** and **R**.

With reference to the type of reaction that **P** has undergone in reaction **I**, explain the sequence in which **Q** and **R** are formed. Support your answer with suitable data from the *Data Booklet*. [3]

- (ii) LiAlH_4 is a powerful reducing agent commonly used in organic chemistry to reduce carbonyl compounds, carboxylic acids and their derivatives. However when LiAlH_4 is used to reduce **S** in reaction **II**, **T** is **not** formed.

Explain these observations. [2]

- (iii) State the reagents and conditions required for reaction **III**. [1]

[Total: 15]

3 The chemistry of Group 15 elements, also known as Pnictogens, is discussed in this question.

- (a) Common phosphorous halides contain phosphorous in oxidation states of +3 or +5 (e.g. PX_3 or PX_5). Such compounds are useful in organic or inorganic syntheses as they can function as both Lewis acids or Lewis bases.

In the synthesis of an aesthetic, Methohexital, phosphorous tribromide is used for the conversion of a secondary alcohol to an alkyl bromide.



The mechanism of the above reaction involves two steps:

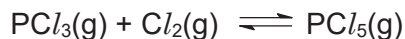
step 1:	<ul style="list-style-type: none"> the secondary alcohol attacks PBr_3 to form the following as an intermediate, along with a bromide ion: $\begin{array}{c} \text{CH}_3 \\ \\ \text{R}-\text{C} \\ \\ \text{O}^+-\text{P} \\ \quad \\ \text{H} \quad \text{Br} \end{array}$
step 2: (rate-determining step)	<ul style="list-style-type: none"> the bromide ion attacks the electrophilic carbon on the intermediate, facilitating the breaking of the C–O bond.

- (i) Using the information given above, draw the mechanism to describe the conversion of the secondary alcohol to an alkyl bromide, showing dipoles, lone pairs, and curly arrows. [3]
- (ii) State and explain if PBr_3 acts as a Lewis acid or Lewis base in the above synthesis. [1]
- (iii) With reference your answer in (i), explain why the reaction of phenol, instead of a secondary alcohol, with PBr_3 will result in the first step of the mechanism being relatively slower. [1]
- (iv) Phenol undergoes substitution when reacted with aqueous bromine. Explain why phenol undergoes substitution instead of addition with aqueous bromine. [1]
- (v) Other than using aqueous bromine or any phosphorous halides, suggest a simple chemical test to distinguish phenol from the secondary alcohol used in (a). [1]

(You can assume that the R group in the molecule does not react in any way.) [2]

- (b) Both phosphorous trichloride and phosphorous pentachloride can be used in the synthesis of tricresylphosphate, a common waterproofing agent.

Phosphorous pentachloride can be formed by reacting phosphorous trichloride with chlorine gas.



2 atm of PCl_3 and 1.5 atm of Cl_2 were left to equilibrate in a closed vessel at 600 K. At equilibrium, the total pressure in the vessel was determined to be 3.3 atm.

- (i) Calculate the K_p of the above equilibrium. [2]
- (ii) Hence, comment on the position of the equilibrium and the sign for the Gibbs free energy change of the forward reaction at 600 K. [2]
- (c) The table below shows common chlorides and oxides of other Group 15 elements.

	Nitrogen	Arsenic
Chlorides	NCl_3	AsCl_3 AsCl_5
Oxides	NO N_2O NO_2	As_2O_3 As_2O_5

- (i) Write an equation to show why arsenic pentachloride (AsCl_5) dissolves in water to give a solution with a very low pH. [1]
- (ii) Draw the dot-and-cross diagram of N_2O and state its bond angle. [2]

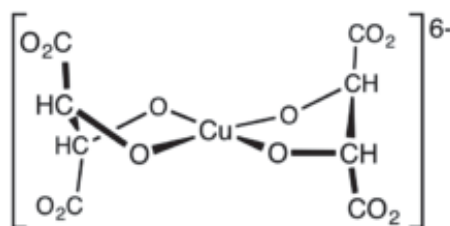
[Total: 15]

- 4 The fragrance of perfume is created using a range of scents such as citrus, fresh, floral, oriental or woody. Hex-3-en-1-ol has a fresh scent with a strong 'leafy' smell of newly cut grass, Geraniol is the main ingredient of rose oil and Linalool has the scent of sweet lavender. Usually, some ethanol and water were also present in a bottle of perfume.

Compound	Molecular formula	Structural formula
Hex-3-en-1-ol	C ₆ H ₁₂ O	CH ₃ CH ₂ CHCHCH ₂ CH ₂ OH
Geraniol	C ₁₀ H ₁₈ O	(CH ₃) ₂ CCH(CH ₂) ₂ C(CH ₃)CHCH ₂ OH
Linalool	C ₁₀ H ₁₈ O	(CH ₃) ₂ CCH(CH ₂) ₂ C(CH ₃)(OH)CHCH ₂

- (a) (i) Geraniol and Linalool are constitutional isomers. Explain what is meant by *constitutional isomers* are. [1]
- (ii) Using skeletal formula, draw the stereoisomers of hex-3-en-1-ol. [1]
- (b) A compound **X**, CH₂CCH₃(CH₂)₃C_aH_bO, is a constitutional isomer of Geraniol. It exhibits stereoisomerism and has a particular functional group that can be tested positively by Fehling's solution, an alkaline solution of complexed Cu²⁺(aq), in a redox reaction.

In Fehling's solution, the tartrate ion forms a *complex* with Cu²⁺ as shown below.



- (i) Suggest why the copper ion needs to be complexed for the test to work. [1]
- (ii) Explain why such a complex can be formed between copper and tartrate ion, while no such complex is formed between potassium and tartrate ion. [2]
- (iii) Suggest the structural formula of the compound **X**. [1]
- (iv) A 2.0 g of fluid sample in a perfume vial containing compound **X** is treated with an excess of the Fehling's solution. The red solid obtained was collected, washed and dried. It had a mass of 0.282 g.

Given that 1 mol of **X** reacts completely with 2 mol of the Fehling's solution, calculate the percentage of compound **X** present in the fluid sample. [2]

- (v) Compound **X** has a citrus scent. The human nose is able to detect the citrus scent at a minimum concentration of 10 ppm (parts per million) by mass in the air. (1 ppm by mass is 1 g in 1×10^6 g).

Assuming that all the fluid were vapourised, using your answer in (iv), calculate the volume of a room above which the smell of compound **X** can no longer be detected by the human nose.

You may assume density of the air in the room is 1.20 kg m^{-3} . [2]

- (c) When copper was added to a solution of copper(II) chloride in concentrated hydrochloric acid, a colourless solution, **Y** was obtained. During the reaction, one mole of copper(II) chloride reacts with exactly two moles of HCl , and no product other than compound **Y** was formed.

(i) Explain why solution **Y** is colourless. [1]

(ii) Write a balanced equation for the reaction. [1]

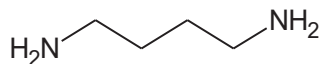
- (d) When solid sodium chloride is added to a solution containing $\text{Cu}^{2+}(\text{aq})$, the colour changes to pale yellow-green. No such colour change occurs when solid sodium sulfate is added to $\text{Cu}^{2+}(\text{aq})$. Addition of water to the yellow-green solution produces the original pale blue colour. Suggest an explanation for these observations. [3]

[Total: 15]

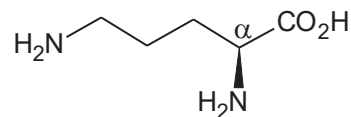
Section B

Answer **one** question from this section.

- 5 (a) A polyamine, butane-1,4-diamine, can be prepared from the decarboxylation of the α -COOH of an amino acid, L-ornithine, under suitable conditions.

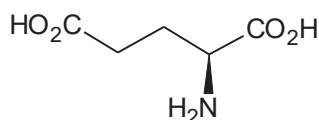


butane-1,4-diamine



L-ornithine

- (i) Deduce the identity of the gaseous by-product of the reaction and hence write an equation for the formation of butane-1,4-diamine from L-ornithine. [1]
- (ii) Draw and name the organic product formed when L-glutamic acid undergoes decarboxylation in a similar manner.



L-glutamic acid

[2]

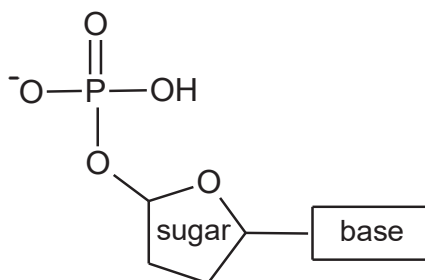
- (iii) α -NH₂ and R-NH₂ of L-ornithine have different base dissociation constants, K_b .

Explain what is meant by the term K_b as applied to a weak base, **B**. [1]

- (iv) State and explain how the K_b values of α -NH₂ and R-NH₂ of L-ornithine would differ. [2]

- (b) Suggest a reaction scheme to synthesise butane-1,4-diamine from ethene. State the reagents and conditions required, and draw the structures of the intermediates formed. [4]

Each strand of deoxyribonucleic acid (DNA) is a macromolecule made by the polymerisation of units called nucleotides. Nucleotides are themselves made from three components (a sugar, a phosphate group and a nitrogen-containing organic base) as shown in the simplified diagram below.



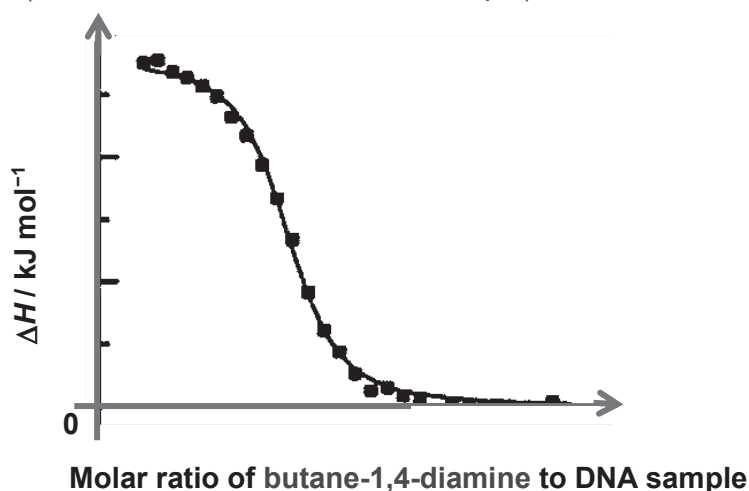
Nucleotide

In this question, the sugar and base group remain unaltered and do not take part in any interaction.

A series of experiments was carried out in a buffer solution of pH 7.0 to investigate how butane-1,4-diamine binds with a DNA sample. The binding of butane-1,4-diamine with DNA sample occurs spontaneously.

- (c) (i) Draw the predominant form of butane-1,4-diamine when it is added to the buffer solution at pH 7.0. [1]
- (ii) Hence suggest the type of interaction that facilitates the binding of butane-1,4-diamine to the DNA sample. [1]

The DNA sample was dissolved in a buffer solution of pH 7.0 before it was titrated with butane-1,4-diamine at 293 K. When butane-1,4-diamine was added to the DNA sample, the following graph showing enthalpy change (kJ per mole of butane-1,4-diamine) against molar ratio (of butane-1,4-diamine to DNA sample) was obtained.



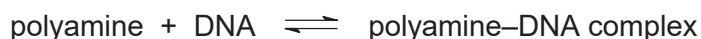
- (d) (i) It is observed from the graph that the enthalpy change is zero at the higher molar ratios. Suggest why this is so. [1]
- (ii) Using the graph above, deduce whether the binding of butane-1,4-diamine with the DNA sample is an endothermic or exothermic process. [1]

(iii) Using your answer in (ii), deduce the sign of the entropy change when butane-1,4-diamine binds with the DNA sample. [2]

(iv) A DNA molecule is closely surrounded by water molecules upon hydration.

Use this information to suggest a reason for the sign of the entropy change in (iii). [1]

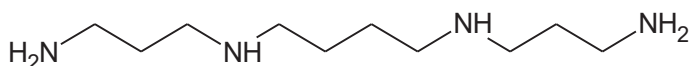
(e) The affinity of a polyamine for a DNA sample can be described by the binding constant, K , for the following equilibrium.



The binding constant, K , is further related to the standard Gibbs free energy change, ΔG^\ominus , for the reaction by the equation below.

$$\Delta G^\ominus = -RT \ln K$$

(i) Given that the numerical value of K for the binding between another polyamine, spermine, and the DNA sample at 290 K is 4.88×10^5 , calculate the standard Gibbs free energy change in J mol^{-1} .



spermine

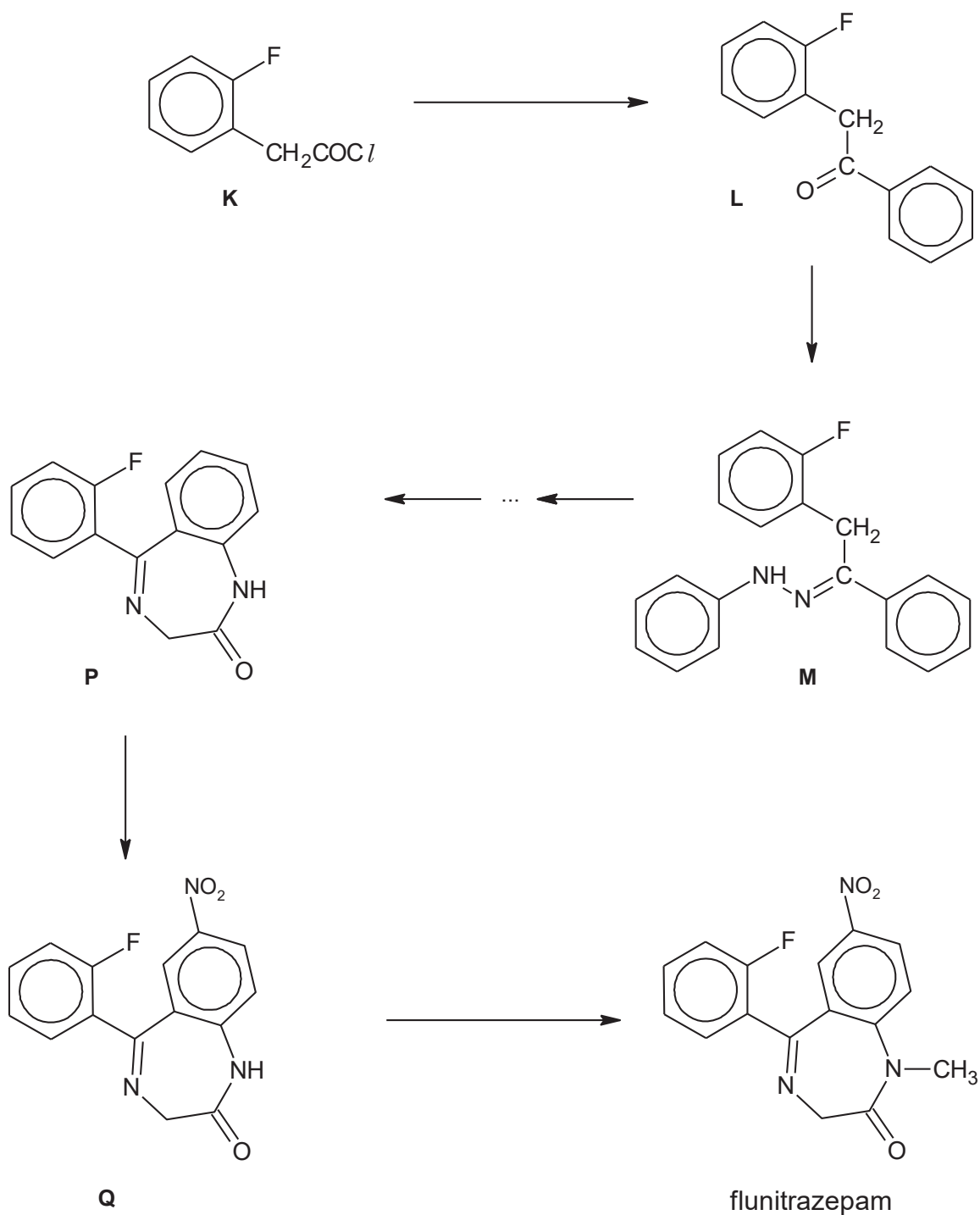
[1]

(ii) When the binding was repeated under similar conditions with butane-1,4-diamine, the standard Gibbs free energy change was found to be $-2.62 \times 10^4 \text{ J mol}^{-1}$.

Deduce the relative strength of interaction of the two polyamines with the same DNA sample. [2]

[Total: 20]

- 6 (a) Flunitrazepam is a potent sleep-inducing drug used to treat severe insomnia. Its use is under strict control in many countries. The reaction scheme below shows the synthesis of flunitrazepam from compound **K**.



- (i) Propose a synthetic route, with no more than four steps, for the synthesis of **K** from 2-fluoromethylbenzene. [5]

(ii) Suggest the reagent(s) and conditions and name the type of reaction for each of the following conversions:

(I) K to L

(II) L to M

(III) P to Q

[6]

(iii) The metabolism of flunitrazepam in human bodies is a first order reaction with a half-life of about 23.5 hours. Suggest an undesirable effect of using flunitrazepam as a sleep-inducing drug. [1]

(iv) A patient suffering insomnia took 1 tablet containing 1mg of flunitrazepam each night for consecutive 3 days. Assuming only about 80% of the flunitrazepam in each tablet can be absorbed by the body, estimate the mass of residual flunitrazepam in the patient's body on the 5th night. [2]

(b) Flunitrazepam acts as a sedative and hypnotic drug by enhancing the effect of the neurotransmitter γ -aminobutyric acid (GABA) at the GABA receptor in the brain. The IUPAC name of GABA is 4-aminobutanoic acid, $C_4H_9NO_2$.

(i) Explain why GABA exists as white crystalline powder. [1]

(ii) Experimentally, it is difficult to determine the melting point of GABA as it decomposes readily under high temperature to form a liquid compound, **R** of molecular formula C_4H_7NO .

By using the following thermochemical data, draw an appropriate energy cycle and calculate the standard enthalpy change of decomposition of GABA.

Standard enthalpy change of formation of solid GABA	$-581.1 \text{ kJ mol}^{-1}$
Standard enthalpy change of formation of gaseous R	$-197.4 \text{ kJ mol}^{-1}$
Standard enthalpy change of vapourisation of R	$+73.6 \text{ kJ mol}^{-1}$
Standard enthalpy change of combustion of hydrogen	-286 kJ mol^{-1}

[4]

(iii) Suggest the structure of compound **R**. [1]

[Total: 20]

Dunman High School
2017 Year 6 H2 Chemistry Preliminary Examination
Paper 1

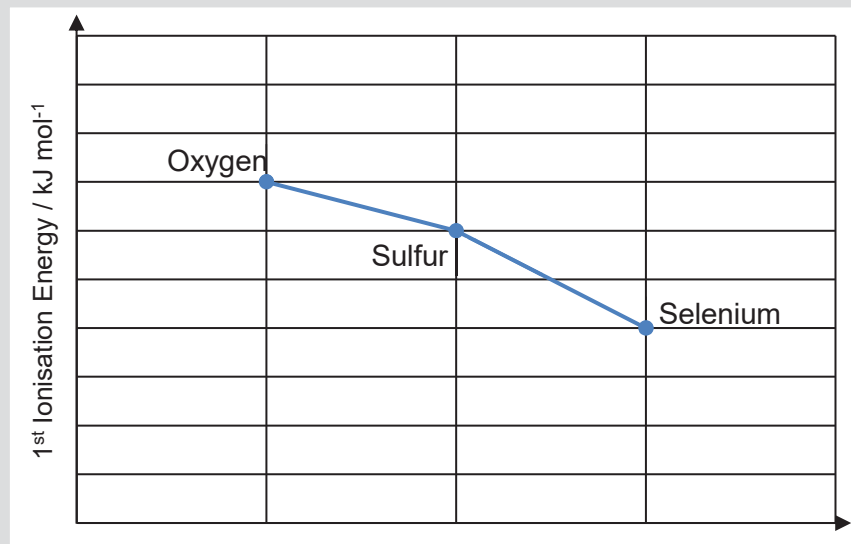
Answer Key

1	2	3	4	5	6	7	8	9	10
D	A	C	A	A	C	D	B	D	C
11	12	13	14	15	16	17	18	19	20
C	B	B	A	B	B	D	C	A	A
21	22	23	24	25	26	27	28	29	30
D	C	B	A	B	C	B	C	D	D

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

1 The chalcogens, or the oxygen family, are the elements in group 16 of the Periodic Table. These elements are common in both organic and inorganic compounds.

(a) The graph below shows the trend in the first ionisation energies of oxygen, sulfur and selenium.



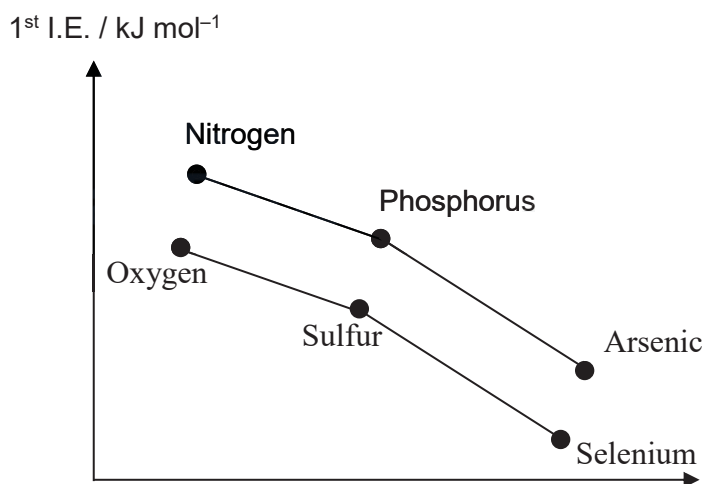
(i) Explain the trend in the first ionisation energies of oxygen, sulfur and selenium.

The first ionisation energy decreases from oxygen to selenium. This is because down the group while the nuclear charge increases, number of quantum shells increases and valence electrons are further away from the nucleus.

Hence, down the group, the valence electrons experience weaker attraction to the nucleus and a smaller amount of energy is required to remove this electron from the atom.

[2]

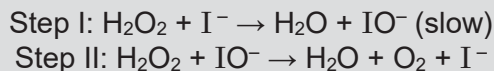
(ii) On the same grid above, sketch the trend in the first ionisation energies of nitrogen, phosphorus and arsenic.



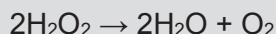
[1]

- (b) A common chalcogen-containing reagent used in both organic and inorganic synthesis is hydrogen peroxide, H_2O_2 . Hydrogen peroxide readily decomposes at room temperature.

Iodide ions, I^- , catalyse this decomposition, as shown below:



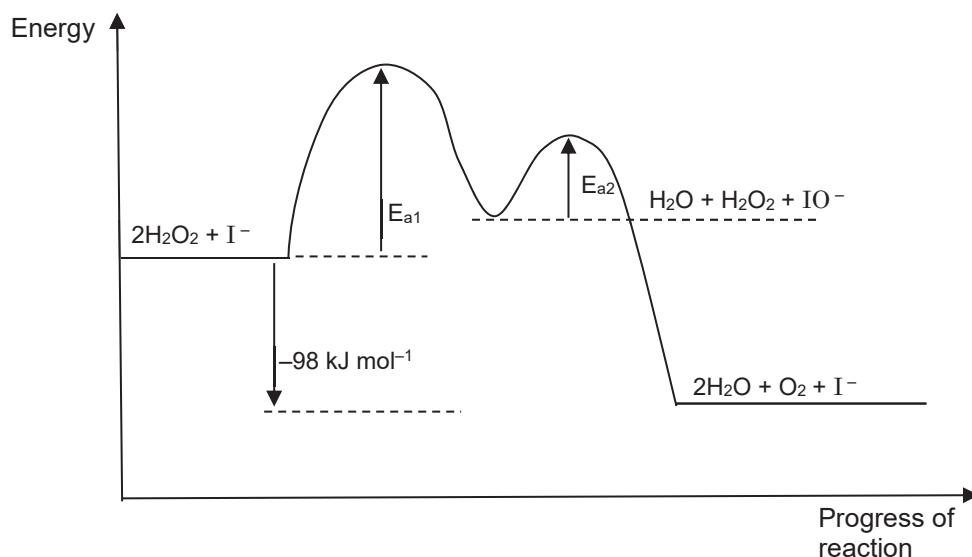
The overall equation for the decomposition of hydrogen peroxide is shown below:



The enthalpy and entropy changes for the reaction above are shown in the table below:

Enthalpy change / kJ mol^{-1}	-98
Entropy change / $\text{J K}^{-1} \text{mol}^{-1}$	+71

- (i) Using the data above, complete the diagram below to show the energy profile diagram for the decomposition of hydrogen peroxide in the presence of iodide ions.



[2]

- (ii) An unknown amount of hydrogen peroxide was allowed to decompose in a 5 dm^3 closed vessel at $120 \text{ }^\circ\text{C}$. When all the hydrogen peroxide was decomposed, a pressure of 177 kPa was measured in the vessel.

Determine the amount of hydrogen peroxide that decomposed in the vessel.
(Assume that H_2O and O_2 are ideal gases under the above reaction conditions)

$$pV = nRT$$

$$\text{Total moles of gas in vessel, } n = \frac{177000 \times 5 \times 10^{-3}}{8.31 \times (273 + 120)} = \underline{\underline{0.27098 \text{ mol}}}$$

$$\begin{aligned} \text{Hence, moles of hydrogen peroxide that decomposed} \\ &= 0.27098 \div 3 \times 2 \\ &= \underline{\underline{0.181 \text{ mol}}} \end{aligned}$$

[2]

- (c) Chalcogens are also very commonly found in organic compounds. Table 1 below shows some common oxygen or sulfur containing organic functional groups.

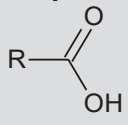
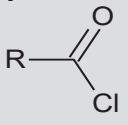
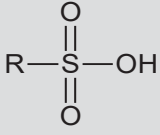
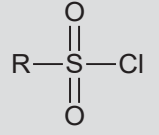
Oxygen-containing functional groups	Alcohols R-OH	Carboxylic Acids 	Acyl chlorides 
Sulfur-containing functional groups	Thiols R-SH	Sulfonic Acids 	Sulfonyl chlorides 

Table 1

- (i) Explain why carboxylic acids are generally more acidic than alcohols.

This is because the lone pair of electrons on the negatively charged oxygen of the carboxylate anion is able to delocalise over two oxygen atoms. This results in the dispersal of the negative charge and hence, the conjugate base of carboxylic acids are more stable than that of alcohols.

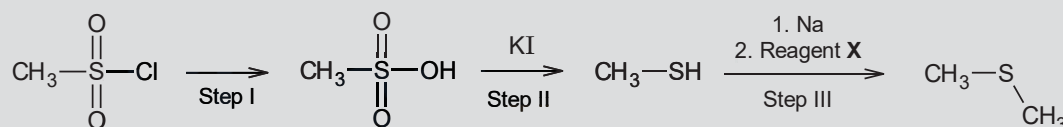
[1]

- (ii) Hence, suggest a reason why carboxylic acids are generally less acidic than their corresponding sulfonic acids.

The conjugate base of the sulfonic acids are more stable due to the presence of an additional (electronegative) oxygen atom, which allows the delocalisation of electrons over more atoms. This reduces the intensity of the negative charge on a single atom.

[1]

- (iii) A reaction scheme for the synthesis of dimethyl sulfide (CH_3SCH_3) from methylsulfonyl chloride ($\text{CH}_3\text{SO}_2\text{Cl}$) is shown below:



Given that sulfur-containing functional groups undergo similar reactions as their corresponding oxygen-containing functional groups (Table 1), suggest:

- I. The reagent(s) and condition(s) required for Step I.

H_2O

[1]

- II. The role of KI in Step II.

Reducing agent

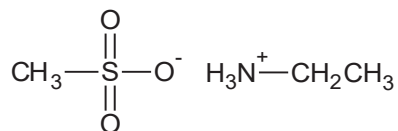
[1]

III. The identity of reagent X in Step III.



[1]

IV. The structure of the product(s) formed when methylsulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) is reacted with ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) at room temperature.



[1]

[Total: 13]

2 The electrolysis of dilute sulfuric acid was carried out using two different currents at room temperature and pressure.

	Current / A	Duration / min
Experiment 1	0.75	90
Experiment 2	0.45	90

Oxygen gas is collected at one of the electrodes.

(a) (i) Calculate the final volume of oxygen produced in experiment 2.

$$Q = I t$$

$$= 0.45 \times (90 \times 60) = 2430 \text{ C}$$



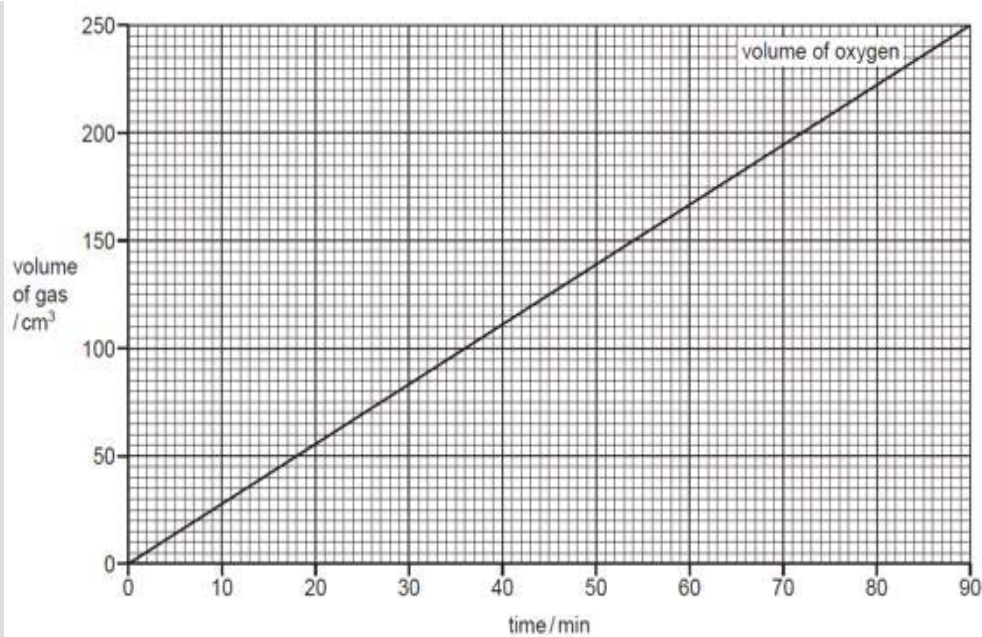
$$4\text{F} \equiv 1\text{O}_2$$

$$\text{Moles of oxygen produced} = \frac{Q}{nF} = \frac{2430}{4 \times 96500} = 6.30 \times 10^{-3}$$

$$\text{Final volume of O}_2 \text{ produced} = (6.30 \times 10^{-3}) \times 24\,000 \text{ cm}^3 = \underline{\underline{151 \text{ cm}^3}}$$

[2]

(ii) The volume of oxygen collect at one of the electrodes for experiment 1 is shown below.



On the graph above, draw a line to show each of the following:

- I. the volume of H₂ gas that would be given off in experiment 1 (Label this line 1)
- II. the volume of oxygen that would be produced in experiment 2 (Label this line 2)

[2]

- I. A straight line from the origin which has double the oxygen volume at a given time.
- II. A straight line from the origin which has 0.45/0.75 of the volume of oxygen at a given time.

(b) In another experiment, electrolysis of aqueous potassium butanedioate, (OOCCH₂CH₂COO)⁻K₂ as the electrolyte was carried out. It was found that two gases, Y and Z, were liberated at the anode in a 2:1 ratio by volume.

Gas Y formed is absorbed by soda lime while gas Z is able to decolourise bromine water.

(i) Suggest the identities of gases Y and Z. [1]

Gas Y is CO₂

Gas Z is C₂H₄

(ii) Construct the half-equation for the reaction that occurs at the anode and the cathode respectively. [2]



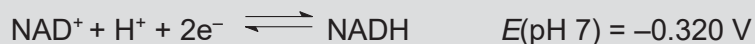
(iii) Predict the main organic product that would be obtained at the anode when a solution of potassium pentanedioate is electrolysed. [1]

Propene

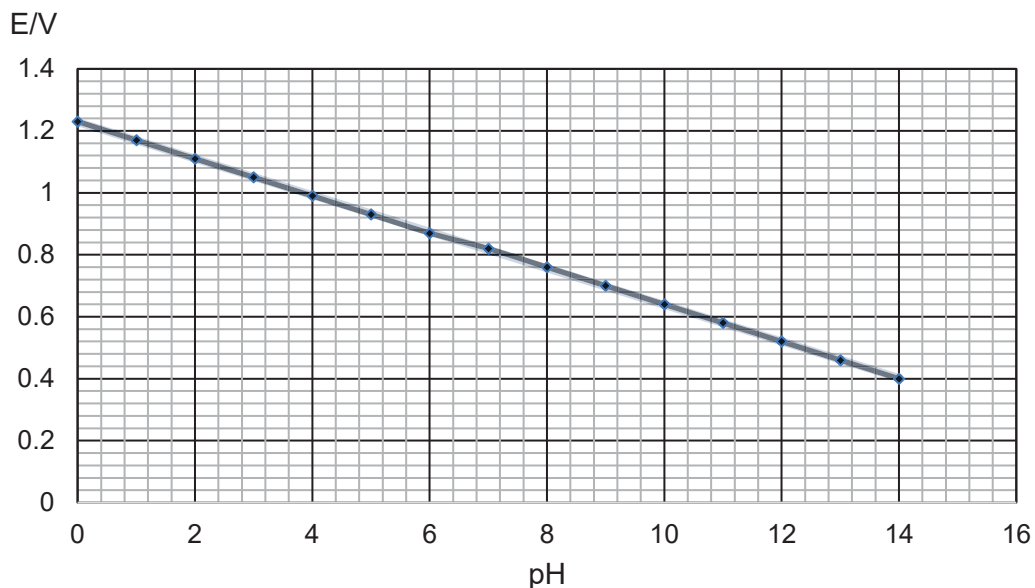
- (c) Nicotinamide adenine dinucleotide (NAD^+) is involved in redox chemistry throughout the respiratory system. Aerobic respiration is the process of producing cellular energy involving oxygen.

The electrode potential for the reduction of NAD^+ in a *biological* system, $E(\text{pH } 7)$, at 1 mol dm^{-3} , 25°C and $\text{pH } 7$, is as shown.

Its oxidised and reduced forms are represented as NAD^+ and NADH respectively.



The reduction electrode potential of oxygen at different pH is given below.

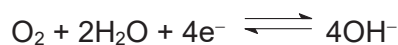


- (i) With reference to the *Data Booklet* and the graph given above, calculate the value of E_{cell} for aerobic respiration. Write a balanced equation for this reaction. [3]

At $\text{pH } 7$, reduction potential of oxygen is **+0.82 V**. That is,

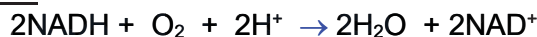


OR

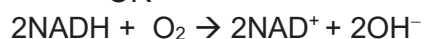


$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.82 - (-0.32) \\ = +1.14 \text{ V}$$

Equation:



OR



- (ii) State how will the E_{cell} differ if the aerobic reaction is performed at a pH of 7.4. [1]

At a higher pH , i.e. lower $[\text{H}^+(\text{aq})]$, the aerobic respiration reaction is *less* favourable and so E_{cell} will be less positive.

- (iii) Based on your answer in (c)(i), calculate $\Delta G(\text{pH } 7)$ for the aerobic respiration process. [1]

$$\begin{aligned}\Delta G(\text{pH } 7) &= -nFE(\text{pH } 7) \\ &= -(4)(96500)(+1.14) \\ &= -440\,040 \text{ J mol}^{-1} \\ &= \underline{\underline{-440 \text{ kJ mol}^{-1}}}\end{aligned}$$

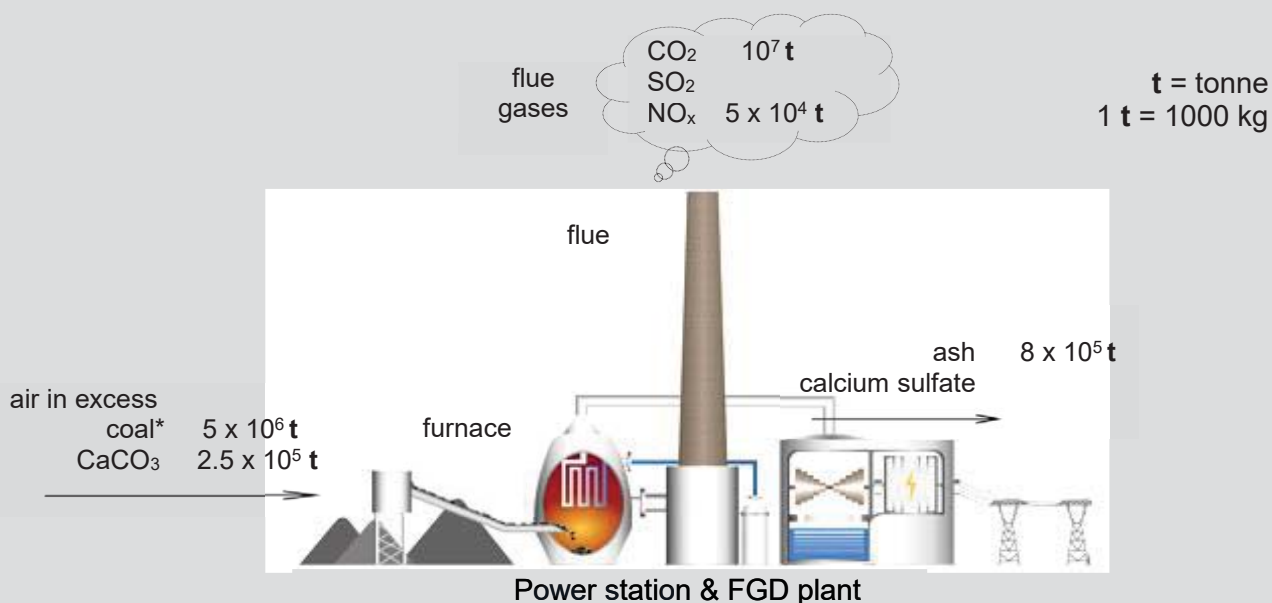
[correct answer + units]

[Total:13]

- 3 A coal-fired power station is fitted with a Flue Gas Desulfurisation (FGD) plant, which removes some of the sulfur dioxide from flue (waste) gases.

In the FGD plant, the flue gases are treated with powdered limestone, CaCO_3 , where sulfur dioxide is absorbed and reacted to produce calcium sulfite, CaSO_3 , which is oxidised by air to form solid calcium sulfate, CaSO_4 .

The diagram below shows the amounts of substances used, and produced, by such a coal-fired power station with an FGD plant in **one** year.



*coal is chiefly hydrocarbons

- (a) (i) State the process that produces the energy in the power station. [1]

Combustion of coal.

- (ii) Identify a gas, not listed in the diagram, which will be a chief component of the flue gases. [1]

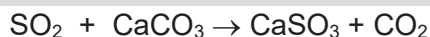
H₂O(g) or water vapour.

- (iii) Explain why oxides of nitrogen (NO_x) are present in the flue gases. [1]

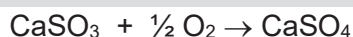
NO_x is likely formed from reaction of oxygen and nitrogen in the air at high temperatures during combustion of coal.

- (b) Write a balanced equation in each case to show how

- sulfur dioxide is removed from flue gases;



- calcium sulfate is formed. [2]



- (c) Using your answer in (b), determine the maximum mass of sulfur dioxide which could be removed in the FGD plant. [1t = 1 tonne = 1000 kg] [1]

Mass of SO_2 that could be removed in FGD plant depends on mass of CaCO_3 used.

Moles of CaCO_3 used = $2.5 \times 10^5 \times 10^6 / 100.1 = 2.4975 \times 10^9$ mol

Maximum moles of SO_2 can be removed = Moles of CaCO_3 used

Maximum mass of SO_2 removed = $2.4975 \times 10^9 \times 64.1$

= 1.60×10^{11} g or 1.60×10^8 kg or 1.60×10^5 t

- (d) Given that your answer in (c) was only 90% of the sulfur dioxide removed from the flue gases, calculate the mass of sulfur dioxide which is released into the atmosphere in **five** years by this power station when the same mass of coal is burnt each year. [1]

Mass of SO_2 released in 5 years = $(1.6009 \times 10^{11} \text{ g} \times \frac{0.10}{0.90}) \times 5$
 = 8.89×10^{10} g or 8.89×10^7 kg or 8.89×10^4 t

- (e) Another method for removing sulfur dioxide from the flue gases is to absorb it in a slurry of magnesium oxide, to produce magnesium sulfite, MgSO_3 .

- (i) Explain why magnesium oxide can also be used to remove sulfur dioxide. [1]

Magnesium oxide is basic and can undergo acid-base reaction with (acidic) sulfur dioxide.

- (ii) Magnesium sulfite decomposes readily, upon heated, to give magnesium oxide and sulfur dioxide. Magnesium oxide could be recycled, while sulfur dioxide could be used to make sulfuric acid.

Explain whether it would be easier to obtain magnesium oxide or calcium oxide from its respective sulfite. [3]

It will require less energy to decompose magnesium sulfite as magnesium sulfite is less thermally stable, due to the higher charge density, hence higher polarising power, of Mg^{2+} ion. The electron cloud of SO_3^{2-} ion will be polarised to a larger

extent by Mg^{2+} , resulting in MgSO_3 decomposing more readily to give MgO . Therefore it will be easier to obtain magnesium oxide from its respective sulfite.

- (f) When 1 mol of magnesium oxide, calcium oxide and other Group 2 metal oxides were separately dissolved in 1 dm^3 of deionised water, the pH of the resulting solutions were obtained.

Some data regarding these Group 2 metal oxides, **MO**, and their resulting solutions are provided in the table below.

ion	ionic radius/ nm	$\Delta H_{\text{hydration}} / \text{kJ mol}^{-1}$	pH of MO in water	Electronegativity difference (ΔEN) in MO
O^{2-}	0.140			
Be^{2+}	0.031	-2370	7.0	1.87
Mg^{2+}	0.065	-2024	9.0	2.13
Ca^{2+}	0.099	-1680	9.5	2.44
Sr^{2+}	0.113	?	11	2.49
Ba^{2+}	0.135	-1314	12	2.55

- (i) Suggest why there is no value for $\Delta H_{\text{hydration}}$ of the oxide ion, O^{2-} . [1]

O^{2-} reacts with water to give OH^- .
OR equation: $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$

- (ii) Using the data given, estimate $\Delta H_{\text{hydration}}$ of Sr^{2+} . [1]

enthalpy change of hydration of $\text{Sr}^{2+} = \underline{\underline{-1538 \text{ kJ mol}^{-1}}}$

- (iii) State and explain the trend in $\Delta H_{\text{hydration}}$ in the table, in terms of the interaction between cations and water. [2]

$\Delta H_{\text{hydration}}$ of cations becomes less exothermic (or its magnitude decreases) with increasing cationic radius. The increase in cationic radius results in decrease in charge density of cations. Cations will polarise the electron cloud of water molecules to a smaller extent, hence there is a decrease in strength of ion-dipole interactions formed between cations and water molecules. This results in less amount of energy evolved when cations are hydrated.

- (iv) With reference to the relevant data given in (f), suggest explanations for the increasing pH of the resulting solution from BeO to BaO in terms of:

(I) Lattice energy and enthalpy change of solution of **MO** [3]

Increasing cationic radius from Be^{2+} to Ba^{2+} , hence lattice energy becomes less exothermic (or magnitude decreases) resulting in a more exothermic (or increasing magnitude of) enthalpy change of solution from BeO to BaO .

Thus, solubility of Group 2 **MO** increases down the group.
As a result, $[\text{OH}^-]$ increases and pH of resulting solution increases.

(II) ΔEN and the nature of the bonding in **MO** [2]

ΔEN increases from BeO to BaO. This means that the metal-oxygen bond gets more ionic from BeO to BaO, thus MO gets more basic / $[OH^-]$ increases, and the pH of the resulting solution becomes higher.

[Total: 20]

- 4 (a)** Vitamin C is an essential nutrient also known as ascorbic acid. A deficiency of vitamin C leads to a disease known as scurvy.

Ascorbic acid is known to have a M_r of 176.0 and contains 40.9% of carbon and 54.5% of oxygen by mass.

- (i)** Determine the molecular formula of ascorbic acid.

	C	O	H
% mass	40.9	54.5	4.6
Divide by A_r	3.41	3.41	4.6
Simplest ratio	3	3	4

The empirical formula of ascorbic acid is $C_3O_3H_4$.

$$n[(3 \times 12.0) + (3 \times 16.0) + (4 \times 1.0)] = 176.0$$

$$n = 2$$

The molecular formula of ascorbic acid is $C_6O_6H_8$.

[2]

- (b)** Ascorbic acid is a monobasic acid, HA , and has a pK_a of 4.10. The amount of ascorbic acid contained in dietary supplement tablets can be verified by titration. A tablet containing 500 mg of ascorbic acid was dissolved in 25.0 cm^3 of deionised water.

- (i)** Calculate the volume of $0.100 \text{ mol dm}^{-3}$ sodium hydroxide required for complete neutralisation.

$$n_{acid} = \frac{0.500}{176.0} = 2.841 \times 10^{-3} \text{ mol}$$

$$v_{NaOH} \times 0.100 = 2.841 \times 10^{-3}$$

$$v_{NaOH} = 28.4 \text{ cm}^3$$

[1]

- (ii)** Calculate the initial pH of the ascorbic acid solution.

$$[HA] = \frac{2.841 \times 10^{-3}}{(25.0) \div 1000} = 0.1136 \text{ mol dm}^{-3}$$

$$K_a = 10^{-4.10}$$

$$[H^+] = \sqrt{K_a \times [HA]} = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\lg[3.00 \times 10^{-3}] = 2.52$$

[2]

- (iii)** Suggest a suitable indicator the titration. Describe the expected colour change at the endpoint.

Phenolphthalein (colorless to pink) or
Thymol blue (yellow to blue)

[1]

(iv) With the aid of a suitable equation, explain your choice of indicator in (iii).



At end point, the salt / conjugate base of ascorbic acid undergoes salt hydrolysis to form hydroxide ions. [1] with equation

The pH of the resultant solution is > 7 .

The pH transition range of selected indicator lies within the range of rapid pH change over the equivalence point of the neutralisation reaction.

[2]

(c) When a vitamin C tablet is swallowed, it dissolves in the stomach. The pH of the stomach is 2.

(i) Determine the percentage of ascorbic acid that is ionised in the stomach.

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

$$10^{-4.10} = \frac{[10^{-2}][A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Alternative method:

$$pH = pK_a + \lg \frac{[A^-]}{[HA]}$$

$$2 = 4.10 + \lg \frac{[A^-]}{[HA]}$$

$$\frac{[A^-]}{[HA]} = 10^{-2.1} = 7.93 \times 10^{-3}$$

Let α represent the percentage ionisation.

$$\frac{\alpha}{100 - \alpha} = 7.93 \times 10^{-3}$$

$$\alpha = 0.788\%$$

Alternative method:

Since $[HA] \gg [A^-]$ or since K_a is small,

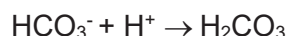
% ionisation = 0.793%

[2]

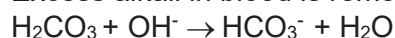
The pH of blood is maintained at 7.35 by a H_2CO_3/HCO_3^- buffer.

(ii) Using appropriate equations, explain how the buffer minimises changes in pH.

Excess acid in blood is removed by hydrogen carbonate.



Excess alkali in blood is removed by carbonic acid.



[2]

(d) Organic acids like ascorbic acid react with amines in aqueous medium.

- (i) State the type of bond formed during the reaction.

Type of bond: Ionic

[1]

- (ii) Account for the increasing basicity of primary, secondary and tertiary amines in gas phase.

As the number of electron-donating alkyl groups increases, electron density on the N atom increases or lone pair of electrons is more available for donation.

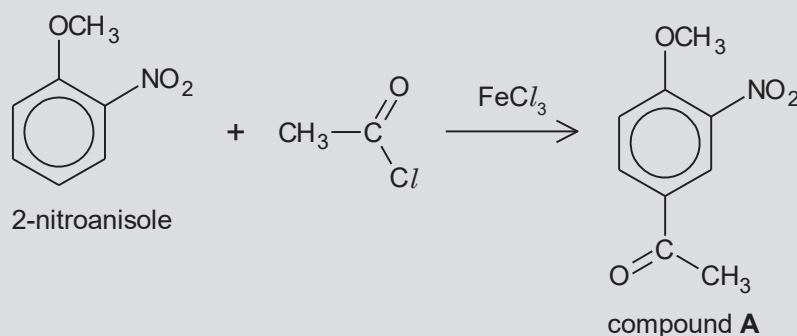
[1]

[Total: 15]

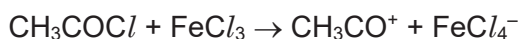
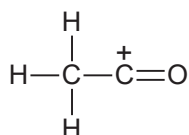
- 5 In Friedel-Crafts acylation, FeCl_3 is employed to attach an acyl group to an aromatic ring via electrophilic substitution.

(a)

For example, compound **A** can be prepared by the reaction of 2-nitroanisole with ethanoyl chloride in the presence of FeCl_3 .

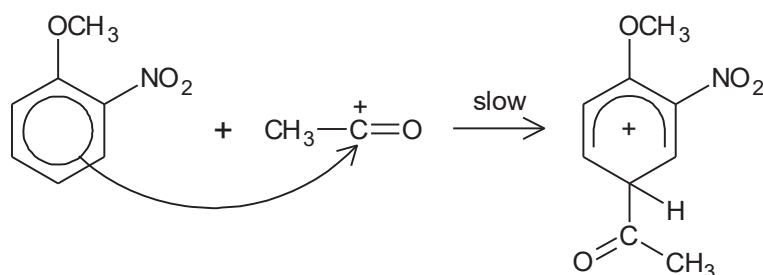


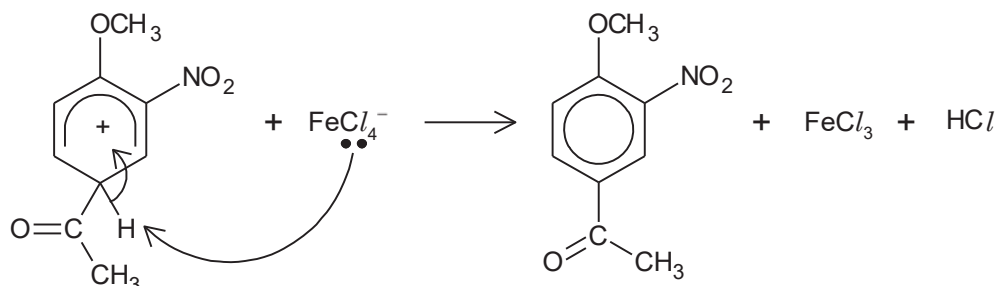
- (i) Draw the displayed formula of the electrophile and write an equation to show how it is generated.



[2]

- (ii) Using your answer in (i), draw the mechanism of the acylation of 2-nitroanisole by ethanoyl chloride. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.





[2]

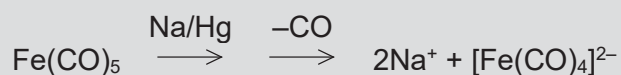
Empirical evidence shows that the electrophile generated in (i) is not exceptionally reactive. As such, the Friedel-Crafts acylation of nitrobenzene by ethanoyl chloride does not take place under any conditions.

(iii) Explain why nitrobenzene does not undergo acylation but the presence of the $-OCH_3$ group in 2-nitroanisole permits acylation.

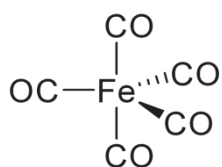
- The $-NO_2$ group is a highly deactivating substituent.
- It reduces the electron density of benzene ring such that it becomes less susceptible to an electrophilic attack by a rather unreactive electrophile like CH_3CO^+ .
- The presence of a second strongly activating group like $-OCH_3$ increases the electron density of benzene ring sufficiently for it to be susceptible to electrophilic attack by CH_3CO^+ .

[2]

(b) Another iron compound, $Na_2[Fe(CO)_4]$, is used in the reaction between alkyl halides and carbon monoxide to synthesise ketones. This iron-based reagent is made as follows.



(i) Draw the structure of $Fe(CO)_5$ to show its shape clearly.



[1]

(ii) The oxidation state of Fe in $Fe(CO)_5$ is 0 and the CO ligands are neutral. Suggest the oxidation state of Fe in the $[Fe(CO)_4]^{2-}$ anion.

-2

[1]

(iii) Besides the oxidation states exhibited in the above reaction, iron also exists in other oxidation states like +2 and +3.

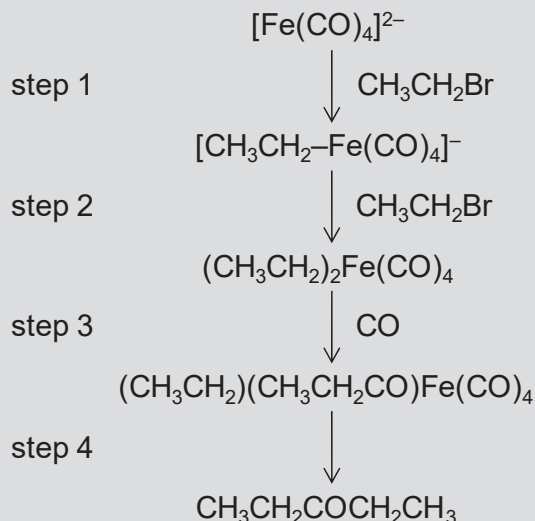
State a property of iron that allows its compounds to behave in this manner and give a reason why this property arises in iron.

- Fe exhibits variable oxidation states.

- In transition elements, 3d and 4s orbitals / electrons are similar in energy OR 3d orbitals which are partially filled, which allows the removal or accepting of electrons without requiring much more energy.

[2]

The reaction between $[\text{Fe}(\text{CO})_4]^{2-}$ and bromoethane takes place under an applied pressure of carbon monoxide via the following steps.



- (iv) Explain what is meant by the term *coordination number* in the context of a metal complex.

State the coordination number of iron in $[\text{Fe}(\text{CO})_4]^{2-}$ and in $(\text{CH}_3\text{CH}_2)(\text{CH}_3\text{CH}_2\text{CO})\text{Fe}(\text{CO})_4$.

The coordination number is the number of dative covalent bonds formed between ligands and the central metal atom or ion.

	coordination number of iron
$[\text{Fe}(\text{CO})_4]^{2-}$	4
$(\text{CH}_3\text{CH}_2)(\text{CH}_3\text{CH}_2\text{CO})\text{Fe}(\text{CO})_4$	6

[2]

- (v) Studies show that steps 1 and 2 proceed via nucleophilic substitution.

If bromoethane were replaced by bromobenzene, the above reaction with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ would not work. With reference to the bonding and structure of bromobenzene, give **two** reasons why both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ cannot occur.

- A p orbital of Br atom overlaps with the p orbitals of C atoms in benzene ring.
- The lone pair of electrons in this p orbital delocalises into the benzene ring to form a delocalised π electron cloud.
- This results in a partial double bond character in the C–Br bond.
- Large amount of energy is needed to break the C–Br bond, making it very difficult for both $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ to occur.
- The rear end of the C–Br bond in bromobenzene is sterically hindered by the

bulky benzene ring.

OR

- The π electron cloud repels the lone pair of electrons of the incoming nucleophile and hinders the rear end attack of the electrophilic C bearing the Br atom.
- This makes it difficult for S_N2 to occur.

[3]

[Total: 15]

Dunman High School
2017 Year 6 H2 Chemistry
Preliminary Examination Paper 3 (Answer Scheme)
Section A

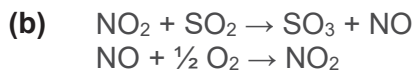
- 1 (a) (i)
1. The gas *particles* have negligible volume compared to the volume of the container.
 2. There are no intermolecular forces of attraction between gas particles.

Its electron cloud size is larger hence volume of NO₂ molecules is significant compared to the volume of the gas, unlike H₂.

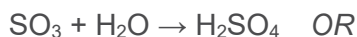
Both NO₂ and H₂ have simple molecular structure. Since NO₂ has stronger permanent dipole-permanent dipole interaction than instantaneous dipole-induced dipole interactions in H₂ OR NO₂ has a larger electron cloud size than H₂, the electron cloud of NO₂ is more polarisable and hence stronger intermolecular forces of attraction.

(ii) $pV = nRT = (m/M)RT$
 $p = (m/V)(RT/M)$
 $\frac{p}{\rho} = RT/M$
At 100 °C and very low pressure,
RT/M = 110.3
M = (8.31 x 373) / 110.3
= 28.1 g mol⁻¹
M_r = 28.1

(iii) CO



NO₂ catalyses by oxidising SO₂ to SO₃, while itself is reduced to NO. NO is rapidly re-oxidised to NO₂ by oxygen, regenerating the catalyst, NO₂.



SO₃ dissolves in the water vapour in the atmosphere/ rain to form sulfuric acid, which causes acid rain.

- (c) (i) Order w.r.t [O₂] is zero as the graph of [O₂] against time is a downward sloping straight line / the gradient of the line, i.e. rate of reaction, is constant with changing [O₂].

When [SO₂] = 0.8 mol dm⁻³,

$$r_1, \text{ rate of reaction} = \left| \frac{0.04 - 0.05}{88} \right| = 1.13 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

When [SO₂] = 1.2 mol dm⁻³,

$$r_2, \text{ rate of reaction} = \left| \frac{0.030 - 0.05}{80} \right| = 2.50 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$r_2/r_1 = 2.21 \approx 2.25$$

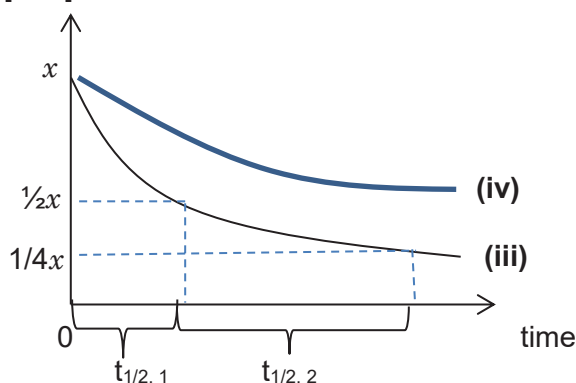
When [SO₂] x 1.5 times, rate of reaction x 2.25 times, reaction is second order w.r.t [SO₂].

(ii) $\text{rate} = k[\text{SO}_2]^2$

When $[\text{SO}_2] = 0.8 \text{ mol dm}^{-3}$,
 $k = 1.77 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

($k = 1.74 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, if $[\text{SO}_2] = 1.2 \text{ mol dm}^{-3}$)

(iii) $[\text{SO}_2] / \text{mol dm}^{-3}$



2 (a) For hexane / cyclohexane mixture,

- Energy produced from instantaneous dipole – induced dipole (id-id) interactions between hexane and cyclohexane molecules after mixing
- is just sufficient to overcome id-id interactions between hexane molecules and between cyclohexane molecules before mixing.
- Thus no heat change is observed.

For hexane / ethanol mixture,

- Energy produced from weak id-id interactions between hexane and ethanol molecules after mixing
- is insufficient to overcome stronger hydrogen bonds between ethanol molecules before mixing.
- Thus heat is absorbed from the surroundings for mixing to occur.

(b) (i)

	bonds broken	bonds formed	$\Delta H / \text{kJ mol}^{-1}$
step 1	1 C=C	1 C-C 1 C-I	$(-350 - 240) + 610 = +20$
step 2	1 H-Cl	1 C-H	$-410 + 431 = +21$

- (ii)
- Only the free radical addition of HBr to an alkene is likely to occur since $\Delta H_{\text{step 1}}$, $\Delta H_{\text{step 2}}$ are all exothermic.
 - This reaction is however unlikely to occur if HCl and HI were used.
 - In each case, there is one propagation step which is endothermic — step 2 for HCl and step 1 for HI.

(iii) $\text{CH}_3\text{CHICH}_3$

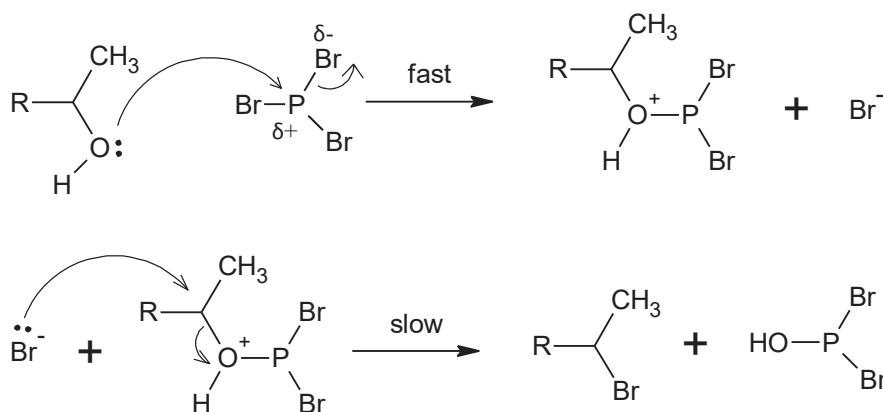
2 (c) (i) Q : AgI
R : AgCl

- Reaction I is the nucleophilic substitution of a halogenoalkane in which C–X bonds (where X = Cl, I) are broken to release X[−] ions into solution to be precipitated as AgX.
- Rate of substitution depends on the strength of C–X bond.

From the *Data Booklet*, BE(C–Cl) : 340 kJ mol^{−1}
BE(C–I) : 240 kJ mol^{−1}

- C–I bond is weaker OR more easily broken than C–Cl bond OR less amount of energy is needed to break C–I than C–Cl bond.
 - Thus, time taken for I[−] ions to be released is shorter than that for Cl[−] ions OR C–I bond is broken first OR AgI is precipitated first.
- (ii)
- LiAlH₄ is a nucleophilic reducing agent OR is electron-rich.
 - It attacks the electrophilic OR electron-deficient carbonyl C atom in carbonyl compounds, carboxylic acids and their derivatives but does not reduce electron-rich C=C bonds in alkenes.
- (iii) Step III: I₂(aq) with NaOH(aq), heat

3 (a) (i)



- 3 (a) (ii) Lewis acid. PBr₃ accepts a lone pair of electrons from oxygen in the first step of the mechanism.
- (iii) For phenol, the lone pair of electron on the oxygen atom is delocalised into the benzene ring and hence less available for donation and hence, phenol will be a weaker nucleophile, resulting in a relatively slower first step.
- (iv) Phenol undergoes electrophilic substitution instead of addition to prevent the loss of its aromaticity (and resonance stability).
- (v) Chemical test 1: Add KMnO₄ and dilute H₂SO₄, heat (in water bath)
Observation for phenol: Purple KMnO₄ does not decolourise
Observation for 2° alcohol used in (a): Purple KMnO₄ decolourises

OR

Chemical test 2: Add I₂ and NaOH, warm/heat (in water bath)
Observation for phenol: No yellow ppt forms
Observation for 2° alcohol used in (a): Yellow precipitate forms

OR

Chemical test 3: Add neutral FeCl₃(aq)
Observation for phenol: Violet colouration observed

Observation for 2° alcohol used in (a): No violet colouration observed

OR

Chemical test 4: Add $K_2Cr_2O_7$ and dilute H_2SO_4 , heat (in a water bath)

Observation for phenol: Solution remains orange

Observation for 2° alcohol used in (a): Orange solutions turns green

3 (b) (i)

	$PCl_3(g)$	+	$Cl_2(g)$	\rightleftharpoons	$PCl_5(g)$
Initial partial pressure / atm	2		1.5		0
Change in partial pressure / atm	-x		-x		+x
Eqm Partial pressure/ atm	$2 - x$		$1.5 - x$		x

Hence, $(2 - x) + (1.5 - x) + x = 3.3$

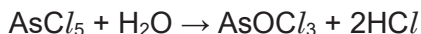
Partial pressure of PCl_5 at eqm, $x = 0.2$ atm

$$K_p = \frac{(0.2)}{(2-0.2)(1.5-0.2)} = 0.0855 \text{ atm}^{-1}$$

(ii) Since K_p is much less than 1, the position of the equilibrium lies to the left (or to the reactant side). This means that the forward reaction is not likely to be spontaneous and hence, ΔG should be positive.

(c) (i) $AsCl_5 + 4H_2O \rightarrow H_3AsO_4 + 5HCl$

Or



$AsCl_5$ completely hydrolyses in water to produce a strong acid, HCl , which is responsible for the very low pH.

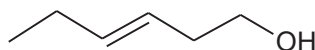
(ii)



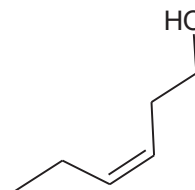
Bond angle: **180°**

4 (a) (i) Constitutional isomers are compounds with the same molecular formula but differs in structural formula.

(ii)



trans



cis

(b) (i) If Cu^{2+} is not complexed, it will form $\text{Cu}(\text{OH})_2$ solid in alkaline medium and hence will not be able to react with the (aldehyde) functional group.

(ii) Cu^{2+} is a transition metal ion while K^+ is not.
 Cu^{2+} has low lying partially-filled orbitals (or vacant subshell of low energy) which allows it to accept lone pair of electrons from tartrate ions to form a dative bond in complex formation.
 K^+ , however, does not have low lying orbitals to form dative bonds with tartrate ligands.

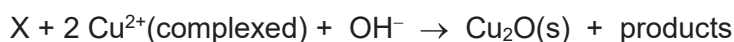
(iii) $\text{CH}_2\text{CCH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$ OR

$\text{CH}_2\text{CCH}_3(\text{CH}_2)_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$ OR

$\text{CH}_2\text{CCH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CHO}$

(iv) Amount of $\text{Cu}_2\text{O} = \frac{0.282}{143} = 0.00197 \text{ mol}$

General equation (unbalanced):



1 X \equiv 2 $\text{Cu}^{2+}(\text{complexed}) \equiv$ 1 $\text{Cu}_2\text{O}(\text{s})$

Amount of X present = 0.00197 mol
 Mass of X present = 0.00197 \times M_r of X
 = 0.00197 \times 154.0
 = 0.3037 g

Percentage of compound X present = $\frac{0.3037}{2.0} \times 100\% = 15.2\%$

(v) From (iv), (max) mass of X vapourised/ present = 0.3037 g

Given that minimum concentration of X in the air to be "detectable" is 10 ppm,

i.e. 10 g of X in 1×10^6 g of air,

$$\begin{aligned} \text{(Max) Mass of air for 0.3037 g of X to be detectable} &= 0.3037 \times \left(\frac{1 \times 10^6}{10} \right) \\ &= 30\,370 \text{ g} \\ &= 30.37 \text{ kg} \end{aligned}$$

Given that the density of air is 1.20 kg m^{-3} ,

$$\text{Volume of air} = \frac{30.37}{1.20} = 25.3 \text{ m}^3$$

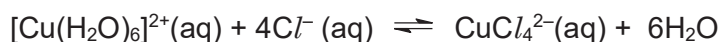
- (c) (i) Copper in solution Y has oxidation state of +1. Electronic configuration of Cu(I) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
The ion has a fully-filled d orbitals (or no vacant or partially-filled d orbitals, hence a d electron from lower energy orbital cannot be promoted to a higher energy d orbital. Therefore, solution Y is colourless.



OR



- (d) $\text{Cu}^{2+}(\text{aq})$ which is $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ is blue in colour. When solid sodium chloride is added, it provides high $[\text{Cl}^-]$, causing H_2O ligands to be displaced by Cl^- ligands, forming $\text{CuCl}_4^{2-}(\text{aq})$ complex, which is yellow in colour. When the following equilibrium is established, the presence of both $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ and $\text{CuCl}_4^{2-}(\text{aq})$ makes the solution appear yellow-green.



Upon addition of water, the equilibrium system is diluted. The aqueous reactants are diluted to a larger extent. By Le Chatelier's Principle, addition of water causes equilibrium position to shift to the left. Thus, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ ion dominates, reproducing the blue colour.

In the presence of sulfate ions, no ligand exchange reaction takes place, hence no change is observed as sulfate is a weaker ligand than H_2O .

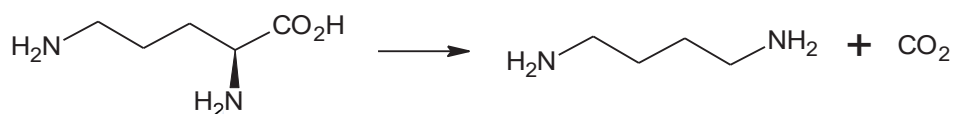
Section B

Answer **one** question from this section.

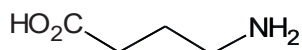
- 5 (a) (i) Gaseous by-product: CO_2

AND

Equation (stereochemistry not required):



- (ii) Structure:



Name: 4-aminobutanoic acid

- (iii) K_b is a measure of the strength/ basicity of a weak base.

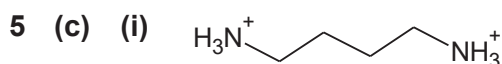
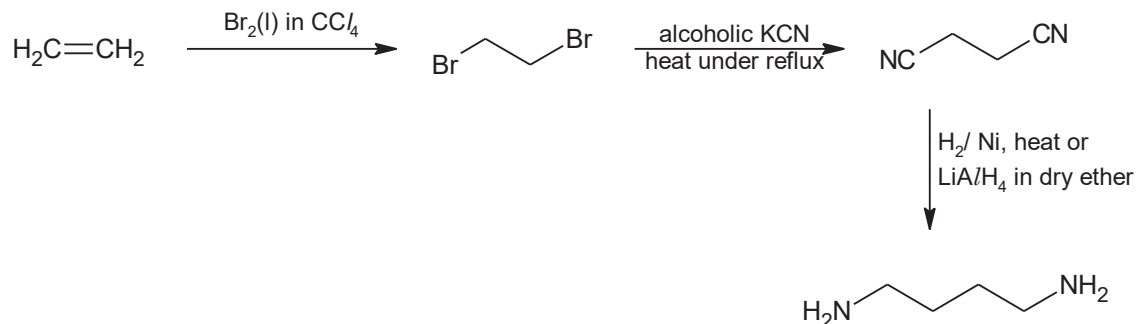
OR

$$K_b \text{ of a weak base, B} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

(iv) K_b : α -NH₂ of L-ornithine < R-NH₂ of L-ornithine

α -NH₂ of L-ornithine is closer to the electron-withdrawing $-\text{CO}_2\text{H}/-\text{CO}_2^-$ group which decreases the availability of the lone pair of electrons on N atom of α -NH₂. Hence, α -NH₂ is a weaker base than R-NH₂ of L-ornithine.

5 (b)



(ii) Ionic bonding

(d) (i) At the higher molar ratios, there is a large excess of unbound butane-1,4-diamine as binding sites of the DNA sample become saturated so energy change per mole of butane-1,4-diamine added is zero.

(ii) Endothermic since enthalpy change is positive when butane-1,4-diamine is added to the DNA sample.

(iii) $\Delta G < 0$ since binding of butane-1,4-diamine with the DNA sample is spontaneous.

Since $\Delta G = \Delta H - T\Delta S$ and $\Delta H > 0$, $\Delta S > 0$ and $|T\Delta S| > |\Delta H|$ in order for $\Delta G < 0$.

(iv) The displacement of water molecules surrounding the DNA molecule disrupts the orderly arrangement which leads to an increase in disorder of the system.
OR

The moles of water molecules displaced from the DNA molecule are more than the moles of butane-1,4-diamine that bind with it, leading to an increase in disorder of the system.

5 (e) (i) $\Delta G^\ominus = -(8.31)(290)(\ln 4.88 \times 10^5)$
 $= -315650$
 $= -31\,600 \text{ J mol}^{-1}$

(ii) Since ΔG^\ominus for butane-1,4-diamine is less negative than that for spermine, the binding constant K for butane-1,4-diamine is smaller than that for spermine.

Hence butane-1,4-diamine interacts/ binds less strongly with the DNA than spermine.

OR

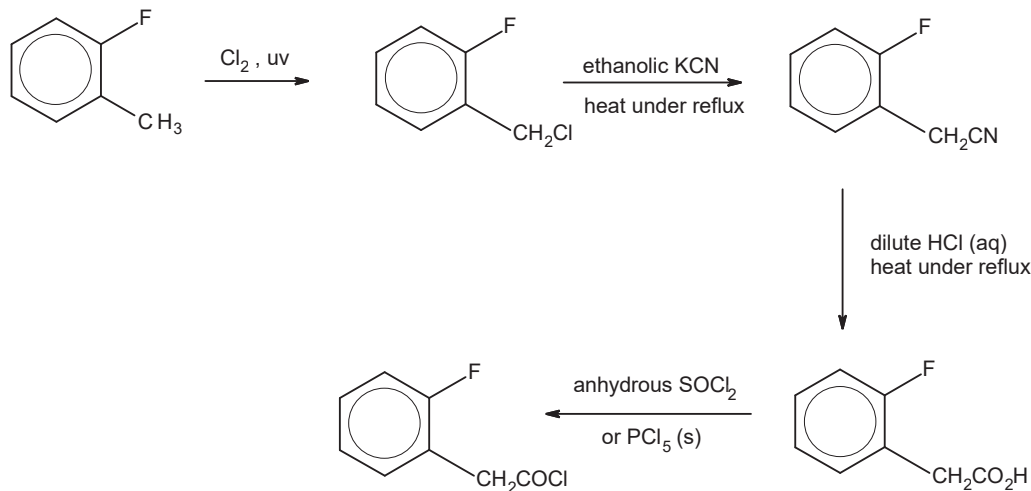
$$-2.62 \times 10^4 = -(8.31)(290)(\ln K)$$

$$K = 52\,671$$

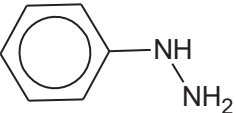
$$= 5.27 \times 10^4$$

Since the magnitude of K for butane-1,4-diamine is lower than that of spermine, butane-1,4-diamine interacts/ binds less strongly with the DNA than spermine.

6 (a) (i)



(ii)

	reagent(s) and conditions	type of reaction
(I)	C_6H_6 , (anhydrous) AlCl_3 or FeCl_3	Electrophilic substitution
(II)	 OR phenylhydrazine	Condensation
(III)	dilute HNO_3	Electrophilic substitution

(iii) The half-life is too long and the patient will still be in a drowsy/ hangover state in the following day. / The effect of taking flunitrazepam at night will persist in the next day. / It takes too long for the sleep inducing effect of the drug to kick in. / There could be an overdose of the drug, due to its slow metabolism which results in accumulation of drug, if the patient continues to take drug on consecutive days.

(iv) Approximating $t_{1/2}$ of 23.5 h as 24 h or a day,

Day	Active mass absorbed / mg	Mass remained from previous day / mg	Total mass left / mg
1	0.8		
2	0.8	0.4	1.2
3	0.8	0.4 + 0.2	1.4
4	-	0.4 + 0.2 + 0.1	0.7
5	-	0.2 + 0.1 + 0.05	0.35

