

RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME		
CLASS	6	
CENTRE NUMBER	S INDEX NUMBER	
H2 CHEM	IISTRY	9729/01
Paper 1 Multipl	e Choice	20 September 2018 1 hour
Additional Mate	rials: Multiple Choice Answer Sheet	

terials: Multiple Choice Answer Sheet Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

Write your name, class and index number on the Optical Answer Sheet in the spaces provided.

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

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

Read the instructions on the Answer Sheet very carefully.

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

Any rough working should be done in this booklet.

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

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

For each question there are four possible answers, **A**, **B**, **C** and **D**.

Choose the **one** you consider to be correct.

1 A mixture of argon and another gas is commonly used during welding. At s.t.p, the density of the gaseous mixture is 1.82 g dm⁻³.

What is the identity of the other gas in the mixture?

[Density of argon = 1.78 g dm^{-3} at s.t.p.]

- A neon
- **B** nitrogen
- **C** oxygen
- **D** carbon dioxide
- 2 Sodium thiosulfate (Na₂S₂O₃) is used in the textile industry to remove an excess of chlorine from bleaching processes by reducing it to chloride ions.

If 10 cm³ of 0.20 mol dm⁻³ of sodium thiosulfate requires 192 cm³ of chlorine for complete reaction at r.t.p., which of the following is a possible formula of the sulfur-containing product?

- 3 Which of the following ions would undergo the smallest deflection in an electric field?

A ${}^{16}O_2{}^+$ **B** ${}^{16}O^{18}O^+$ **C** ${}^{16}O^{18}O^{2+}$ **D** ${}^{18}O^{2+}$

4 The table below shows the fourth ionisation energies of five consecutive elements in the Periodic Table.

Element	V	W	Х	Y	Z
Fourth ionisation energy / kJ mol ⁻¹	10450	11710	4350	5030	4580

What is the formula of the bromide of V?

A VBr B VBr ₂ C VBr ₃ D VE	A VBr
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5 Two identical bulbs at the same temperature contain ideal gases P and Q separately. The density of gas P is half that of gas Q while the molecular mass of gas P is twice that of gas Q.

What is the ratio of the pressure of gas P to that of gas Q?

A 1:1 **B** 1:2 **C** 1:4 **D** 2:1

6 The auto-ionisation of bromine trifluoride is represented by the equation:

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Which of the following statements is correct?

- **A** BrF₃ is planar while BrF_{4^-} is non-planar.
- **B** BrF_{2^+} is linear while BrF_{4^-} is tetrahedral in shape.
- **C** The F–Br–F bond angle in BrF_3 is smaller than that in BrF_2^+ .
- **D** There are more lone pairs of electrons around the Br atom in BrF_3 than that in BrF_2^+ .
- 7 Dimerisation is described as a process in which two identical molecules combine to give a single product. Some examples include Al₂Cl₆, N₂O₄ and (CH₃CO₂H)₂.

Which of the following statements about the above dimers are correct?

- 1 Hydrogen bonds hold the CH₃CO₂H molecules together in the dimer.
- 2 All the nitrogen-oxygen bonds in N_2O_4 are of equal length.
- 3 The bond angle around each aluminium atom in Al_2Cl_6 is 109.5°.
- **A** 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3

8 Vaporisation is the process when a liquid is converted to a gas.

Given that the enthalpy change of vaporisation of water is +40.8 kJ mol⁻¹, what is the entropy change when 36.0 g of water boil to form water vapour?

- A +109 J K⁻¹
- **B** -109 J K⁻¹
- **C** +219 J K⁻¹
- **D** –219 J K⁻¹

9 At T °C and a total pressure of 6.00 atm, N₂O₄ is 60.0% dissociated into NO₂. What is the $K_{\rm p}$ value at T °C?

A 3.0 **B** 5.4 **C** 13.5 **D** 21.6

10 H₂A is a weak acid which undergoes partial dissociation.

$$H_2A(aq) \rightleftharpoons 2H^+(aq) + A^{2-}(aq)$$

Given that the pH of 1.00 mol dm⁻³ H₂A(aq) solution is 2.3, what is the degree of dissociation of H₂A?

A 2.50×10^{-3} **B** 5.01×10^{-3} **C** 1.26×10^{-5} **D** 1.26×10^{-7}

11 The auto-ionisation of water is an endothermic process.

 $H_2O(I) \rightleftharpoons H^+(aq) + OH^-(aq)$ $\Delta H = +6.5 \text{ kJ mol}^{-1}$

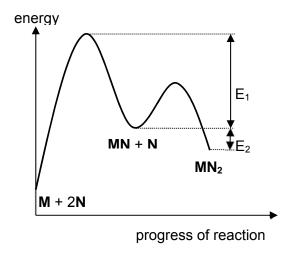
Which of the following statements are correct?

- 1 K_{w} increases as temperature increases.
- 2 pH of solution decreases as temperature increases.
- 3 Acidity of water increases as temperature increases.
- **A** 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3
- **12** What is the pH of a saturated solution of aluminium hydroxide, $Al(OH)_3$, if its solubility product is 2.53×10^{-18} mol⁴ dm⁻¹²?

A 4.28 B 5.44 C 9.60	D D 9.72
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13 The energy profile diagram of the reversible reaction between M and N is shown below.



Which of the following statements are correct?

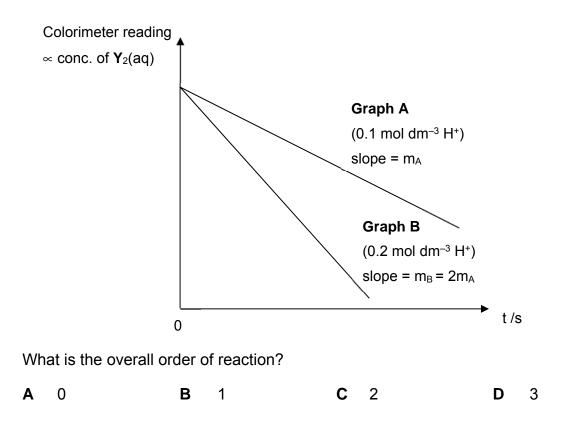
- 1 The activation energy of the reverse reaction is $E_1 + E_2$.
- 2 Rate equation of the reaction is rate = $k[\mathbf{M}][\mathbf{N}]^2$.
- 3 The equilibrium [**MN**₂] increases as temperature increases.
- **A** 1 and 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

14 The acid-catalysed reaction between X and Y_2 in aqueous solution has been investigated.

$$X + Y_2(aq) \xrightarrow{H^+} XY(aq) + HY(aq)$$

It has been found that rate equation is rate = $k[X][Y_2]^m[H^+]^n$.

The change in concentration of Y_2 remaining for this reaction is measured by using a photoelectric colorimeter. **Graph A** is obtained when the concentration of hydrogen ions used is 0.1 mol dm⁻³.



- **15 W** and **X** are 2 different elements in Period 3. The following are some of their properties:
 - The oxide of **W** is insoluble in water, but is soluble in both NaOH(aq) and HC*l*(aq).
 - The chloride of **X** dissolves completely in water to give a colourless solution of pH = 2.

Which of the following is the likely identity of element **W** and **X**?

	W	X
Α	Al	Р
В	Al	Si
С	Mg	Р
D	Mg	Si

16 Y and Z are two different elements from the same Group. The chlorides of both Y and Z have giant ionic lattice structure.

Which of the following statements is inconsistent with the other options?

- **A** The first ionisation energy of **Y** is less endothermic compared to **Z**.
- **B** The oxide of **Y** is less soluble in water compared to the oxide of **Z**.
- **C** The magnitude of the lattice energy of chloride of **Y** is higher compared to the chloride of **Z**.
- **D** The carbonate of **Y** decomposes at a lower temperature compared to the carbonate of **Z**.

17 Purification of copper involves placing the impure copper at the anode of an electrolytic cell of CuSO₄(aq) and running a current though the setup. Over time, pure copper will be deposited on the cathode.

In a particular setup, a copper sample with zinc and silver impurities was placed at the anode and a current of 6.00 A was passed through the circuit for 11 min. The cathode was then found to have an increase of mass of 1.12 g.

Which of the following statement is likely to be incorrect?

- A Less time is needed if [CuSO₄] is increased.
- **B** Anodic sludge containing silver would be formed.
- **C** The maximum mass of copper that can be purified is 1.30 g.
- **D** There would be Zn^{2+} ions found in the solution after the purification process.
- **18** Use of the Data Booklet is relevant to this question.

Patterns or designs can be etched on copper objects as a way to improve its aesthetics. Etching of copper objects are can be done chemically, where a solution of etching chemical is poured over copper surface to dissolve part of the copper.

Which of the following solution cannot be used as an etching chemical?

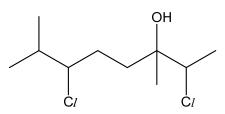
- A Fe²⁺(aq)
- **B** Fe³⁺(aq)
- C Mn³⁺(aq)
- **D** acidified $Cr_2O_7^{2-}(aq)$

19 Which of the following galvanic cell information is incorrect?

You may assume that all ions stated are at 1.00 mol dm^{-3} and all measurements are made at standard conditions.

	Half-	cell 1	Half-	cell 2		
	Electrolyte	Electrode (Anode)	Electrolyte	Electrode (Cathode)	<i>E</i> ⊖ _{cell} / V	
A	H⁺ Mn²⁺ MnO₄⁻	Pt	Fe ²⁺ Fe ³⁺	Pt	+0.75	
в	Mn ²⁺	Mn	Fe ²⁺ Fe ³⁺	Pt	+1.95	
С	Mn ²⁺	Mn	Fe ²⁺	Fe	+0.74	
D	Fe ²⁺	Fe	Mn ²⁺ Mn ³⁺	Pt	+1.98	

20 The following molecule is a derivative of linalool.



How many isomers may be formed when the molecule is heated under reflux with excess ethanolic potassium hydroxide?

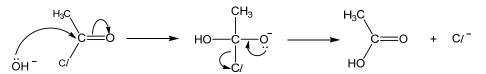
Α	2	В	4	С	6	D	8
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21 Ethane reacts with chlorine gas in the presence of ultraviolet light to form a mixture via free radical substitution.

Which statement about this reaction is true?

- **A** Homolytic fission occurs only in the initiation step.
- **B** Bond formation occurs only in the termination step.
- **C** Chloroethane is formed only in the propagation step.
- **D** Small quantities of butane is formed only in the termination step.

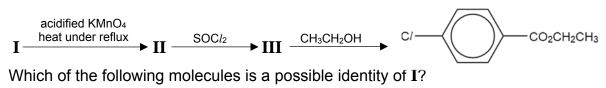
- **22** Which of the following compounds are formed in the reaction between ethene and aqueous bromine in the present of sodium ethoxide (CH₃CH₂O⁻Na⁺)?
 - 1 BrCH₂CH₂OH
 - 2 BrCH₂CH₂OCH₂CH₃
 - 3 CH₃CH₂OCH₂CH₂OCH₂CH₃
 - **A** 1 and 2 only **B** 2 and 3 only **C** 1 and 3 only **D** 1 only
- **23** Which of the following sequence of steps is expected to give the best yield for the synthesis of 3-bromo-4-methylphenylamine from benzene?
 - A alkylation, nitration, bromination, reduction
 - **B** alkylation, nitration, reduction, bromination
 - **C** bromination, alkylation, nitration, reduction
 - **D** nitration, alkylation, reduction, bromination
- **24** In which of the following pairs of compounds is the compound on the left more volatile than that on the right?
 - 1 propylamine and propan-1-ol
 - 2 pentan-2-one and pentan-2-ol
 - 3 cyclohexylamine and aminoethanoic acid
 - **A** 1 only **B** 1 and 2 only **C** 2 and 3 only **D** 1, 2 and 3
- **25** The two-stage reaction given below shows a possible mechanism for the reaction between hydroxide ions and ethanoyl chloride.



Which of the following best describes the overall reaction mechanism?

- A electrophilic substitution
- **B** electrophilic addition
- **C** nucleophilic substitution
- **D** nucleophilic addition

26 Consider the reaction scheme below:



Α	В
с	D

27 A compound **X**, with molecular formula $C_9H_{10}O_2$, is heated under reflux with NaOH(aq) and the resulting mixture then cooled and acidified with $H_2SO_4(aq)$. The final products include a compound that turns blue litmus solution red, and another which gives a violet colouration when tested with neutral FeC $l_3(aq)$.

What is a possible identity of X?

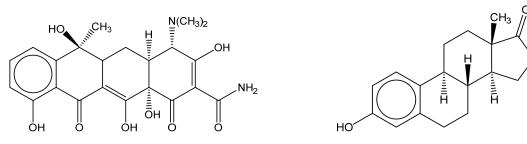
- A C₆H₅OCOCH₂CH₃
 B C₆H₅CH₂OCOCH₃
 C C₆H₅COOCH₂CH₃
 D C₆H₅CH₂COOCH₃
- **28** Ascorbic acid, commonly known as vitamin C, is a water-soluble molecule that traps

radicals formed in the aqueous environments of the cell and in the blood plasma.

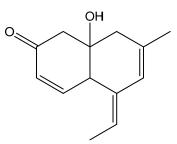
Which of the following statements is correct?

- **A** Ascorbic acid molecule is planar.
- **B** Ascorbic acid can exhibit cis-trans isomerism.
- **C** Ascorbic acid can react with hot hydrochloric acid.
- **D** Ascorbic acid can react with 2,4-dinitrophenylhydrazine.

29 Which of the following procedures can be used to distinguish between the two molecules below?



- A Add 2,4-dinitrophenylhydrazine at room temperature.
- **B** Add aqueous bromine at room temperature.
- **C** Add silver(I) diammine solution and warm.
- **D** Add dilute sodium hydroxide and warm.
- 30 Which of the following statements are true about molecule Y below?



- 1 1 mol of **Y** reacts with excess HBr(g) to yield a major product with 7 chiral centres.
- 2 1 mol of **Y** reacts with hot acidified KMnO₄(aq) to give a tribasic carboxylic acid as one of the products.
- 3 When heated, 1 mol of **Y** reacts with 4 mol of $H_2(g)$ in the presence of Ni catalyst to yield a saturated compound.
- **A** 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 3 only

- End of Paper -

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



RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME							
CLASS							
CENTRE NUMBER	S 3 0	4 4		INDEX NUMBER			
H2 CHEN	IISTRY						9729/02
Paper 2 Structu	red Questions						12 Sep 2018 2 hours
Additional Mate	rials:	Data Bookle	et				
_	READ THESE INSTRUCTIONS FIRST.						
	THIS BOOKLET		AR		SO. PAPE	R 2	
•	e, class and inde the top of this pag			QUESTION 1			
Write in dark blue	•	for only					9
diagrams or grap	an HB pencil hs.			QUESTION 2			9
Do not use highlighters, glue	staples, pape or correction flui		QUESTION 3			8	
			QUESTION 4			14	
Answer all qu provided on the (spaces	QUESTION 5			12	
The use of an ap is expected, whe	proved scientific re appropriate.	calculator	QUESTION 6		10		
A Data Booklet is	s provided.		QUESTION 7			13	
The number of r	marks is given in of each questio		Units				
question.			s.f.				
PAPER 1	PAPER 2	PAPER 3		TOTAL	PA	PER 4	GRADE
30	75	8	0	185		55	

This paper consists of **20** printed pages.

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

2

1 Magnesium, aluminium, **W** and **X** are 4 different elements in the 3rd Period. The following are some of their properties:

The chloride of ${\bf W}$ dissolves in water to give a strongly acidic solution and the oxide of ${\bf W}.$

The chloride of \mathbf{X} reacts with ethanoic acid to form ethanoyl chloride as one of the products.

(a) Identify the elements, **W** and **X**, and write the balanced equations for the reactions described above.

W:

Chloride of **W** dissolved in water (equation):

.....

X:

Chloride of **X** reacting with ethanoic acid (equation):

.....

- (b) Aluminium oxide is a white solid that is soluble in NaOH(aq) to give a colourless solution.
 - (i) Write a balanced equation, with state symbols, to describe the reaction of aluminium oxide with NaOH(aq).

.....[1]

(ii) Describe the observations made when HCl(aq) is carefully added to this colourless solution, until HCl(aq) is in excess.

.....[2]

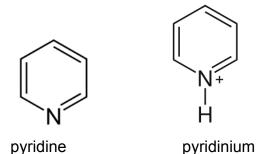
(c) State and explain how the decomposition temperature of BaCO₃ compares with that of MgCO₃.

[3] Explain why the 1st ionisation energy of aluminium is of lower magnitude

(d) Explain why the 1st ionisation energy of aluminium is of lower magnitude compared to that of magnesium.

[1] [Total: 9] **2** Pyridine C₅H₅N is a weak alkali with a distinctive, unpleasant fish-like smell. Pyridine reacts readily with hydrochloric acid to form pyridinium chloride only. Pyridinium chloride is commercially available in a form of 98.0% purity by mass.

4



Pyridinium chloride has a pK_a value of 5.25.

(a) Calculate the mass of 98.0% pyridinium chloride that must be added to 1.00 dm³ of water to give a solution of pH 3.5.

(You may assume no change in volume of solution upon addition of the salt.)

(b) Calculate the pH of the reaction mixture when 5.00 cm^3 of $0.0125 \text{ mol dm}^{-3}$ hydrochloric acid is added to 25.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ of pyridine.

(c) With the aid of **two** equations, explain how a solution of pyridinium chloride and pyridine can control pH.

[3] [Total: 9]

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3 Nitrosoyl chloride, NOC*l*, is a yellow gas that can be formed between nitryl chloride and nitric oxide in the following reversible reaction:

 $NO_2Cl(g) + NO(g) \rightleftharpoons NOCl(g) + NO_2(g)$ ΔH is negative

(a) A 3:1 molar ratio mixture of NO₂Cl(g) and NO(g), at a total initial pressure of 5 atm, was allowed to react in a closed vessel at 800 K. When equilibrium was reached at time *t*₁, the partial pressure of NO₂Cl was found to be 2.90 atm.

Calculate the value of the equilibrium constant, K_p , of the reaction at 800 K.

(b) At time t₂, more NO₂Cl gas was introduced into the vessel at 800 K, causing the partial pressure of NO₂Cl to increase to 3.25 atm. The system was allowed to reach equilibrium before the temperature was increased to 1000 K at t₃. A new equilibrium was established at t₄.

In the pressure-time axes below, sketch the graph that would be observed from time = 0 to time = t_4 , clearly indicating the values of the partial pressure of NO₂C*l* at time = 0, t_1 and t_2 .



River Valley High School 2018 Preliminary Examinations (c) Given that nitrogen is the central atom, draw the dot-and-cross diagram for NOC*l*.

7

(d) NOC*l* reacts with CH₃CH=CH₂ to give a product as predicted by Markovnikov's rule. When the organic product is heated with NaOH(aq), followed by acidification and addition of AgNO₃(aq), a white precipitate is obtained.

Given that the oxidation state of chlorine in NOCl is +1, state and draw the mechanism for the reaction between NOCl and CH₃CH=CH₂.

[3]

[Total: 8]

4 (a) Sucrose, or table sugar, is the most common natural food sweetener. In acidic medium, sucrose is readily hydrolysed to a mixture of glucose and fructose. The reaction is also acid-catalysed.

 $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+(aq)} C_6H_{12}O_6 + C_6H_{12}O_6$ (sucrose) (fructose)

A series of experiments was carried out at room temperature to investigate the kinetics of this reaction, using 0.850 mol dm^{-3} sucrose solution and 1.23 mol dm^{-3} hydrochloric acid.

Expt	Volume of sucrose / cm ³	Volume of HC <i>l</i> / cm ³	Volume of water / cm ³	Initial rate of reaction / mol dm ⁻³ min ⁻¹
1	20	30	0	1.77 × 10 ^{−3}
2	20	20	10	1.18×10^{-3}
3	10	30	10	8.85 × 10 ⁻⁴
4	40	20	10	?

(i) Using the data given above, determine the order of reaction with respect to sucrose and HC*l*.



- Hence, write the rate equation and deduce the rate constant of the (ii) reaction, stating its units.
- [2] (iii) Using your answer in (a)(ii), calculate the initial rate of reaction for Experiment 4.
- In bacteria, sucrose is broken down into glucose and fructose by the (b) enzyme, invertase. Experiments were done to measure the rate of the enzyme-catalysed hydrolysis reaction for different concentrations of sucrose.
 - Sketch a graph to show how the rate of this enzyme-catalysed (i) hydrolysis reaction varies with the concentration of sucrose until sucrose is in large excess.

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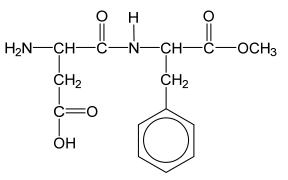
[2]

[1]

[Turn over

(ii) Explain the shape of the graph in (b)(i). In your answer, make reference to the order of reaction with respect to sucrose.

(c) Aspartame, an artificial sweetener, is 200 times sweeter than sucrose. The structure of aspartame is as follows.



(i) Draw the structure in which aspartame exists in water.

[2]

.....[1]

(iii) Draw the structural formulae of all the organic products formed when aspartame is heated with aqueous NaOH.

Label any chiral carbon in each product with an asterisk.

[3]

[Total: 14]

5 Manganese exhibits the widest range of oxidation states among the 1st set of transition elements from titanium to copper.

In deaerated aqueous solution and in the presence of excess CN^- ions, pale pink $Mn^{2+}(aq)$ forms blue $[Mn(CN)_6]^{4-}$ ion. $[Mn(CN)_6]^{4-}$ ion reacts with 3% solution of hydrogen peroxide to form red $[Mn(CN)_6]^{3-}$ ion.

In the visible spectrum, red is the lowest energy light while violet is the highest energy light.

(a) Explain why transition elements exhibit variable oxidation states.

.....[1]

(b) Explain why there is a difference in the colour observed for $[Mn(CN)_6]^{4-}$ and $[Mn(CN)_6]^{3-}$ ions.

(c) Given that:

 $[Mn(CN)_6]^{3-} + e \rightleftharpoons [Mn(CN)_6]^{4-}$

 $E^{\ominus} = -0.24 \text{ V}$

Use the *Data Booklet* to suggest why Mn(III) ion exhibits stronger oxidising power in aqueous solution than in concentrated cyanide solution in terms of

- E^{\ominus} and
- effect of ligand exchange on E^{\ominus} .

[2]

River Valley High School 2018 Preliminary Examinations [Turn over

[2]

(d) The figure below gives the splitting diagram of the d-orbitals in the presence of an octahedral ligand field.

A transition metal complex can exist in a 'high spin' state or in a 'low spin' state.

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

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

Electrons usually prefer to occupy orbitals singly, rather than in pairs, to minimise coulombic repulsion, also known as the pairing energy.

In this question, only one of the cyanido-complexes of manganese is high-spin.

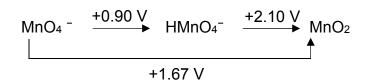
(i) Using this information, and compare the colour of the cyanidocomplexes of manganese, deduce and draw the electronic configuration of the [Mn(CN)₆]³⁻ on the splitting diagram.

energy		
	 _	

(ii) Explain the spin-state of [Mn(CN)₆]³⁻ in (d)(i) in terms of the energy gap between the d-orbitals in both manganese cyanido-complexes and pairing energy.

[1]

(e) Standard reduction potentials are often presented in the form of a potential diagram. The figure below gives the potential diagram of manganese under the condition of $[H^+] = 1 \mod dm^{-3}$.



(i) Given that HMnO₄⁻ undergoes disproportionation, construct a balanced equation for the reaction.

.....[1]

(ii) Calculate ΔG^{\ominus} for the reaction.

.....[2]

(f) It is necessary to carry out reactions involving Mn(II) in deaerated solution as Mn(II) may react with aerated solutions.

Consider the data given below and appropriate values from the *Data Booklet*, calculate the E^{\ominus}_{cell} values for the oxidation of Mn(II) to Mn(III) in aerated solutions at pH = 0 and pH = 14.

Comment on what the signs of E^{Θ}_{cell} indicate about the stability of Mn(II) in acidic and alkaline aerated solutions.

 $Mn(OH)_3(s) + e^- \rightleftharpoons Mn(OH)_2(s) + OH^-(aq)$ $E^{\ominus} = +0.18 V$

[Total: 12]

[2]

[Turn over

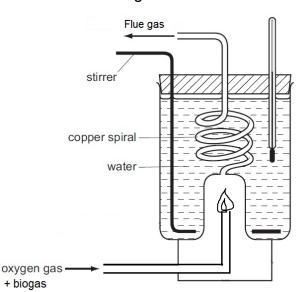
6 Anaerobic digestion is a natural form of waste-to-energy that uses the process of fermentation to break down organic matter in the absence of oxygen. Typically, 50 to 75% of biogas can be combusted, therefore it produces a deep blue flame and can be used as an energy source.

Biogas is primarily made up of methane, along with carbon dioxide. Depending on the type of biodegradable material involved, hydrogen sulphide (H₂S), hydrogen and nitrogen may be produced.

The composition of a sample of biogas by mass is given in the following table, along with the enthalpy change of combustion for each gas.

Biogas component	Percentage mass	$\Delta H_{\rm c}$ / kJ mol ⁻¹	
methane	72.2 ?		
carbon dioxide	21.6	0.00 - 482 - 386 - 43.1	
hydrogen sulfide	1.2		
hydrogen	2.7		
nitrogen	2.3		

The total energy evolved from the combustion of biogas can be determined using a calorimeter as shown in Figure 6.1.





(a) (i) The cooled flue gas contains carbon dioxide, sulfur dioxide and nitrogen gas.

Two gases present in the sample of biogas do not react with oxygen. Identify the two gases and explain why they do not react.

.....[2]

(iii) An experiment was carried out to determine the fuel value of a sample of biogas using a calorimeter as shown in Figure 6.1. Fuel value is defined as the amount of energy generated by complete combustion of one gram of the fuel.

In this experiment, biogas was mixed with excess oxygen at room temperature and pressure before it was passed into the calorimeter.

Assuming that the efficiency of heat transferred to water is 100%, use the *Data Booklet* and the following information to determine the energy evolved. Hence determine the fuel value of biogas.

Volume of biogas used = 1.00 dm^3

Density of biogas is $6.44 \times 10^{-4} \text{ g cm}^{-3}$

Volume of water heated = 200 cm^3

Density of water = 1.00 g cm⁻³

Initial temperature of water = 29.6 °C

Maximum temperature of water reached = 64.7 °C

(iv) Use the information provided, calculate the amount of each gas that combusted. Hence, determine the enthalpy change of combustion of methane.

(c) To determine the fuel values of biogas, the apparatus in Figure 6.1 can simply be replaced with a beaker of water with lid and a thermometer.

Suggest how the design of the apparatus in Figure 6.1 improves the efficiency of heat transfer to the water.

..... [1]

(d) Cooled flue gas was passed through a tube containing anhydrous calcium oxide, as shown in Figure 6.2, before being discharged into the atmosphere.

Figure 6.2

anhydrous calcium oxide

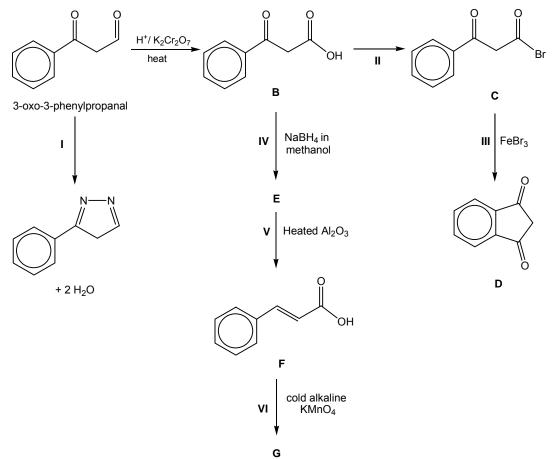


Explain why it is important for the cooled flue gas to be passed through anhydrous calcium oxide.

.....[1]

[Total: 10]

7 (a) A student carried out a series of tests on 3-oxo-3-phenylpropanal.



(i) Suggest the reagents and conditions required for reactions I and II.

Reaction I:

- (ii) Draw the structures of **E** and **G**.

E	G

[2]

(iii) Describe the mechanism for reaction III, and provide the name of the mechanism.

[3]

(b) Suggest simple laboratory tests to distinguish between compounds B, C and F. State the expected observations for each compound.

[4]

(c) Describe what the student will observe when 3-oxo-3-phenylpropanal is warmed with Fehling's solution. Write an equation for this reaction.

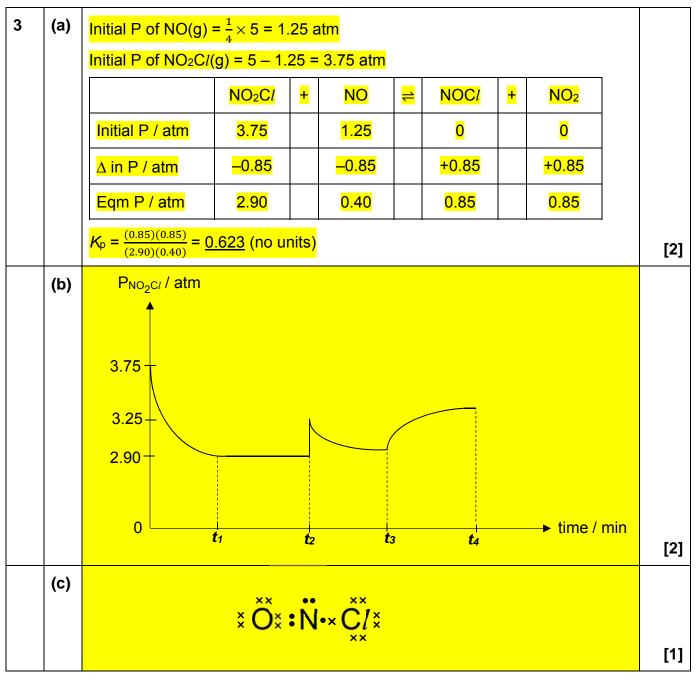
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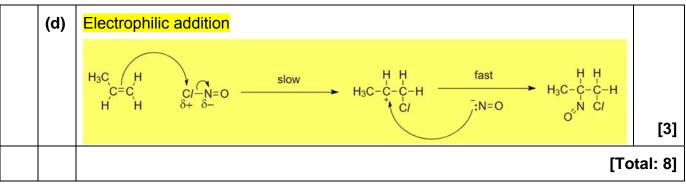
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MARK SCHEME

1	(a)	W: Si		
	$\frac{\text{SiC}_{l_4} + 2\text{H2O} \rightarrow \text{SiO}_2 + 4\text{HC}_l}{\text{SiC}_2 + 2\text{H2O}}$			
		X : P PC l_5 + CH ₃ COOH \rightarrow POC l_3 + CH ₃ COC l_1		
		OR		
		$\frac{3CH_{3}COOH + PCI_{3} \longrightarrow 3CH_{3}COCI + H_{3}PO_{3}}{COCI + H_{3}PO_{3}}$	[4]	
	(b) (i)	$A_{l_2O_3}(s) + 2NaOH(aq) \rightarrow 2Na[A_l(OH)_4](aq) + H_2O(l)$		
		OR		
		$Al_2O_3(s) + 2OH^-(aq) \rightarrow 2[Al(OH)_4]^-(aq) + H_2O(I)$	[3]	
	(b) (ii)	On addition of HC <i>l</i> (aq), <u>a white ppt is formed</u> . <u>Ppt would dissolve in excess</u> <u>HC<i>l</i>(aq) to give a colourless solution</u> .		
	(c)	BaCO ₃ has a higher thermal decomposition temperature.		
		Ba ²⁺ has a <u>larger ionic radius</u> compared to Z^{2+}/Mg^{2+} . Ba ²⁺ hence <u>has a lower</u> charge density, and <u>polarise the CO₃²⁻ anion to a lower extent</u> (compared to		
		Z ²⁺ /Mg ²⁺), and the <u>C–O bonds are weakened to a smaller extent</u> , resulting in a higher thermal decomposition temperature.		
	(d)	The <u>3p electron to be removed from Al is at a higher energy level compared</u> to the 3s electron to be removed from Mg, hence the p electron is less		
		strongly attracted to the nucleus and require less energy to remove.	[1]	
		[To	tal: 9]	

		On addition of a <u>small amount of base</u> (OH [−]) to the buffer solution, nearly all the <u>added OH[−] ions are neutralised</u> by the large amount of C ₅ H ₅ NH ⁺ . Hence [OH [−]] does not increase appreciably and the pH is kept approximately	
		C_5H_5N (aq) + H ⁺ (aq) $\rightarrow C_5H_5NH^+$ (aq)	
	(c)	On addition of a <u>small amount of acid</u> (H ⁺) to the buffer solution, nearly all the <u>added H⁺ ions are neutralised</u> by the large amount of C_5H_5N . Hence [H ⁺] does not increase appreciably and the <u>pH is kept approximately constant</u> .	
	(-)	pH = 14 - 7.16 = 6.84	[3]
		$pOH = 8.75 + lg (2.08 \times 10^{-3} / 0.0813) = 7.16$	
		$pOH = pK_b + lg [salt]/[base]$	
		$pK_b = 14 - pK_a = 8.75$	
		[pyridinium chloride] = $(0.0125 \times 0.005) / 0.03 = 2.08 \times 10^{-3} \text{ mol dm}^{-3}$	
	(b)	[C₅H₅N] = [(0.100 × 0.025) – (0.0125 × 0.005)] / 0.03 = <u>0.0813 mol dm⁻³</u>	
		= <u>2.13 g (or 2.10 g)</u>	[3]
		Mass to be added = $(0.0181 \times (12.0 \times 5 + 1.0 \times 6 + 14.0 + 35.5)) \div 0.98$	
		= <u>0.0178 mol</u>	
		$\mathbf{Y} = [(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}]$	
		$(3.16 \times 10^{-4})^2$ / Y = 5.62×10^{-6}	
		<u>Or</u>	
		$Y = [(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}] + (3.16 \times 10^{-4})$ = 0.0181 mol	
		$(3.16 \times 10^{-4})^2$ / Y – (3.16×10^{-4}) = 5.62 × 10 ⁻⁶	
		Since $pK_a = 5.25$, $K_a = 10^{-5.25} = 5.62 \times 10^{-6}$	
		Let the number of moles of C_5H_5NHCl be Y mol	
2	(a)	For pH = 3.5 [H ⁺] = $10^{-3.5} = 3.16 \times 10^{-4} \text{ moldm}^{-3}$	





River Valley High School 2018 Preliminary Examinations [Turn over

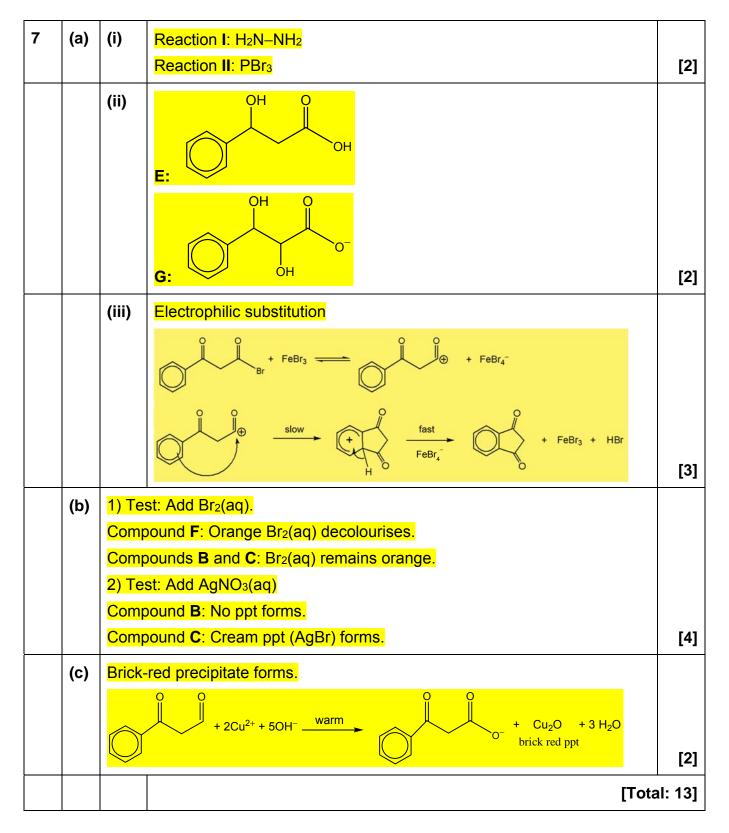
4	(a)	When the volume/concentration of HC <i>l</i> increases to 1.5 times, rate increases to 1.5 times.						
			Hence, reaction is first order with respect to HCI.					
			Comparing Experiments 1 and 3, When the volume/concentration of sucrose doubles, rate doubles					
			When the volume/concentration of sucrose doubles, rate doubles. Hence, reaction is first order with respect to sucrose.					
		(ii)	Rate = k [sucrose] [HC l]					
		()	From Experiment 1,					
			[sucrose] = $0.850 \times \frac{20}{50}$ = 0.340 mol dm ⁻³					
			$[HC/] = 1.23 \times \frac{30}{50} = 0.738 \text{ mol dm}^{-3}$					
			$k = \frac{1.77 \times 10^{-3}}{(0.340)(0.738)} = 7.05 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$	[2]				
	(iii) [sucrose] = $0.850 \times \frac{40}{70}$ = 0.486 mol dm ⁻³							
			$[\text{HC}/] = 1.23 \times \frac{20}{70} = 0.351 \text{ mol dm}^{-3}$					
			Both concentrations for					
			Initial rate of reaction = $7.05 \times 10^{-3} \times 0.486 \times 0.351$					
			= 1.20 × 10 ⁻³ mol dm ⁻³ min ⁻¹	[2]				
	(b)	(i)	Initial rate					
			(sucrose)	[1]				
				[1]				

	(ii)	<u>When [sucrose] is low, reaction is first order</u> with respect to sucrose due to the <u>availability of active sites on the enzyme molecules</u> for binding.				
		When [sucrose] is high, all active sites on the enzyme molecules are occupied. The rate of reaction then is independent of [sucrose] and the reaction is zero order with respect to sucrose.				
(c)	(c) (i) $H_{3}N - CH - C - N - CH - C - OCH_{3}$ $H_{3}N - CH - C - N - CH - C - OCH_{3}$ $CH_{2} - CH_{2}$ C = 0 O^{-}					
	<i>(</i>)					
	(ii)	The zwitterions of aspartame form ion-dipole interactions with water.				
	(iii)	$H = N = CH = C = ONa$ $H = N = CH = CH^{2} = ONa$ $H = N = CH^{2} = ONa$ $H = ONa$ $H = N = CH^{2} = ONa$ $H = ONa$				
			[3]			
		[Tota	al: 14]			

5	(a)	transi	Due to the <u>similar energy/ close proximity of the 3d and 4s electrons</u> in the transition elements, transtion element can form ions of approximately the similar stability by losing different number of electrons. In the presence of octahedral <u>ligand</u> field, the <u>degenerate d-orbitals in the metal complex were spilt into two energy levels</u> . The <u>colour observed is due to the difference in energy levels</u> . The <u>difference in electronic configuration due to different oxidation state affect ΔE. Light of different <u>energies/ different wavelengths are absorbed for the promoion of electrons from the lower energy orbital to the vacant/partially filled higher energy <u>orbital/ d-d transition</u>, different complementary colour is observed.</u></u>				
	(b)	<u>metal</u> <u>to</u> th <u>confic</u> <u>energ</u> <u>from</u>					
	(c)	show: cynai	\ln^{3+}/Mn^{2+}) is <u>more positive</u> than $E^{\ominus}([Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-})$, which s that Mn^{3+} is <u>more readily reduced</u> , hence a weaker oxidising agent in de solution than in water. <u>More energy</u> is required to <u>add an electron to</u> egatively charged [Mn(CN)_6]^{3-} due to repulsion.	[2]			
	(d)	(i)	Figure 1.1 energy				
			11 1 1	[1]			
		(ii)	Since $[Mn(CN)_6]^{3-}$ ions are red, the <u>energy gap between the 2 sets of</u> <u>d-orbitals in $[Mn(CN)_6]^{3-}$ is bigger</u> . This suggests that $[Mn(CN)_6]^{3-}$ is the low spin complex, as its <u>energy gap</u> , ΔE , is greater than the <u>pairing energy</u> / <u>Coulombic repulsion/ repulsion energy</u> , electrons in $[Mn(CN)_6]^{3-}$ would pair up.	[1]			
	(e)	(i)	[O] HMnO ₄ ⁻ \rightarrow MnO ₄ ⁻ + H ⁺ + e [R] 3H ⁺ + 2e + HMnO ₄ ⁻ \rightarrow MnO ₂ + 2H ₂ O Overall equation: 3HMnO ₄ ⁻ + H ⁺ \rightarrow MnO ₂ + 2 MnO ₄ ⁻ +2H ₂ O	[1]			
		(ii)	$E_{cell} = +2.10 - (+0.90) = +1.20 V$ $\Delta G = -nFE_{cell} = -(2)(96500)(1.20) = -232 \text{ kJ mol}^{-1}$	[2]			
	(f)	<mark>In aci</mark>	dic condition,				
		O ₂ + 4H ⁺ + 4e \Rightarrow 2H ₂ O E^{\ominus} = +1.23 V					
		$Mn^{3+} + e \rightleftharpoons Mn^{2+} \qquad E^{\ominus} = +1.54 V$					
		E [⊖] _{cell} = +1.23 – (+1.54) = −0.31 V					
				[2]			

In alkaline solution,	
$O_2 + 2H_2O + 4e \Rightarrow 4OH^ E^{\ominus} = +0.40 V$	
E [⊖] _{cell} = +0.40 – (+0.18) = +0.22 V	
Since the <u>E^{$\Theta_{cell > 0$ in alkaline}</u> environment and <u>E^{Θ_{cell}} < 0 in acidic</u>	
environment, <u>Mn(II) is more stable in acidic environment</u> than in alkaline environment.	
[Total:	12]

6	(a)	(i)	CO ₂ : Carbon in CO ₂ has attained maximum oxidation state. N ₂ : N=N is very strong resulting high activation energy.	[2]
		(ii)	Methane: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(I)$ Hydrogen sulfide: $H_2S(g) + 1\frac{1}{2}O_2(g) \rightarrow SO_2(g) + H_2O(I)$ Hydrogen: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(I)$	[2]
		(iii)	Energy evolved = $200 \times 4.18 \times (64.7 - 29.6) = 29.34 \text{ kJ}$ mass of biogas used = $1000 \times 6.44 \times 10^{-4} = 0.644 \text{ g}$ Fuel value of biogas = $29.34 \div 0.644 = 45.6 \text{ kJ g}^{-1}$	[2]
		(iv)	Amount of methane in 1 dm ³ biogas = $0.644 \times 0.722 \div (12.0 \pm 4.0)$ = 0.0291 mol Amount of H ₂ S in 1 dm ³ biogas = $0.644 \times 0.012 \div (2.0 \pm 32.1)$ = 0.000227 mol Amount of H ₂ in 1 dm ³ biogas = $0.644 \times 0.027 \div 2.0$ = 0.00869 mol Energy evolved = 29.34 kJ = $(0.0291 \times \Delta H_{c}(CH_{4})) \pm (0.000227 \times 482) \pm (0.00869 \times 386)$ $\Delta H_{c}(CH_{4}) = -890$ kJ mol ⁻¹	[2]
	(c)	• Sp • cc • th	onger time for hot flue gas to pass through spiral copper coil piral copper coil increase the surface area for energy transfer opper is a good conductor of heat e combustion takes place inside the apparatus, not affected by aught.	[1]
	(d)		emove sulfur dioxide gas as low concentration of this gas can also as the respiratory system.	[1]
			[Tota	al: 10]



- End of Paper -



RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME				
CLASS	6			
CENTRE NUMBER	S		INDEX NUMBER	
H2 CHEMISTRY 9729/03				
Paper 3 Free	Respons	se		18 September 2018 2 hours
Candidates an	swer on	separate paper.		
Additional Mat	erials:	Answer Paper		
		Cover Page		
		Data Booklet		

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in. Write in dark blue or black pen on both sides of paper.

You may use a soft pencil for any diagrams, graphs or rough working. Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A

Answer **all** questions.

Section B Answer one question.

Begin each question on a fresh sheet of paper. The use of an approved scientific calculator is expected, where appropriate. A Data Booklet is provided. Do not write anything on it. You are reminded of the need for good English and clear presentation in your answers.

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

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

Section A

Answer **all** the questions in this section.

- 1 (a) (i) Phosphorus reacts with
 - F_2 to produce PF_5 as the only product.
 - Cl_2 to give both PCl_5 and PCl_3 .
 - Br₂ and I₂ to give PBr₃ and PI₃ respectively.

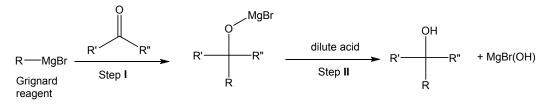
With reference to the *D*ata *B*ooklet, explain the difference in oxidation states of phosphorus in the phosphorus-containing compounds formed.

(ii) The table below gives the pK_a values of the hydrogen halides.

hydrogen halide	р <i>К</i> а
HF	3.17
HCl	-7
HBr	-9
HI	-10

Explain the trend in the pK_a values.

(b) The following reaction scheme shows the formation of an alcohol via the Grignard reaction.



- (i) Suggest the type of reaction undergone in Step II.
- (ii) Suggest the identities of a suitable carbonyl compound and Grignard reagent to form 1-methylcyclohexan-1-ol. [2]
- (iii) The reaction between the carbonyl compound and the Grignard reagent suggested in (b)(ii) is a nucleophilic addition.

Propose the mechanism for this reaction, assuming that the Grignard reagent (R-MgBr) produces the :R⁻, as the reacting species to form 1-methylcyclohexan-1-ol. [3]

[2]

[1]

[3]

- (c) Calcium phosphate, Ca₃(PO₄)₂, is a sparingly soluble salt. ..
 - (i) Write the expression for the solubility product of calcium phosphate. [1]
 - (ii) Given that the solubility of calcium phosphate in water is 1.14×10^{-7} mol dm⁻³, calculate the solubility product of calcium phosphate, stating its units.
 - (iii) Calculate the solubility of calcium phosphate in the presence of 0.150 mol dm⁻³ of potassium phosphate. [2]
 - (iv) A saturated solution was prepared by dissolving two sparingly soluble salts, calcium phosphate and calcium sulfate, CaSO₄, in tap water. The tap water used was found to be contaminated with trace amounts of SO₄²⁻.

Explain the impact of the contamination on the solubilities of calcium phosphate and calcium sulfate.

[Total: 18]

[2]

[2]

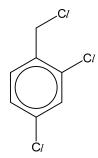
River Valley High School 2018 Preliminary Examinations

2 Strepsils[®] is a line of throat lozenges used to relieve discomfort caused by mouth and throat infections.

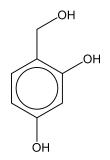
The table below shows the main active and non-active ingredients found in one lozenge.

primary active ingredients	2,4-dichlorobenzyl alcohol	OH C/
	amylmetacresol	OH
	(–)-menthol	ОН
non-active ingredients	tartaric acid	
	propylene glycol	ОН

(a) 2,4-dichlorobenzyl alcohol can be prepared from 2,4-dichlorobenzyl chloride (shown below) via a one-step synthesis.



- (i) State the reagent and condition for the reaction.
- (ii) Explain why the molecule below will not be obtained as a by-product.



[1]

[2]

[1]

(iii) A student carries out the synthesis using the reagent in (a)(i) that has been contaminated with sodium ethoxide.

Draw the structure of the possible by-product that may result.

(iv) Describe a simple chemical test that can distinguish between 2,4-dichlorobenzyl alcohol and amylmetacresol.

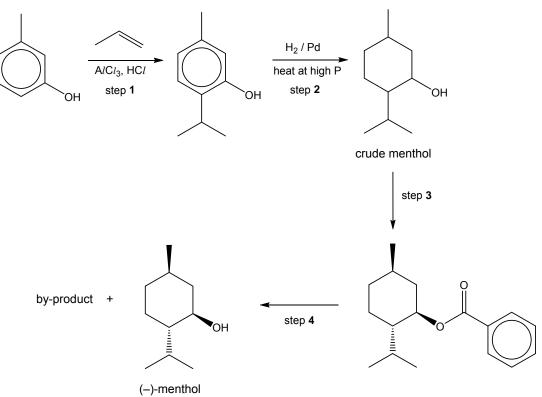
State the expected observations for each compound.

(b) Arrange amylmetacresol, menthol and tartaric acid in increasing order of acidity.

Explain your answer.

You only need to consider the first acid dissociation of tartaric acid. [3]

(c) Menthol is produced commercially via the Haarmann-Reimer process. A modified version of the process is shown below.



- (i) Suggest the types of reactions occurring in steps 1 and 2. [2]
- (ii) Given that crude menthol does not exhibit optical activity, determine the number of enantiomers crude menthol has.

Hence, calculate the proportion of each enantiomer formed. [2]

- (iii) Draw the structure of the by-product formed.
- (d) (i) A 25.0 cm³ solution of 0.0100 mol dm⁻³ tartaric acid in a conical flask is titrated with 0.0100 mol dm⁻³ NaOH(aq) from a burette.

Given that $pK_{a1} = 2.89$ and $pK_{a2} = 4.40$, and ignoring the autoionisation of water, determine the pH of the solution when the following volumes of NaOH(aq) are added:

- 0.00 cm³
- 12.50 cm³
- 50.00 cm³
- (ii) When the second equivalence point is reached, the solution is heated to dryness. The residue left is a white solid.

Explain, using structure and bonding, why the boiling point of the solid residue is higher than that of tartaric acid. [2]

[Turn over

[1]

[4]

- (e) Propylene glycol can be produced from gaseous propene.
 - (i) State the reagent and condition required for propene to form propylene glycol. [1]
 - (ii) When propene is reacted with the reagent in (e)(i) under a different set of condition, an organic liquid and an inorganic gas are formed.

Draw the displayed formula of the organic liquid.

(iii) The inorganic gas is collected in an evacuated glass bulb at 30 °C. It is found that the mass of the 500 cm³ glass bulb increased by 0.36 g.

Identify the inorganic gas and determine the pressure of the gas collected. [2]

[Total:23]

3 Transition elements and their compounds have found many applications in industries as both homogeneous and heterogeneous catalysts.

For example, nickel is used as a catalyst for hydrogenation of alkenes and vanadium pentoxide (V_2O_5) is used in the manufacture of sulfuric acid.

- (a) Explain what is meant by the term heterogeneous catalyst.
- (b) The following table list the colours of various vanadium ions in aqueous solution:

ion	oxidation state	colour
V ²⁺	+2	violet
V ³⁺	+3	green
VO ²⁺	+4	blue
VO ₃ -	+5	yellow

When a sample of yellow VO_3^- solution is mixed with an excess of zinc powder, the solution undergo a series of colour changes over time.

Using relevant E^{\ominus} values from the *Data Booklet*, account for all the observed colour changes. There is no need to write any balanced chemical equation.

[3]

[1]

[2]

(c) A similar process as (b) was carried out as follows:

100 cm³ of 0.0500 mol dm⁻³ of NaVO₃ is reacted completely with zinc powder. The final colour of the solution is blue-green.

25.0 cm³ of this blue-green solution requires 20.63 cm³ of 0.0200 mol dm⁻³ of KMnO₄ for complete reaction under acidic conditions.

(i) There are 2 different vanadium containing ions in this blue-green solution, of which one of them is VO²⁺.

State the identity of the other ion.

- (ii) Write a balanced chemical equation between VO²⁺ and MnO₄⁻ under acidic conditions.
 [1]
- (iii) Calculate the amount of KMnO₄ that has undergone reaction. [1]

- (iv) Given that:
 - 5 mol of the ion identified in (c)(i) reacts exactly with 2 mol of KMnO₄
 - $x \mod \text{OV}^{2+}$ is present in 25.0 cm³ of the blue-green solution

Show that the total amount of KMnO₄ reacted = $\frac{2}{5}(0.00125 - x) + \frac{1}{5}x$.

Hence, calculate the mass of zinc powder added to the original mixture.

(d) Vanadium pentoxide can be used as a catalyst in a reaction known as oxidative esterification. In this reaction, an aldehyde can react with an alcohol or phenol to form an ester:

$$R_1$$
-CHO + HO- $R_2 \rightarrow R_1$ -COO- R_2 + 2[H]

Compound **A**, $C_8H_8O_2$ undergoes oxidative esterification in the presence of V_2O_5 catalyst to form a neutral compound **B**, $C_8H_6O_2$. On heating **B** under reflux with NaOH(aq), the sodium salt of compound **C**, $C_8H_8O_3$, was formed. Compounds **A**, **B** and **C** reacts with LiA/H₄ in dry ether to form compound **D**, $C_8H_{10}O_2$, while compounds **A**, **C** and **D** are able to decolourise aqueous bromine.

Draw the structures of A, B, C and D, and explain your reasoning.

[7]

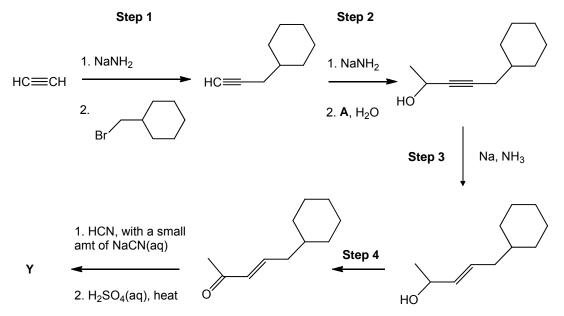
[4]

[Total: 19]

Section B

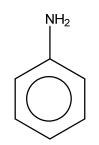
Answer **one** question from this section.

4 (a) Compound **Y** can be obtained from ethyne using the following synthesis pathway:



- (i) Given that $HC \equiv C^-$ is formed, state the role of NaNH₂ in Step 1.
- (ii) Name and outline the mechanism for the reaction in Step 1 Part 2. Show relevant lone pairs and dipoles, using curly arrows to indicate the movement of electron pairs.

(iii)



phenylamine

Suggest why phenylamine is unable to carry out the role of sodium amide, NaNH₂, in Step **1**.

- (iv) Suggest the reagent A in Step 2, and reagents and conditions for Step 4.
- (v) Draw the structure of Compound Y.
 Explain why HCN reacts with C=O but not with C=C in the same compound.
 [3]

[1]

[3]

(b) Sodium borohydride, NaBH₄, is another inorganic sodium compound that is often used in organic synthesis. It is also used to make the prototypes of direct borohydride fuel cell. Aqueous sodium borohydride undergoes catalytic decomposition to produce the hydrogen needed for the fuel cell.

 $NaBH_4(s) + 2H_2O(I) \rightarrow NaBO_2(s) + 4H_2(g)$ $\Delta H^{\ominus} = -210 \text{ kJ mol}^{-1}$

Boron is similar to carbon in its ability to form stable covalently bonded molecular network.

- (i) What do you understand by the term *lattice energy*?
- (ii) With the aid of an energy cycle, use the following data and appropriate data from the *Data Booklet* to calculate the lattice energy of sodium borohydride.

enthalpy change of formation of H ₂ O(g)	−241 kJ mol ⁻¹
standard enthalpy change of atomisation of Na	+107 kJ mol ^{−1}
standard enthalpy change of formation of $BH_4^-(g)$	−78.2 kJ mol ⁻¹
standard enthalpy change of vapourisation of $H_2O(I)$	+40.8 kJ mol ⁻¹
standard enthalpy change of formation of NaBO ₂ (s)	−1059 kJ mol ⁻¹

[5]

(c) A breathalyzer does not directly measure blood alcohol content or concentration, which involves the analysis of blood sample. It measures the blood alcohol content by measuring the amount of alcohol in the exhaled breath instead.

Ethanol is a volatile compound. In lungs, the ethanol dissolved in blood can change its state from liquid to gaseous and it is exhaled with air. When a user breathes into the breathlyzer, the ethanol in the exhaled air is passed through a solution of potassium dichromate. The ethanol is oxidised to ethanoic acid.

 $3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$

The direct oxidation of ethanol by potassium dichromate is carried out in an electrochemical cell and the current generated can be used to estimate the alcohol content of blood.

(i) When a user breathes into the breathlyzer which contains potassium dichromate, a current of 0.12 A is recorded for 1 min.

Determine the mass of ethanol per breath.

(ii) A partition ratio of "2100:1" is used to estimate the blood alcohol content in blood from the amount of alcohol in a breath. This partition ratio implies that 2100 cm³ of breath contains the same amount of ethanol as 1 cm³ of blood.

Given that the volume of exhaled air in (c)(i) is 65 cm^3 , calculate the amount of ethanol per cm³ of blood.

[Total: 20]

[3]

5 (a) Most plants do not thrive in highly acid or highly alkaline soil, though a few have adapted to such extremes. Soil pH may be adjusted using suitable chemicals.

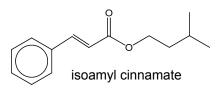
Describe, with the aid of balanced equations, the actions of acid and/or base on the oxides of magnesium and phosphorus, if any.

Hence, suggest why oxides of phosphorus should not be used to adjust soil pH.

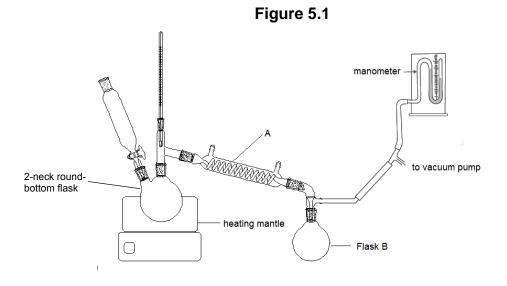
(b) RVCM[®]Calmag is a solid fertiliser containing calcium nitrate and magnesium nitrate in a fixed mole ratio of 2:1.

Two equal masses of fertiliser samples were heated at 575 K and 949 K respectively until there is no more change to their masses. For both samples, brown fumes were observed and a gas that rekindled a glowing splint was evolved.

- (i) Write a balanced equation to represent any one reaction that occurred. [1]
- (ii) The loss in mass for sample 1 heated at 949 K is three times that of sample 2 heated at 575 K. Account for this observation. [3]
- (c) Isoamyl cinnamate extracted from several types of trees from the genus *Cinnamomum* has a balsamic odour, reminiscent of cinnamon with an amber note.



Isoamyl cinnamate can be oxidised to give different products depending on the choice of oxidising agents and the reaction conditions. A pure sample of isoamyl cinnamate was heated with acidified potassium dichromate using the apparatus setup as shown in **Figure 5.1**.



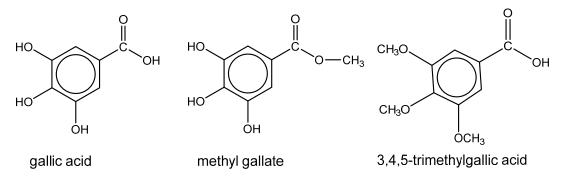
[3]

- (i) State the function of the apparatus A.
- (ii) Name and write balanced equations for two major reactions that occur in the 2-neck round-bottom flask.

You may use [O] or [H] to balance the equations.

- (iii) Identify the first organic compound that is likely to be collected in flask **B**. [1]
- (iv) Draw the skeletal structures of all the organic products formed if acidified potassium manganate(VII) is used instead of acidified potassium dichromate.
 [2]
- (d) Pu'erh (Chinese: 普洱) is a variety of fermented tea produced in Yunnan province, China. Black Pu'erh tea is known to contain more gallic acid than green Pu'erh tea. Gallic acid and its derivatives have been reported to elicit antioxidant, anti-cancer and anti-diabetic activities.

The structures of gallic acid and its derivatives are given below:



(i) Gallic acid can dissolve in water and diethyl ether. The partition coefficient for the separation of gallic acid in the two immiscible phases is given below:

 $K_{partition} = \frac{[gallic \ acid]_{aqueous}}{[gallic \ acid]_{diethyl \ ether}}$

In an experiment, 1.00 g sample of pure gallic acid was dissolved in 100 cm³ of water. This aqueous solution of gallic acid and 50.0 cm³ of diethyl ether were placed in a separatory funnel which is shaken to mix well. The mixture was then allowed to stand for 30 minutes before the two immiscible layers were separated.

It was found that 20.0 cm^3 of the aqueous layer required 20.25 cm^3 of 0.180 mol dm⁻³ sodium hydroxide for complete neutralisation.

Calculate the amount of gallic acid in each layer, and hence the partition coefficient.

[3]

[1]

[2]

(ii) A sample containing both gallic acid and 3,4,5-trimethylgallic acid are dissolved in 50 cm³ of diethyl ether.

Describe and explain how would you modify the solvent extraction method in **d(i)** such that mainly 3,4,5-trimethylgallic acid is left in the diethyl ether layer.

(iii) Suggest a chemical test to distinguish methyl gallate from gallic acid. [2]

[Total: 20]

[2]

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			Section A	
1	(a)	(i)	Element <u>E</u> ^O / V	
			$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$ +2.87	
			$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$ +1.36	
			$\frac{1}{2}$ Br ₂ + e ⁻ ⇒ Br ⁻ +1.07	
			$\frac{1}{2} I_2 + e^- \rightleftharpoons I^- \qquad +0.54$	
			The order of oxidising strength of the halogens, as observed from the E^{Θ} values above, <u>decreases down the Group.</u>	
			Due to the strong oxidising power of F2, the oxidation number of	
			Phosphorus +5 in PF ₅ , +5 and +3 in PC l_5 and PC l_3 , +3 in PBr ₃ and PI ₃ respectively.	[3]
				[9]
		(ii)	The smaller the pK_a , the stronger the acid, indicating HI is the strongest acid, followed by HBr, HC <i>l</i> and HF. Down the group from F to C <i>l</i> to Br to I, atomic radius increases, effectiveness of orbital overlap between H and X decreases. The H–X bond becomes	
			increasingly weaker, making it easier to lose the H ⁺ .	[2]
	(b)	(i)	(Acidic) hydrolysis	[1]
		(ii)		
			and CH ₃ MgBr	[2]

Section A

	(iii	$:CH_3^{-} \xrightarrow{\delta - 0} \xrightarrow{Slow} H_3^{-} \xrightarrow{O_{-}^{-}} \xrightarrow{H_3^{-} O_{-}^{-}} \xrightarrow{H_3^{-}} \xrightarrow{H_3^{-} O_{-}^{-}} \xrightarrow{H_3^{-} O_{-}^{-}} \xrightarrow{H_3^{-}} $	[3]
((c) (i)	$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$	[1]
	(ii)	$[Ca^{2+}] = 1.14 \times 10^{-7} \times 3 = 3.42 \times 10^{-7} \text{ mol dm}^{-3}$ $[PO_4^{3-}] = 1.14 \times 10^{-7} \times 2 = 2.28 \times 10^{-7} \text{ mol dm}^{-3}$ $K_{sp} = (3.42 \times 10^{-7})^3 (2.28 \times 10^{-7})^2 = 2.08 \times 10^{-33} \text{ mol}^5 \text{ dm}^{-15}$	[2]
	(iii	Let the solubility of calcium phosphate in the presence of potassium phosphate be y. $2.08 \times 10^{-33} = (3y)^3(0.15 + y)^2$ Assume that y is small such that $0.15 + y \approx 0.15$ $2.08 \times 10^{-33} = (3y)^3(0.15)^2$ $y = 1.51 \times 10^{-11} \text{ mol dm}^{-3}$	[2]
	(iv	An increase in $[SO_4^{2-}]$ causes the <u>equilibrium position of</u> $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$ to shift left, decreasing the solubility of $CaSO_4$. Since the solubility of CaSO_4 is lowered, there will be <u>less Ca^{2+}</u> from dissolution of CaSO_4. <u>Equilibrium position of</u> $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$ shifts right, increasing the solubility of $Ca_3(PO_4)_2$.	[2]
		[Tota	l: 18]

2	(a)	(i)	NaOH(aq), heat under reflux	[1]
		(ii)	The <u>C–Cl bond has a partial double bond character</u> as the <u>lone pair of</u> electrons in the p orbital of the Cl atom can delocalise into the π electron cloud of the benzene ring. This strengthens the C–Cl bond, making it more difficult to break.	[1]
		(iii)	OCH ₂ CH ₃ C/	[1]
		(iv)	Add PC15 / SOC12	
			2,4-dichlorobenzyl alcohol: white fumes (of HCl) observed	
			amylmetacresol: no white fumes observed	
			or	
			Add Br ₂ (aq)	
			2,4-dichlorobenzyl alcohol: Br2(aq) remains orange	
			amylmetacresol: orange Br ₂ (aq) decolourises	
			or	
			Add neutral FeCl ₃	
			2,4-dichlorobenzyl alcohol: no violet complex formed	
			amylmetacresol: violet complex formed	[2]

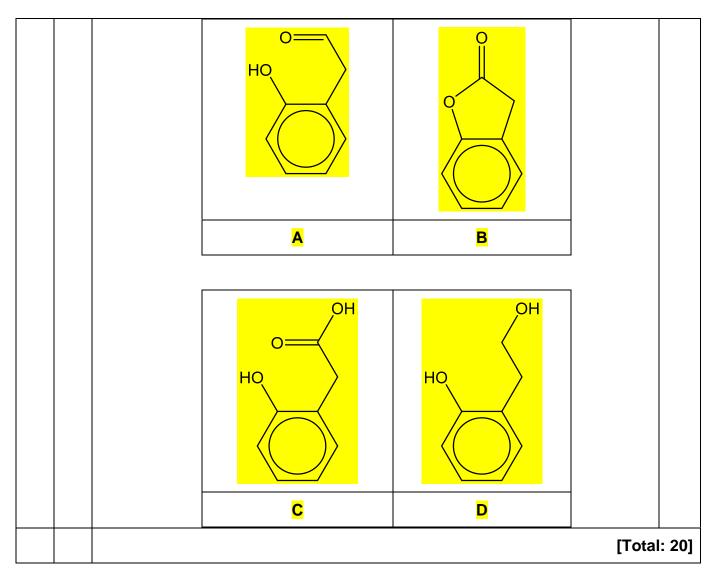
((b)	Menth	nol < amylmetacresol < tartaric acid	
		<u>electr</u>	nol is the weakest acid. <u>is the least stable anion</u> as the <u>on-donating alkyl group intensifies the negative charge</u> on the oxygen in the anion.	
		anion	netacresol is more acidic than menthol as the <u></u>	
		stable	ric acid is the most acidic as the <u>anion is the most</u> anion is the most acidic as the <u>anion is the most</u> anion is the most anion is the most	
			anion.	[3]
	(c)	(i)	Step 1: electrophilic substitution / electrophilic addition Step 2: reduction (Note: for step 1, the catalyst aids in the formation of CH ₃ CHCH ₃ ⁺ electrophile)	[2]
		(ii)	8 enantiomers	[2]
			Proportion = 0.125 / 12.5%/ 1/8	[2]

(d)	(iii)	(Accept: benzoate salt) When 0.00 cm ³ of NaOH is added, solution contains only tartaric acid. $[H^*] = \sqrt{(0.0100)(10^{-2.89})} = 3.59 \times 10^{-3} \text{ mol dm}^{-3}$ $pH = -lg(3.59 \times 10^{-3}) = 2.45$ When 12.50 cm ³ of NaOH is added, solution contains equal concentration of unreacted tartaric acid and tartrate mono-anion, giving rise to a <u>buffer at its maximum buffering capacity</u> . Hence, $pH = pK_{a1} = 2.89$. When 50.00 cm ³ of NaOH is added, solution only contains tartrate di-anion which undergoes hydrolysis to form OH ⁻ . [Tartrate di-anion] = $(\frac{25.00}{1000} \times 0.0100) \div \frac{75.00}{1000} = 0.00333 \text{ mol dm}^{-3}$	[1]
		$[OH^{-}] = \sqrt{(0.00333)(\frac{1.00 \times 10^{-14}}{10^{-4.40}})} = 9.15 \times 10^{-7} \text{ mol dm}^{-3}$ $pOH = -\lg(9.15 \times 10^{-7}) = 6.04$ $pH = 14 - 6.04 = \underline{7.96}$	[4]
	(ii)	The solid has a <u>giant ionic lattice structure</u> while tartaric acid has a <u>simple covalent structure</u> . <u>More energy</u> is needed to overcome the <u>stronger electrostatic attraction between the cations and anions</u> than the weak <u>hydrogen bonds between tartaric acid molecules</u> .	[2]
(e)	(i)	Cold dilute acidified / alkaline KMnO4(aq)	[1]
	(ii)		[1]

	(iii)	The gas is CO ₂ .	
		pV = nRT	
		p(500 × 10 ⁻⁶) = (^{0.36} / _{44.0})(8.31)(30 + 273)	
		p = <u>4.12 × 10⁴ Pa</u>	[2]
		[Total	: 23]

3	(a)	the ra	substance that is at a <u>different phase</u> as the reactants, and it <u>speeds up</u> ate of the reaction by <u>providing an alternative reaction pathway</u> with a activation energy.	[2]
	(b)	VO ₃ ^{-/} VO ^{2+/} V ³⁺ /V ³ <u>(VO₃⁻</u> Zn is spont <u>(VO²</u> Zn is spont <u>(V³⁺/</u>	h^{2+} half-cell $E \ominus = -0.76 \text{ V}$ VO^{2+} half-cell $E \ominus = +1.00 \text{ V}$ V^{3+} half-cell $E \ominus = +0.34 \text{ V}$ P^{2+} half-cell $E \ominus = -0.26$ $VO^{2+}//Zn/Zn^{2+}) E \ominus_{cell} = +1.76 \text{ V}$ is able to reduce VO_3^- to $VO^{2+}/$ reduction of VO_3^- to VO^{2+} by Zn is caneous. $P^{2+}/V^{3+}//Zn/Zn^{2+}) E \ominus_{cell} = +1.10 \text{ V}$ is able to reduce VO^{2+} to $V^{3+}/$ reduction of VO^{2+} to V^{3+} by Zn is caneous. $V^{2+}//Zn/Zn^{2+}) E \ominus_{cell} = +0.50 \text{ V}$ able to reduce V^{3+} to $V^{2+}/$ reduction of V^{3+} to V^{2+} by Zn is spontaneous.	
		Henc	e, the solution changes from <u>yellow to blue to green to violet</u> .	[3]
	(c)	(i)	<mark>V³⁺(aq)</mark>	[1]
		(ii)	$5VO^{2+} + MnO_4^- + 6H_2O \rightarrow 5VO_3^- + Mn^{2+} + 12H^+$ OR $5VO^{2+} + MnO_4^- + H_2O \rightarrow 5VO_2^+ + Mn^{2+} + 2H^+$	[1]
		(iii)	$n_{KMnO_4} = \frac{20.63}{1000} \times 0.02 = 0.000413 \text{ mol}$	[1]

	(iv)	$n_{V^{3+}} + n_{VO^{2+}} = \frac{25}{1000} \times 0.05 = 0.00125 \text{ mol}$ $n_{V^{3+}} = 0.00125 - x$ $n_{KMnO_4} \text{ reacted with } VO^{2+} = \frac{1}{5}x$ $n_{KMnO_4} \text{ reacted with } V^{3+} = \frac{2}{5}(0.00125 - x)$ $\frac{2}{5}(0.00125 - x) + \frac{1}{5}x = 0.000413$ $0.0025 - 2x + x = 0.002063$ $x = 0.000437 \text{ mol}$ $\ln 100 \text{ cm}^3 \text{ of solution:}$ $n_{V^{3+}} = 4(0.00125 - 0.000437) = 0.003252 \text{ mol}$	
		$n_{VO^{2+}} = 4x = 0.001748 \text{ mol}$ $m_{Zn} = 0.5[(65.4)(0.001748) + (65.4)(2)(0.003252)]$ = 0.270 g	[4]
(d)	C [.] H r	atio of A , B , C and D \approx 1:1	L 'J
(4)	<u>-</u>	Contains a benzene ring	
	Comp	oound A undergo oxidative esterification:	
	- -	 A has an aldehyde group / phenol / alcohol group. B has an ester group (also accept B being ester due to neutral nature) 	
	Comp	bound B undergo (alkaline) hydrolysis to form the sodium salt of C	
	-	B is a <u>cyclic</u> ester C has a carboxylic acid and alcohol / phenol group.	
	A, B	and C undergo reduction to form D	
	-	D contains 2 –OH group, of which one is a primary alcohol.	
	<mark>А, В</mark> а	and D can undergo electrophilic substitution with Br ₂ (aq)	
	-	A, B and D contains a phenol	
			[7]

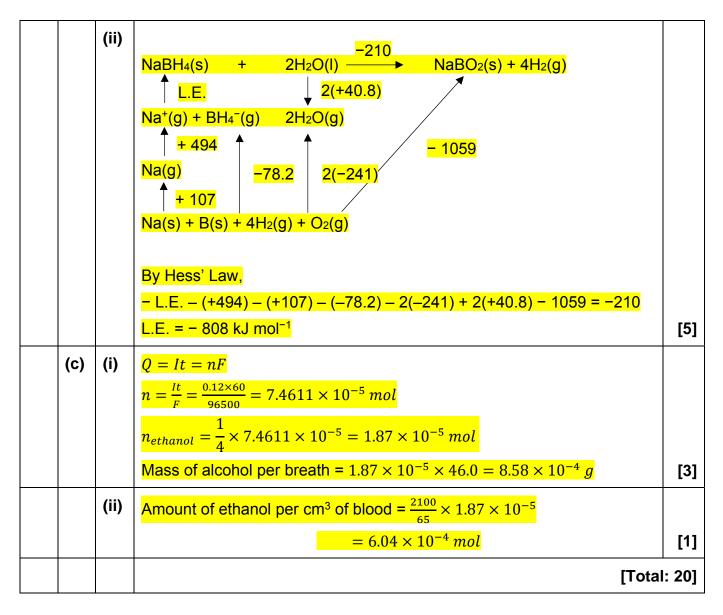


Section B

10

Answer **one** question from this section.

4	(a)	(i)	Base	[1]
		(ii)	S _N 2 nucleophilic substitution	
			$HC = \overline{C}: \qquad H \qquad HC = C \qquad H \qquad HC = C \qquad H \qquad HC = C \qquad HC $	
			Br ⁻	[3]
		(iii)	Phenylamine is a weaker base. The lone pairs of electrons on the –NH ₂ group is <u>delocalised into the benzene ring</u> , this <u>makes the lone pair less</u> available for protonation.	[1]
		(iv)	Step 2: ethanal	
			Step 4: Acidified K ₂ Cr ₂ O ₇ , heat (under reflux)	[2]
		(v)	HO COOH	
			The <u>C=C is electron rich</u> hence C=C does not attract CN ⁻ nucleophiles.	
			The carbonyl <u>C in C=O is electron-deficient</u> (or electrophilic) as it is bonded to highly electronegative O atom, attracting <u>CN⁻ nucleophiles</u> .	[3]
	(b)	(i)	Lattice energy is the enthalpy change when <u>one mole of the solid ionic</u> <u>compound</u> is formed <u>from its constituent gaseous ions</u> <u>under standard</u> <u>conditions.</u>	[1]



5	(a)	MgC	O(s) reacts with acid to form neutral salt and water.	
		MgC	$D(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2O(I)$	
		wate	$P_6(s)$ (or $P_4O_{10}(s)$) react violently/vigorously with alkali to form salt and er. $P_{10}(s) + 12OH^{-}(aq) \rightarrow 4PO_4^{3-}(aq) + 6H_2O(I)$	
		<mark>P₄O</mark>	$D_6(s) + 8OH^-(aq) \rightarrow 4HPO_3^{2-}(aq) + 2H_2O(I)$	
		root	0 ₆ (s) (or P ₄ O ₁₀ (s)) reactions with alkali is too exothermic (could burn the is of the plant), OR produces conjugate base which makes the soil aline.	[3]
	(b)	(i)	$Mg(NO_3)_2(s) \rightarrow MgO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$	
			$Ca(NO_3)_2(s) \rightarrow CaO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$	[1]
		(ii)	Mg(NO ₃) ₂ decomposed at 575 K but not Ca(NO ₃) ₂ .	
			Both Mg(NO ₃) ₂ and Ca(NO ₃) ₂ decomposed at 949 K.	
			Mg^{2+} has a <u>smaller ionic radius</u> than Ca^{2+} while their ionic charges are the same. <u>Charge density of Mg^{2+} is higher</u> and hence has higher polarising power than Ca^{2+} . Mg^{2+} is able to <u>polarise / distort the electron</u> <u>cloud of NO_3^{2-} and weaken the covalent bonds in NO_3^{2-} to larger extent.</u>	
			Since the mole ratio of Mg(NO ₃) ₂ and Ca(NO ₃) ₂ in the samples is 2:1, Sample at 575 K lost x g from Mg(NO ₃) ₂	
			Sample at 949 K lost x g from Mg(NO ₃) ₂ and 2 x g from Ca(NO ₃) ₂ (3 x g in total).	[3]
	(c)	(i)	To condense the product formed so that it can be collected.	[1]
		(ii)	Hydrolysis:	
			Oxidation: HO + $[O]$ + H_2O	[2]
		(iii)	3-methylbutanal (lowest b.p. compared to the isoamyl cinnamate, cinnamic acid and 3-methylbutanol, deduce using chem bonding knowledge)	[1]

	(iv)		[2]
(d)	(i)	Total amount of gallic acid (GA) = $\frac{1.00}{170}$ = 0.005882 mol	
		GA = 4NaOH	
		Amount of GA in 100 cm ³ aqueous layer = $\frac{20.25}{1000} \times 0.180 \times \frac{1}{4} \times 5$	
		$= 4.556 \times 10^{-3}$ mol	
		Amount of GA in 50 cm ³ organic layer = $0.005882 - 4.556 \times 10^{-3}$	
		$= 1.326 \times 10^{-3} \text{ mol}$	
		$\frac{K_{partition}}{K_{partition}} = \frac{\left(\frac{4.556 \times 10^{-3}}{0.100}\right)}{(1.326 \times 10^{-3})} = 1.72$	
			[3]
	(ii)	Add (100 cm ³ of / an excess of) aqueous NaOH and the (50 cm ³ of) diethyl ether containing both gallic acid and 3,4,5-trimethylgallic acid to a separatory funnel. Shake the two layers to ensure all the gallic acid are neutralised by NaOH. Vent the separatory funnel periodically to prevent pressure build up. <u>Salt of gallic acid much more soluble in</u> aqueous layer than diethyl ether layer as it can form more ion-dipole interaction with water molecules. Thus, mainly 3,4,5-trimethylgallic acid is left in the diethyl ether layer.	
		modification: use of aqueous NaOH to neutralise the gallic acid and its derivatives	
		explanation: explain why mainly 3,4,5-trimethoxygallic acid is left in diethyl ether layer	
		gallic acid forms anion with more charge (+4) than anion from 3,4,5- trimethoxygallic acid, therefore more ion-dipole interaction	
		bulky 3,4,5-trimethoxybenzyl group hinders the formation of ion-dipole, thus anion from 3,4,5-trimethoxygallic acid form significant pd-pd with diethyl ether	[2]
	(iii)	Test: Add acidified KMnO4, heat. Bubble gaseous product into limewater.	
		For methyl gallate, purple KMnO ₄ is decolourised and a colourless, odourless gas evolved gives white ppt in limewater.	
		For gallic acid, KMnO ₄ remained purple.	[2]
		[Total	: 20]