

RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

| H2 CHEN Paper 1 Multipl | IISTRY e Choice | | 9729/01 20 September 2018 1 hour |
|----------------------------|--------------------|-----------------|--|
| CENTRE NUMBER | S | INDEX NUMBER | |
| CLASS | 6 | | |
| CANDIDATE NAME | | | |

Additional Materials: 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?

| | Α | S | В | SO ₂ | С | HSO₄ [−] | D | H_2S |
|--|---|---|---|-----------------|---|-------------------|---|--------|
|--|---|---|---|-----------------|---|-------------------|---|--------|

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 |
|---|
|---|

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_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** 9.72

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.

$$\mathbf{X} + \mathbf{Y}_2(aq) \xrightarrow{\mathbf{H}^+} \mathbf{X}\mathbf{Y}(aq) + \mathbf{H}\mathbf{Y}(aq)$$

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 | Х |
|---|----|----|
| 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 | |
| А | H⁺ Mn ²⁺ 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 | Mn²⁺ Mn³⁺ | 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?

A 2 **B** 4 **C** 6 **D** 8

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
 - $3 \qquad CH_3CH_2OCH_2CH_2OCH_2CH_3$
 - 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:



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?

| Α | $C_6H_5OCOCH_2CH_3$ | В | $C_6H_5CH_2OCOCH_3$ |
|---|--|---|---|
| С | C ₆ H ₅ COOCH ₂ CH ₃ | D | C ₆ H₅CH ₂ COOCH ₃ |

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

| H2 CHEN | /IST | RY | | | | | 9729 | /02 |
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| CENTRE NUMBER | S | 3 | 0 | 4 | 4 | INDEX NUMBER | | |
| CLASS | | |] | | | | | |
| CANDIDATE NAME | | | | | | | | |

Paper 2 Structured Questions

Additional Materials:

Data Booklet

READ THESE INSTRUCTIONS FIRST.

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

| Write your name | , class and inde | | | PAPE | R 2 | | | |
|---|---------------------------------------|-----------------------|------------|-------------------|-----|-------|------|----|
| in the spaces at t Write in dark blue | he top of this pag e or black pen. | Je. | | QUESTION 1 | | | | 9 |
| You may use diagrams or grap | an HB pencil hs. | for any | | QUESTION 2 | | | | 9 |
| Do not use highlighters, glue | staples, pape or correction flui | er clips, d. | | QUESTION 3 | | | | 8 |
| 0 0 /0 | | | | QUESTION 4 | | | | 14 |
| Answer all qu provided on the (| iestions in the Question Paper. | 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 | narks is given in of each questio | brackets n or part | | Units | | | | |
| question. | or each queene | n or part | | s.f. | | | | |
| PAPER 1 | PAPER 2 | PAPER 3 | 3 | TOTAL | PA | PER 4 | GRAD |)E |
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| 30 | 75 | 8 | 30 | 185 | | 55 | | |
| | | | | | | | | |

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

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12 Sep 2018

2 hours

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

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):

.....

- [2]
- (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) compared to that of magnesium. [1] [Total: 9] **2** Pyridine C_5H_5N 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 cm³ of 0.0125 mol dm⁻³ hydrochloric acid is added to 25.00 cm³ of 0.100 mol dm⁻³ of pyridine.

[3]

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

[3] [Total: 9] **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 NO₂C*l*(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 NO₂C*l* 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 t_2 , 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 t_3 . A new equilibrium was established at t_4 .

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 NO₂Cl at time = 0, t_1 and t_2 .



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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

- [1]
- (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.

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*.



(ii) Hence, write the rate equation and deduce the rate constant of the reaction, stating its units.



- (b) In bacteria, sucrose is broken down into glucose and fructose by the enzyme, invertase. Experiments were done to measure the rate of the enzyme-catalysed hydrolysis reaction for different concentrations of sucrose.
 - (i) Sketch a graph to show how the rate of this enzyme-catalysed hydrolysis reaction varies with the concentration of sucrose until sucrose is in large excess.

(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.

.....[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.

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

(b) Explain why there is a difference in the colour observed for $[Mn(CN)_6]^{4-}$ and [Mn(CN)₆]³⁻ ions.

..... [2]

Given that: (C)

 $[Mn(CN)_6]^{3-} + e \rightleftharpoons [Mn(CN)_6]^{4-} \qquad E^{\ominus} = -0.24 \text{ V}$

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]

[Turn over

[1]

(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-orbtials 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.



(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.

(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 mol 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^{Θ}_{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.

$$Mn(OH)_{3}(s) + e^{-} \rightleftharpoons Mn(OH)_{2}(s) + OH^{-}(aq) \qquad E^{\ominus} = +0.18 V$$

[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 (H_2S), 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 |
| hydrogen sulfide | 1.2 | - 482 |
| hydrogen | 2.7 | - 386 |
| nitrogen | 2.3 | - 43.1 |

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



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.

 Identity of gases:
 and

 Identity of gases:
 [2]

 (ii)
 Write balanced equations to show the reaction for 1 mole of each component of biogas that reacted under standard conditions.

 Identity of gases:
 [2]

 (iii)
 [2]

 (iii)
 [2]

 (iii)
 [2]

 (iii)
 [2]

 (iii)
 [2]

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(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.

18

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



(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] |
|---------|

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.

[Total: 13]

- End of Paper -

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MARK SCHEME

| 1 | (a) | W: Si | |
|---|-------------|---|---------|
| | | $\frac{\text{SiC}l_4 + 2\text{H2O} \rightarrow \text{SiO}_2 + 4\text{HC}l}{1}$ | |
| | | X: P | |
| | | $PCl_5 + CH_3COOH \to POCl_3 + CH_3COCl$ | |
| | | OR | |
| | | $3CH_{3}COOH + PCI_{3} \longrightarrow 3CH_{3}COCI + H_{3}PO_{3}$ | [4] |
| | (b) (i) | $A_{l_2}O_3(s) + 2NaOH(aq) \rightarrow 2Na[A_l(OH)_4](aq) + H_2O(I)$ | |
| | | OR | |
| | | Al₂O₃(s) + 2OH⁻(aq) → 2[Al(OH)₄]⁻(aq) + H₂O(I) | [3] |
| | (b) (ii) | On addition of HCl(aq), <u>a white ppt is formed</u> . <u>Ppt would dissolve in excess</u> <u>HCl(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 polarise the CO_3^{2-} anion to a lower extent (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] |

| | | | 1 |
|---|-----|---|-----|
| 2 | (a) | For pH = 3.5 | |
| | | [H ⁺] = 10 ^{-3.5} = <u>3.16 x 10⁻⁴ moldm⁻³</u> | |
| | | Let the number of moles of C ₅ H ₅ NHC <i>l</i> be Y mol | |
| | | Since p $K_a = 5.25$, $K_a = 10^{-5.25} = 5.62 \times 10^{-6}$ | |
| | | | |
| | | $(3.16 \times 10^{-4})^2$ / Y – (3.16×10^{-4}) = 5.62 × 10 ⁻⁶ | |
| | | $Y = [(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}] + (3.16 \times 10^{-4})$ | |
| | | = <u>0.0181 mol</u> | |
| | | <u>Or</u> | |
| | | $(3.16 \times 10^{-4})^2$ / Y = 5.62 × 10 ⁻⁶ | |
| | | $Y = [(3.16 \times 10^{-4})^2 / 5.62 \times 10^{-6}]$ | |
| | | = <u>0.01/8 mol</u> | |
| | | | |
| | | Mass to be added = $(0.0181 \times (12.0 \times 5 + 1.0 \times 6 + 14.0 + 35.5)) \div 0.98$ | [2] |
| | | | ျာ |
| | (b) | $[C_{5}H_{5}N] = [(0.100 \times 0.025) - (0.0125 \times 0.005)] / 0.03 = 0.0813 \text{ mol dm}^{-3}$ | |
| | | [pyridinium chloride] = $(0.0125 \times 0.005) / 0.03 = 2.08 \times 10^{-3} \text{ mol dm}^{-3}$ | |
| | | | |
| | | $pK_{b} = 14 - pK_{a} = \frac{8.75}{1000}$ | |
| | | $pOH = p_{Ab} + lg [sall/[base]$ | |
| | | $pOH = 6.75 + lg (2.08 \times 10^{-7} 0.0813) = 7.10$ pH = 14 - 7.16 = 6.84 | [3] |
| | | | [3] |
| | (c) | On addition of a <u>small amount of acid</u> (H ⁺) to the buffer solution, nearly all the added H ⁺ ions are neutralised by the large amount of C ₅ H ₅ N. Hence [H ⁺] | |
| | | does not increase appreciably and the pH is kept approximately constant. | |
| | | C_5H_5N (aq) + H ⁺ (aq) $\rightarrow C_5H_5NH^+$ (aq) | |
| | | 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 | |
| | | constant. | |
| | | $C_5H_5NH^+$ (aq) + OH ⁻ (aq) $\rightarrow C_5H_5NH$ (aq) + H ₂ O(I) | [3] |
| | | [Total: 9] | |
| | | | - |





River Valley High School 2018 Preliminary Examinations

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[Turn over
| 4 | (a) | (i) | Comparing Experiments 1 and 2, 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 HC <i>l</i> . Comparing Experiments 1 and 3, | |
|---|-----|-------|--|-----|
| | | | Hence, reaction is first order with respect to sucrose. | [2] |
| | | (ii) | Rate = k [sucrose] [HC/] From Experiment 1, [sucrose] = $0.850 \times \frac{20}{50} = 0.340 \text{ mol dm}^{-3}$ [HC/] = $1.23 \times \frac{30}{50} = 0.738 \text{ mol dm}^{-3}$ $k = -\frac{1.77 \times 10^{-3}}{50} = 7.05 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^{3} \text{ min}^{-1}$ | |
| | | | $K = \frac{10}{(0.340)(0.738)} = 7.05 \times 10^{-5}$ moles differ filling | [2] |
| | | (111) | [sucrose] = $0.850 \times \frac{40}{70} = 0.486 \text{ mol dm}^{-3}$ [HC/] = $1.23 \times \frac{20}{70} = 0.351 \text{ mol dm}^{-3}$ Both concentrations for Initial rate of reaction = $7.05 \times 10^{-3} \times 0.486 \times 0.351$ = $1.20 \times 10^{-3} \text{ mol dm}^{-3} \text{ min}^{-1}$ | [2] |
| | (b) | (i) | [sucrose] | [1] |

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

| 5 | (a) | Due t transi simila | 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. | | | | | |
|---|-----|---|---|-----|--|--|--|--|
| | (b) | In the <u>metal</u> <u>to</u> th <u>confic</u> <u>energ</u> <u>from</u> <u>orbita</u> | In the presence of octahedral <u>ligand</u> field, the <u>degenerate d-orbitals in the</u> <u>metal complex were spilt into two energy levels</u> . The <u>colour observed is due</u> <u>to</u> the difference in energy levels, ΔE . The <u>difference in electronic</u> <u>configuration due to different oxidation state affect ΔE. Light of different</u> <u>energies/ different wavelengths are absorbed for the promoion of electrons</u> <u>from the lower energy orbital to the vacant/partially filled higher energy</u> <u>orbital/ d-d transition</u> , different complementary colour is observed. | | | | | |
| | (c) | E [⊖] (M shows cynaio <u>the n</u> e | $E^{\ominus}(Mn^{3+}/Mn^{2+})$ is <u>more positive</u> than $E^{\ominus}([Mn(CN)_6]^{3-}/[Mn(CN)_6]^{4-})$, which shows that Mn^{3+} is <u>more readily reduced</u> , hence a weaker oxidising agent in cynaide solution than in water. <u>More energy</u> is required to <u>add an electron to the negatively charged [Mn(CN)_6]^{3-} due to repulsion</u> . | | | | | |
| | (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] $3H^+ + 2e + HMnO_4^- \rightarrow MnO_2 + 2H_2O$ Overall equation: $3HMnO_4^- + H^+ \rightarrow MnO_2 + 2 MnO_4^- + 2H_2O$ | [1] | | | | |
| | | (ii) | $E_{cell} = +2.10 - (+0.90) = +1.20 \text{ V}$ $\Delta G = -nFE_{cell} = -(2)(96500)(1.20) = -232 \text{ kJ mol}^{-1}$ | [2] | | | | |
| | (f) | In acidic condition, | | | | | | |
| | | $O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23 V$ | | | | | | |
| | | Mn^{3+} + e \Rightarrow Mn^{2+} E [⊖] = +1.54 V | | | | | | |
| | | E [⊖] _{cell} | <mark>= +1.23 – (+1.54) = −0.31 V</mark> | | | | | |
| | | | | | | | | |

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| | <mark>In alk</mark> | aline solution, | |
|--|--------------------------------|--|--------|
| | <mark>O₂ + 2</mark> | 2H₂O + 4e ⇒ 4OH⁻ | |
| | E [⊖] _{cell} | = +0.40 - (+0.18) = +0.22 V | |
| | | | |
| | <mark>Since</mark> | the <u>E[⊖]_{cell} > 0 in alkaline</u> environment and <u>E[⊖]_{cell} _< 0 in acidic</u> | |
| | enviro enviro | onment, <u>Mn(II) is more stable in acidic environment</u> than in alkaline | |
| | envire | | |
| | | [Tota | l: 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: | | | |
| | | | $CH_4(g) + 2O_2(g) \to CO_2(g) + 2H_2O(I)$ | | | |
| | | | 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 × 4.18 × (64.7 – 29.6) = 29.34 kJ | | | |
| | | | mass of biogas used = $1000 \times 6.44 \times 10^{-4}$ = 0.644 g | | | |
| | | | Fuel value of biogas = 29.34 ÷ 0.644 = 45.6 kJ g ⁻¹ | [2] | | |
| | | (iv) | Amount of methane in 1 dm ³ biogas = $0.644 \times 0.722 \div (12.0 + 4.0)$ | | | |
| | | = 0.0291 mol | | | | |
| | | Amount of H ₂ S in 1 dm ³ biogas = $0.644 \times 0.012 \div (2.0 + 32.1)$ | | | | |
| | | | = 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 | | | |
| | | | $= (0.0291 \times \Delta H_{c}(CH_{4})) + (0.000227 \times 482) + (0.00869 \times 386)$ | | | |
| | | | $\Delta H_{\rm c}(\rm CH_4) = -890 \ \rm kJ \ mol^{-1}$ | [2] | | |
| | (c) | • Lo | onger time for hot flue gas to pass through spiral copper coil | | | |
| | | • Sp | piral copper coil increase the surface area for energy transfer | | | |
| | | • th | e combustion takes place inside the apparatus, not affected by | | | |
| | | dr | aught. | [1] | | |
| | (d) | To <u>re</u> irritate | move sulfur dioxide gas as low concentration of this gas can also | [4] | | |
| | | | | | | |
| | | [Total: 10] | | | | |

| 7 | (a) | (i) | Reaction I: H ₂ N–NH ₂ Reaction II: PBr ₃ | | | |
|---|-----|---|---|--------|--|--|
| | | (ii) | | | | |
| | | | G: OH O OH O OH O OH O OH | [2] | | |
| | | (iii) | Electrophilic substitution | | | |
| | | | $ \begin{array}{c} $ | | | |
| | | | $ \begin{array}{c} & & \\ & & $ | [3] | | |
| | (b) | <mark>1) Te</mark> s | 1) Test: Add Br ₂ (aq). | | | |
| | | Comp | Compound F : Orange Br ₂ (aq) decolourises. | | | |
| | | Comp | Compounds B and C : Br ₂ (aq) remains orange. | | | |
| | | Z) Tes | 2) Test: Add AgNU ₃ (aq) | | | |
| | | Comp | ound C : Cream ppt (AgBr) forms. | [4] | | |
| | (c) | Brick-red precipitate forms. | | | | |
| | | $ + 2Cu^{2+} + 5OH^{-} $ warm $ - + Cu_2O + 3H_2O $ brick red ppt [2] | | | | |
| | | | [Tota | l: 13] | | |

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RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

| CANDIDATE NAME | | | | |
|-------------------|---------|-----------------|-----------------|------------------------------|
| CLASS | 6 | | | |
| CENTRE NUMBER | S | | INDEX NUMBER | |
| H2 CHEN | IISTR | Y | | 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. [1]
- (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]

- (c) Calcium phosphate, $Ca_3(PO_4)_2$, 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 SO_4^{2-} .

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

[Total: 18]

[2]

[2]

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 |
| non octivo | (–)-menthol | ОН |
| 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. [1]

(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.

[4]

[2]

- (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 |
| VO₃ [−] | +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]

[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. [1]
 (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 mol of VO²⁺ 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.

[Total: 19]

[7]

[4]

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 $NaNH_2$ 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.
 [3]

(iii)



phenylamine

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

- (iv) Suggest the reagent A in Step 2, and reagents and conditions for Step 4. [2]
- (v) Draw the structure of Compound Y.

Explain why HCN reacts with C=O but not with C=C in the same compound. [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.

NaBH₄(s) + 2H₂O(I)
$$\rightarrow$$
 NaBO₂(s) + 4H₂(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 cm³, calculate the amount of ethanol per cm³ of blood. [1]

[Total: 20]

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**.



- (i) State the function of the apparatus A. [1] Name and write balanced equations for two major reactions that occur (ii) in the 2-neck round-bottom flask. You may use [O] or [H] to balance the equations. [2] (iii) Identify the first organic compound that is likely to be collected in flask **B**. [1] Draw the skeletal structures of all the organic products formed if (iv) 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.

(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. [2]

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

[Total: 20]

- End of Paper -

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16

| Section . | Α |
|-----------|---|
|-----------|---|

| 1 | (a) | (i) | Element E ^O / V | |
|---|-----|------|--|-----|
| | | | $\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$ +2.87 | |
| | | | $\frac{1}{2}Cl_{2} + e^{-} \rightleftharpoons Cl^{-} + 1.36$ | |
| | | | <mark>½Br₂ + e⁻ ≓ Br⁻</mark> +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 <i>E</i> [⊖] values above, <u>decreases down the Group.</u> | |
| | | | Due to the strong oxidising power of F_2 , the oxidation number of Phosphorus +5 in PEr, +5 and +3 in PC/r and PC/r +3 in PBr, and | |
| | | | $\frac{PI_3 \text{ respectively.}}{PI_3 \text{ respectively.}}$ | [3] |
| | | (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 CH2MgBr | [2] |

| | (iii) | $:CH_3^{-} \longrightarrow H_3^{-} \longrightarrow H_$ | [3] |
|-----|-------|--|--------|
| (c) | (i) | $K_{\rm sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$ | [1] |
| | (ii) | $[Ca^{2+}] = 1.14 \times 10^{-7} \times 3 = 3.42 \times 10^{-7} \text{ mol dm}^{-3}$ $[PO_4^{3-}] = 1.14 \times 10^{-7} \times 2 = 2.28 \times 10^{-7} \text{ mol dm}^{-3}$ $K_{m} = (3.42 \times 10^{-7})^3 (2.28 \times 10^{-7})^2 = 2.08 \times 10^{-33} \text{ mol}^5 \text{ dm}^{-15}$ | [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> $CaSO_4 \Rightarrow Ca^{2+} + SO_4^{2-}$ 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> $Ca_3(PO_4)_2 \Rightarrow 3Ca^{2+} + 2PO_4^{3-}$ 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</u> bond has a partial double bond character as the lone pair of 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) | | [1] |
| | | (iv) | Add PCI ₅ / SOCI ₂ | |
| | | | 2,4-dichlorobenzyl alcohol: white fumes (of HC <i>l</i>) observed | |
| | | | amyImetacresol: no white fumes observed | |
| | | | <u>or</u> | |
| | | | Add Br ₂ (aq) | |
| | | | 2,4-dichlorobenzyl alcohol: Br ₂ (aq) remains orange | |
| | | | amylmetacresol: orange Br ₂ (aq) decolourises | |
| | | | | |
| | | | Add neutral FeC/3 | |
| | | | 2,4-dichioropenzyl alconol: no violet complex formed | [0] |
| | | | amyimetacresoi: violet complex formed | [2] |



| | (iii) | | |
|-----|-------|--|-----|
| | | | |
| | | | |
| | | (Accept: benzoate salt) | [1] |
| (d) | (i) | 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 cm³ of NaOH is added, solution only contains tartrate di-anion which undergoes hydrolysis to form OH⁻. | |
| | | [Tartrate di-anion] = $\left(\frac{25.00}{1000} \times 0.0100\right) \div \frac{75.00}{1000} = 0.00333 \text{ mol dm}^{-3}$ | |
| | | $[OH^{-}] = \sqrt{(0.00333)(\frac{1.00 \times 10^{-14}}{10^{-4.40}})} = 9.15 \times 10^{-7} \text{ mol dm}^{-3}$ | |
| | | $pOH = -lg(9.15 \times 10^{-7}) = 6.04$ | |
| | | pH = 14 – 6.04 = <u>7.96</u> | [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 stronger electrostatic attraction between the cations and anions than | |
| | | the weak hydrogen bonds between tartaric acid molecules. | [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] |
| | | [Tota | : 23] |

| 3 | (a) | lt is a the ra lower | 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) | Zn/Zn VO ₃ ^{-/} VO ^{2+/} V ³⁺ /V ³ <u>(VO₃⁻</u> Zn is spont <u>(VO²</u> Zn is spont <u>(V³⁺/</u> Zn is | 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 $E \ominus = -0.26$ $VO^{2+}//Zn/Zn^{2+}) E \ominus_{cell} = +1.76 \text{ V}$ A able to reduce VO_3^- to $VO^{2+}/$ reduction of VO_3^- to VO^{2+} by Zn is aneous. $V^{3+}//Zn/Zn^{2+}) E \ominus_{cell} = +1.10 \text{ V}$ A able to reduce VO^{2+} to $V^{3+}/$ reduction of VO^{2+} to V^{3+} by Zn is aneous. $V^{2+}//Zn/Zn^{2+}) E \ominus_{cell} = +0.50 \text{ V}$ 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) | V ³⁺ (aq) | [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) | $n_{KMnO_4} = \frac{20.63}{1000} \times 0.02 = 0.000413 \ mol$ | [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} reacted with VO ²⁺ = $\frac{1}{5}x$ | |
| | | n_{KMnO_4} 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 mol | |
| | | In 100 cm ³ of solution: | |
| | | $n_{V^{3+}} = 4(0.00125 - 0.000437) = 0.003252$ mol | |
| | | $n_{VO^{2+}} = 4x = 0.001748$ mol | |
| | | $m_{Zn} = 0.5[(65.4)(0.001748) + (65.4)(2)(0.003252)]$ | |
| | | = 0.270 g | [4] |
| (d) | <mark>C:H</mark> r | atio of A , B , C and D ≈ 1:1 | |
| | - | Contains a benzene ring | |
| | <mark>Comp</mark> | 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) | |
| | <mark>Com</mark> p | 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. | |
| | <mark>A, B</mark> a | and C undergo reduction to form D | |
| | - | D contains 2 –OH group, of which one is a <u>primary alcohol</u> . | |
| | A, B a | and D can undergo electrophilic substitution with Br ₂ (aq) | |
| | - | A, B and D contains a phenol | |
| | | | |
| | | | [7] |



Section B

Answer **one** question from this section.



| | (ii) | -210 | |
|-----|------|---|-------|
| | | NaBH ₄ (s) + $2H_2O(I) \xrightarrow{-210}$ NaBO ₂ (s) + $4H_2(g)$ | |
| | | L.E. 2(+40.8) | |
| | | $Na^{+}(g) + BH_{4}^{-}(g) = 2H_{2}O(g)$ | |
| | | [↑] + 494 [↑] [↑] − 1059 | |
| | | Na(g) -78.2 2(-241) + 107 | |
| | | $Na(s) + B(s) + 4H_2(g) + O_2(g)$ | |
| | | By Hess' Law, | |
| | | - L.E (+494) - (+107) - (-78.2) - 2(-241) + 2(+40.8) - 1059 = -210 | |
| | | <mark>L.E. = − 808 kJ mol⁻¹</mark> | [5] |
| (c) | (i) | Q = It = nF | |
| | | $n = \frac{It}{F} = \frac{0.12 \times 60}{96500} = 7.4611 \times 10^{-5} mol$ | |
| | | $n_{ethanol} = \frac{1}{4} \times 7.4611 \times 10^{-5} = 1.87 \times 10^{-5} mol$ | |
| | | Mass of alcohol per breath = $1.87 \times 10^{-5} \times 46.0 = 8.58 \times 10^{-4} g$ | [3] |
| | (ii) | Amount of ethanol per cm ³ of blood = $\frac{2100}{65} \times 1.87 \times 10^{-5}$ | |
| | | $= 6.04 \times 10^{-4} mol$ | [1] |
| | | [Total | : 20] |

| 5 | (a) | <mark>MgO</mark> | o(s) reacts with acid to form neutral salt and water. | | | | | |
|---|-----|---------------------------|---|-----|--|--|--|--|
| | | <mark>MgO</mark> | $MgO(s) + 2H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2O(I)$ | | | | | |
| | | P₄O wate P₄O P₄O | P ₄ O ₆ (s) (or P ₄ O ₁₀ (s)) <u>react violently/vigorously with alkali</u> to form salt and water. P ₄ O ₁₀ (s) + 12OH ⁻ (aq) → 4PO ₄ ³⁻ (aq) + 6H ₂ O(I) P ₄ O ₆ (s) + 8OH ⁻ (aq) → 4HPO ₃ ²⁻ (aq) + 2H ₂ O(I) | | | | | |
| | | P₄O root alka | ₆ (s) (or P ₄ O ₁₀ (s)) reactions with alkali is too exothermic (could burn the s of the plant), OR produces conjugate base which makes the soil line. | [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 Mg²⁺ is higher</u> and hence has higher polarising power than Ca ²⁺ . Mg ²⁺ is able to <u>polarise / distort the electron</u> cloud of NO ₃ ²⁻ and weaken the covalent bonds in NO ₃ ²⁻ to larger extent. 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 2x g from Ca(NO ₃) ₂ (3x g in total). | [3] | | | | |
| | (c) | (i) | To <u>condense the product</u> formed so that it can be collected. | [1] | | | | |
| | | (ii) | Hydrolysis: | | | | | |
| | | | $+ [0] \longrightarrow + H_2O$ | [2] | | | | |
| | | (iii) | 3-methylbutanal (lowest b.p. compared to the isoamyl cinnamate, cinnamic acid and 3-methylbutanol, deduce using chem bonding knowledge) | [1] | | | | |

12

| | | | |
|------|-------|--|-------|
| | (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 × 10 ⁻³ mol Amount of GA in 50 cm ³ organic layer = 0.005882 - 4.556 × 10 ⁻³ = 1.326 × 10 ⁻³ mol $K_{partition} = \frac{\left(\frac{4.556 \times 10^{-3}}{0.100}\right)}{\left(\frac{1.326 \times 10^{-3}}{0.050}\right)} = 1.72$ | [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. Salt of gallic acid much more soluble in 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 KMnO ₄ , 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] |
| | | ITotal | : 201 |
| | | | •1 |


H2 CHEMISTRY 9729

23 AUGUST 2018

2 HOURS 30 MINUTES

NAME

CLASS 6 ()

INDEX NO.

INSTRUCTIONS TO CANDIDATES

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Read these notes carefully.

Write your name, class and index number in the spaces at the top of this page. Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in dark blue or black pen.

You may use a 2B pencil for any diagrams or graph. Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

| Shift |
|------------|
| |
| Laboratory |
| |

| For Examiner's Use | | | |
|--------------------|----|--|--|
| 3 s.f. | | | |
| Units | | | |
| Total | 55 | | |

This Question Paper consists of **22** printed pages and **0** blank page.

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

1 To investigate the kinetics of the reaction between iron(III) ions and iodide ions

You will investigate the rate of oxidation of iodide by iron(III) ions in **reaction 2**. The chemical changes in this experiment can be presented by the following equations:

Reaction 1: $Fe^{3+}(aq) + S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)]^+(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

The reaction is started by mixing acidic solution of iron(III) chloride with sodium thiosulfate, potassium iodide, and starch.

The iodine, I_2 , produced in **reaction 2** reacts immediately with thiosulfate ions, $S_2O_3^{2-}$ in **reaction 3**.

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black. The rate of the reaction can therefore be determined by finding the time for the blue-black colour to appear.

FA 1 is 0.030 mol dm⁻³ iron(III) chloride, FeCl₃.

FA 2 is 0.060 mol dm⁻³ potassium iodide, KI.

FA 3 is 0.0060 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃. starch indicator

You are advised to read the instructions before starting any practical work and draw a table, in an appropriate format, for your results in the space on page 4.

You will need to include volume of **FA 1**, volume of water, reaction time and calculated rate of reaction for each of the five experiments. Record all calculated values to 3 significant figures.

(a) Method

Experiment 1

- 1. Use the measuring cylinders to place the following in a 100 $\rm cm^3$ beaker.
 - 10 cm³ of **FA 2**
 - 20 cm³ of **FA 3**
 - 10 cm³ of starch indicator
- 2. Using a measuring cylinder, transfer 20 cm³ of **FA 1** rapidly into the same 100 cm³ beaker. Start the stopwatch during this addition.
- 3. Stir the mixture and place the beaker on a white tile.
- 4. The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this blue-black colour appears. Record the time to the nearest 0.1 second.
- 5. Wash the beaker thoroughly with water and carefully dry the beaker.

For

Examiner's

Use

Experiment 2

- 6. Repeat step 1 in Experiment 1.
- Using a measuring cylinder, add 12 cm³ of FA 1, and make up the volume to 20 cm³ using deionised water. Transfer the solution rapidly into the same 100 cm³ beaker. Start the stopwatch during this addition.
- 8. Stir the mixture and place the beaker on the white tile.
- 9. Stop timing when a blue-black colour appears.
- 10. Wash the beaker thoroughly with water and carefully dry the beaker.

Experiments 3–5

Carry out three further experiments to investigate the effect of changing the concentration of $Fe^{3+}(aq)$ by altering the volume of aqueous $FeCl_3$, **FA 1**, used.

You should use a volume of **FA 1** that is at least 12 cm^3 and the total volume of the reaction mixture must always be 60 cm^3 .

(b) Show, by means of calculation, that the change in the concentration of Fe^{3+} , $\Delta[Fe^{3+}]$, which occurred when the blue-black colour appeared was 2.00×10^{-3} mol dm⁻³.



(c) Results

For Examiner's Use

The rate of the reaction can be calculated as shown.

rate =
$$\frac{\Delta [Fe^{3+}]}{\text{reaction time}} \times 10^6$$

Calculate the rate of reaction for each experiment and complete your table.

| 2 | |
|---|--|
| 3 | |
| 4 | |
| 5 | |





River Valley High School Practical Examination II 2018

| | (ii) Explain why the volume of FA 1 in each experiment can be us as [Fe ³⁺]. | | For Examiner's Use | | er's |
|-----|---|--|--------------------------|---|------|
| | | | 9 | | |
| | (iii) | Deduce the order of reaction with respect to Fe ³⁺ . Use evidence from your graph to support your deduction. | | | |
| | | | | | |
| | | | 10 | | |
| (e) | (i) | Use your graph to calculate the time that the reaction would have taken if 4.0 cm ³ of FA 1 had been used. Show your working clearly. | | | |
| | | | 11 | | |
| | (ii) | time = Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions if 4.0 cm ³ of FA 1 had been used. | | | |
| | | initial [Fe ³⁺] = | | | |
| | | initial [I ⁻] = | 12 | Τ | |
| | | | 12 | | |

| (e) | (iii) | Given that the reaction is second order with respect to iodide, calculate the rate constant. | F Exan U | ōor niner's Ise | | |
|-----|--|---|----------------|-----------------------|--|--|
| | | rate constant = | 13 | | | |
| (f) | i) The complex $[Fe(S_2O_3)]^+$ formed in reaction 1 is purple. | | | | | |
| | Consi solutio Suggo involv | der the colour change observed when FA 1 was added to the on prepared in Step 1 before the blue-black colour appeared. est an explanation for the colour change in terms of the chemistry red. | | | | |
| | | | | | | |
| | | | | 1 | | |
| | | | 14 | | | |
| | | | 15 | | | |
| | | [Total: 15] | | | | |

| 2 | Dete | rmining the percentage purity of calcium carbonate | For Examiner's | | | |
|---|---|---|-------------------|--|--|--|
| | In this question, you will determine the percentage purity of an industrial grade calcium carbonate, $CaCO_3$, by two different methods. | | | | | |
| | (a) | Method 1 | | | | |
| | | The percentage purity of calcium carbonate can be determined by measuring the change in mass when the sample of calcium carbonate reacts with hydrochloric acid. | | | | |
| | | $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(I) + CO_2(g)$ | | | | |
| | | FA 4 is industrial grade calcium carbonate, CaCO₃. FA 5 is 2.00 mol dm⁻³ dilute hydrochloric acid. | | | | |
| | | You do not need to carry out Method 1 . | | | | |
| | | Procedure: | | | | |
| | | Weigh accurately about 2.0 g of FA 4 in a small weighing bottle. Measure about 25 cm³ of FA 5 in a small conical flask. Add FA 4 to FA 5 and swirl the mixture continuously until no more bubbles is observed. | | | | |
| | | Reweigh the weighing bottle with its residual FA 4. Reweigh the conical flask and its content. | | | | |
| | | A student performed a series of experiments by repeating the above procedure with different masses of FA 4 . | | | | |
| | | The results from her series of experiment are plotted on the grid in Fig 2.1. | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |





| Procedure: | For |
|--|------------|
| 1. Pipette 25.0 cm ³ of FA 5 into flask X . | Examiner's |
| 2. Weigh accurately about 0.6 g of FA 4 in a weighing bottle. | Use |
| 3. Add the FA 4 into flask X . | |
| 4. Reweigh the weighing bottle with its residual FA 4 . | |
| 5. Swirl the mixture until no more bubbles are observed. | |
| 6. Transfer all the contents of flask X and the washings into a 250 cm ³ volumetric flask. | |
| 7. Add deionised water up to the mark, stopper the volumetric flask and mix the contents thoroughly. Label this solution FA 7 . | |
| 8. Fill the burette with FA 6 . | |
| 9. Wash and rinse the pipette then use it to transfer 25.0 cm ³ of FA 7 into a conical flask. | |
| 10. Add about 5 drops of thymolphthalein indicator. | |
| 11. Titrate FA 7 with FA 6 . | |
| 12. Repeat the titration as many times as you think necessary to obtain consistent results. | |
| Record in the space below, all of your mass readings, burette readings and the volume of FA 6 added. | |
| | |

Results





| (d) | From your accurate titration results, obtain a suitable value for the volume of FA 6 to be used in your calculations. Show clearly how you obtained this value. | | |
|------|--|--|----|
| Calc | ulatio | Volume of FA 6 used = | 26 |
| (e) | (i) | Calculate the number of moles of sodium hydroxide, NaOH, present in volume of FA 6 calculated in (d) . | |
| | (ii) | amount of NaOH = Calculate the number of moles of hydrochloric acid remaining in flask X after the reaction with FA 4 has completed. | 27 |
| | (iii) | amount of HC <i>l</i> remaining in flask $X =$ Calculate the number of moles of hydrochloric acid that reacted with the FA 4 used. | 28 |
| | | amount of HC <i>l</i> reacted = | 29 |

| | (iv) | Calculate the mass of $CaCO_3$ in the sample of FA 4 used, and hence the percentage purity of the industrial grade $CaCO_3$. | Fo Exam Us | or iner's se |
|-----|---------------|--|------------------|--------------------|
| | | [<i>A_r</i> : Ca, 40.1; C, 12.0; O,16.0] | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | percentage purity of the industrial grade $CaCO_3$ = | 30 | |
| (f) | The indu | two different methods were used to find the percentage purity of strial grade calcium carbonate. | | |
| | lt is reac | found that the samples of FA 4 used contain calcium oxide which ts with dilute hydrochloric acid. | | |
| | How Expl | would this affect the percentage purity calculated for each method? ain your answers. | | |
| | Meth | nod 1: | | |
| | | | | |
| | | | | |
| | | | | |
| | Meth | nod 2: | | |
| | | | | |
| | | | | |
| | | | | |
| | | | 31 | |
| | | | 32 | |
| (g) | Expl | ain why sulfuric acid cannot be used in both methods. | | |
| | | | | |
| | | | 33 | |
| | | | | |
| | | | I | |

(h) Planning

Unlike the acid-base titration in **Part (c)** that uses acid-base indicator to mark the end-point, thermometric titration uses heat evolved or temperature change of solution. In thermometric titration, the titre value can be determined from the graph of energy evolved against volume of titrant (solution from the burette) added.

Since neutralisation reaction is exothermic, thermometric titration can be used to determine the amount of excess hydrochloric acid in flask X from **Part (c)**.

(i) Given that the concentration of undiluted excess hydrochloric acid in flask X is about 1.7 mol dm⁻³, and the desired titre is around 24 cm³, calculate the concentration of sodium hydroxide required for the thermometric titration.

Concentration of NaOH =

(ii) You are to plan a thermometric titration to determine the concentration of hydrochloric acid. The results obtained should allow the titre value to be determined graphically.

You may assume that you are provided with

- 50 cm³ of hydrochloric acid, HC*l*, of concentration around 1.7 mol dm⁻³
- standard solution of sodium hydroxide solution, NaOH, of the same concentration calculated in (h)(i)
- apparatus commonly found in a school or college laboratory

In your plan you should include the following:

- a diagram of the apparatus set-up that may be used
- the procedure that you would follow and the measurements you would take
- the precautions and measures that you would take to minimise heat loss to the surroundings

For Examiner's Use

34

| For |
|------------|
| Examiner's |
| Use |

| | | | F Exar | For niner's |
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| | | | 38 | |
| | | | 39 | |
| | | | 40 | |
| | | | | |
| (h) | (iii) | Your procedure in (h)(ii) should allow the graph of total energy evolved against volume of titrant to be plotted. Briefly describe how you would use the results obtained to determine the total energy evolved from the start of the experiment for each data point. | | |
| | | | | |
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| | | | | |
| | | | 41 | |
| | | | | |

| (h) | (iv) | Sketch, on the axes in Fig. 2.2, the graph you would expect to obtain and show how you would use this graph to determine the titre value. | F Exan U | For niner's Ise |
|--------|---------|---|----------------|-----------------------|
| | | Explain the shape of your graph. | | |
| | | Fig. 2.2 | | |
| Energy | / evolv | ed/ J | | |
| | | | | |
| | 0 | Volume of NaOH added/ cm ³ | | |
| | Expla | anation [.] | | |
| | Слри | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | 1 |
| | | | 42 | |
| | | | 43 | |
| | (v) | Sketch, on the same axes in Fig. 2.2, the graph you would expect to obtain if aqueous ammonia of the same concentration as aqueous NaOH is used as the titrant instead. | | |
| | | Label this graph clearly as Graph B . | | |
| | | Explain the shape of Graph B . | | |
| | | | | |
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| | | | | |
| | | | 44 | |
| | | | 45 | |
| | | [Total: 30] | | |

3 Inorganic qualitative analysis

In this experiment you are to explore the chemistry of some compounds of an unknown transition element **W**. You are provided with 4 samples, **FA 8**, **FA 9**, **FA 10** and **FA 11**.

- **FA 8** is a solid sample of a common dioxide of the unknown transition element **W**.
- $\label{eq:FA9} \textbf{FA9} \qquad \text{is a dilute sulfuric acid, } H_2SO_4.$
- $\label{eq:FA10} \textbf{FA10} \quad \text{is a solid sample of sodium ethanedioate, } Na_2C_2O_4.$
- **FA 11** is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

Carry out the following experiments. Carefully record your observations. Test for any gases produced.

| | Test | Observations |
|--------|--|--------------|
| (a)(i) | Transfer all of the solid sample of FA 10 into a 100 cm ³ beaker. Add 25 cm ³ of FA 9 to this beaker. | |
| | Gently heat the beaker until the temperature of the mixture reaches about 60°C. | |
| | Stir the mixture carefully. Place the beaker on the white tile. | |
| | Add 2-3 spatulas of FA 8 to the mixture, stir the mixture carefully with a thermometer and observe any changes in the temperature of the mixture. | |
| | Filter the mixture into a boiling tube when you think the reaction is complete. Leave the filtrate to stand. The filtrate contains compound X . | |
| | Retain this filtrate for use in (a)(ii) . | |
| | | |
| | | |

| 46 | |
|----|--|
| 47 | |

For Examiner's Use

| (a) | (ii) | You are to investigate the effect of the addition of aqueous sodium hydroxide, and the addition of aqueous ammonia, to separate portions of the filtrate from (a)(i) and FA 11 . | For Examiner's Use |
|-----|--------------|--|--------------------------|
| | | In the space below, record the details of the tests performed and the observations made in a suitable table. | |
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| | | | |
| | | | 48 |
| | | | 49 |
| (b) | Expl shou | ain how you determined when the reaction is completed in 4(a)(i) . You Ild support your answer by referring to your observations. | 50 |
| | | | |
| | | | 51 |
| | | | |

| (c) | (i) | Consider your observations in (a)(ii). | F | or vinor'o |
|-----|------------------------|--|-----------|---------------|
| | | Identify the transition metal ion formed in (a)(i) . Justify your choice by making reference to your observations in (a)(ii) . | Exan U | se |
| | ion pr | resent is | | |
| | justifi | cation | | |
| | | | | |
| | | | 52 | |
| | (ii) | In (a)(i), the reaction between FA 8 and FA 10 occurs under acidic conditions. | | |
| | | Write a balanced equation for this reaction. | | |
| | | | 53 | |
| | (iii) | State the role of FA 8 in the reaction and support your answer by referring to your observations. | | |
| | | | | |
| | | | | |
| | | | | |
| | | | 54 | |
| (d) | Dedu (c) , o | ce the nature of reaction, other than the type of reaction identified in ccurring in (a)(i) . | | |
| | Justif | y by referring to your observations. | | |
| | | | | |
| | | | | |
| | | | 55 | |
| | | [Total: 10] | L | |
| | | | | |

END OF PAPER

Qualitative Analysis Notes [ppt. = precipitate] 9

9(a) Reactions of aqueous cations

| and in the | reaction with | | | |
|---|---|---|--|--|
| cauon | NaOH(aq) | NH₃(aq) | | |
| aluminium, A <i>t</i> ³*(aq) | white ppt. soluble in excess | white ppt. insoluble in excess | | |
| ammonium, NH₄⁺ (aq) | ammonia produced on heating | - | | |
| barium, no ppt. Ba ²⁺ (aq) (if reagents are pure) no ppt. | | no ppt. | | |
| calcium, white. ppt. with high Ca ²⁺ (aq) [Ca ²⁺ (aq)] no ppt. | | no ppt. | | |
| chromium(III), Cr ³⁺ (aq) | grey-green ppt. soluble in excess giving dark green solution | grey-green ppt. insoluble in excess | | |
| copper(II), Cu ²⁺ (aq), | pale blue ppt. insoluble in excess | blue ppt. soluble in excess giving dark blue solution | | |
| iron(II), Fe ²⁺ (aq) | green ppt., turning brown on contact with air insoluble in excess | green ppt., turning brown on contact with air insoluble in excess | | |
| iron(III), Fe ³⁺ (aq) | red-brown ppt. insoluble in excess | red-brown ppt. insoluble in excess | | |
| magnesium, Mg ²⁺ (aq) | white ppt. insoluble in excess | white ppt. insoluble in excess | | |
| manganese(II), Mn ²⁺ (aq) | off-white ppt., rapidly turning brown on contact with air insoluble in excess | off-white ppt., rapidly turning brown on contact with air insoluble in excess | | |
| zinc, Zn ²⁺ (aq) | white ppt. soluble in excess | white ppt. soluble in excess | | |

9(b) Reactions of anions

| anion | reaction | |
|---|--|--|
| carbonate, CO3 ²⁻ | CO ₂ liberated by dilute acids | |
| chloride, C <i>l</i> ⁻(aq) | gives white ppt. with $Ag^{+}(aq)$ (soluble in $NH_{3}(aq)$) | |
| bromide, Br ⁻ (aq) | gives pale cream ppt. with Ag ⁺ (aq) (partially soluble in NH ₃ (aq)) | |
| iodide, I⁻(aq) | gives yellow ppt. with $Ag^{+}(aq)$ (insoluble in $NH_{3}(aq)$) | |
| nitrate, NO ₃ ⁻ (aq) | NH_3 liberated on heating with $OH^-(aq)$ and Al foil | |
| nitrite, NO ₂ ⁻ (aq) | NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless $NO \rightarrow$ (pale) brown NO_2 in air) | |
| sulfate, SO_4^{2-} (aq) | gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids) | |
| sulfite, SO_3^{2-} (aq) | SO ₂ liberated with dilute acids; gives white ppt. with Ba ²⁺ (aq) (soluble in dilute strong acids) | |

9(c) Tests for gases

| gas | test and test result | | |
|---------------------------------|--|--|--|
| ammonia, NH ₃ | turns damp red litmus paper blue | | |
| carbon dioxide, CO ₂ | gives a white ppt. with limewater (ppt. dissolves with excess CO ₂) | | |
| chlorine, Cl ₂ | bleaches damp litmus paper | | |
| hydrogen, H ₂ | "pops" with a lighted splint | | |
| oxygen, O ₂ | relights a glowing splint | | |
| sulfur dioxide, SO ₂ | turns aqueous acidified potassium manganate(VII) from purple to colourless | | |

9(d) Colour of halogens

| halogen | colour of element | colour in aqueous solution | colour in hexane |
|---------------------------|----------------------------|----------------------------|------------------|
| chlorine, Cl ₂ | greenish yellow gas | pale yellow | pale yellow |
| bromine, Br ₂ | reddish brown gas / liquid | orange | orange-red |
| iodine, I_2 | black solid / purple gas | brown | purple |



RIVER VALLEY HIGH SCHOOL YEAR 6 PRACTICAL EXAMINATION II

H2 CHEMISTRY 9729

23 AUGUST 2018

2 HOURS 30 MINUTES

NAME

CLASS 6 ()

INDEX NO.

INSTRUCTIONS TO CANDIDATES

DO NOT OPEN THIS BOOKLET UNTIL YOU ARE TOLD TO DO SO.

Read these notes carefully.

Write your name, class and index number in the spaces at the top of this page. Give details of the practical shift and laboratory where appropriate, in the boxes provided. Write in dark blue or black pen.

You may use a 2B pencil for any diagrams or graph.

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

Answer **all** questions in the spaces provided on the Question Paper.

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

You may lose marks if you do not show your working or if you do not use appropriate units.

| Shift |
|------------|
| |
| Laboratory |
| |

| For Examiner's Use | | | |
|--------------------|----|--|--|
| 3 s.f. | | | |
| Units | | | |
| Total | 55 | | |

This Question Paper consists of **14** printed pages and **1** blank page.

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

1 To investigate the kinetics of the reaction between iron(III) ions and iodide ions

For Examiner's Use

You will investigate rate of oxidation of iodide by iron(III) ions in **reaction 2**. The chemical changes in this experiment can be presented by the following equations:

Reaction 1: $Fe^{3+}(aq) + S_2O_3^{2-}(aq) \rightleftharpoons [Fe(S_2O_3)]^+(aq)$

Reaction 2: $2Fe^{3+}(aq) + 2I^{-}(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Reaction 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

The reaction is started by mixing acidic solution of iron(III) chloride with sodium thiosulfate, potassium iodide, and starch. The iodine, I_2 , produced in **reaction 2** reacts immediately with thiosulfate ions, $S_2O_3^{2-}$ in **reaction 3**.

When all the thiosulfate has been used, the iodine produced will turn starch indicator blue-black. The rate of the reaction can therefore be determined by finding the time for the blue-black colour to appear.

FA 1 is 0.030 mol dm⁻³ iron(III) chloride, FeCl₃.

FA 2 is 0.060 mol dm^{-3} potassium iodide, KI.

FA 3 is 0.0060 mol dm⁻³ sodium thiosulfate, Na₂S₂O₃.

starch indicator

You are advised to read the instructions before starting any practical work and draw a table, in an appropriate format, for your results in the space on page 4.

You will need to include volume of **FA 1**, volume of water, reaction time and calculated rate of reaction for each of the five experiments. Record all calculated values to 3 significant figures.

(a) Method

Experiment 1

- 1. Use the measuring cylinders to place the following in a 100 cm³ beaker.
 - 10 cm³ of **FA 2**
 - 20 cm³ of **FA 3**
 - 10 cm³ of starch indicator
- 2. Using a measuring cylinder, transfer 20 cm³ of **FA 1** rapidly into the same 100 cm³ beaker. Start the stopwatch during this addition.
- 3. Stir the mixture and place the beaker on a white tile.
- 4. The mixture turns brown and then yellow before turning a blue-black colour. Stop timing when this blue-black colour appears. Record the time to the nearest 0.1 second.
- 5. Wash the beaker thoroughly with water and carefully dry the beaker.



Examiner's



(c) Results

The rate of the reaction can be calculated as shown.

rate =
$$\frac{\Delta [Fe^{3+}]}{\text{reaction time}} \times 10^{6}$$

Calculate the rate of reaction for each experiment and complete your table.

| <mark>Expt</mark> | V _{FA1} / cm³ | V _{H2O} /cm³ | Reaction time, t /s | Rate/ mol dm⁻³ s⁻¹ |
|-------------------|------------------------|-----------------------|-------------------------------|-----------------------|
| <mark>1</mark> | <mark>20.00</mark> | <mark>0.00</mark> | <mark>12.9</mark> | <mark>155</mark> |
| 2 | <mark>12.00</mark> | <mark>8.00</mark> | <mark>28.8</mark> | <mark>69.4</mark> |
| <mark>3</mark> | <mark>14.00</mark> | <mark>6.00</mark> | <mark>20.7</mark> | <mark>96.6</mark> |
| <mark>4</mark> | <mark>16.00</mark> | <mark>4.00</mark> | 17.3 | <mark>115</mark> |
| <mark>5</mark> | <mark>18.00</mark> | <mark>2.00</mark> | <mark>14.7</mark> | <mark>136</mark> |

| | 2 | | |
|--|---|--|--|
| | 3 | | |
| | 4 | | |
| | 5 | | |

(d) (i) Plot the rate (y-axis) against the volume of **FA 1** (x-axis) on the grid. Draw a line of best fit through the points.

Your chosen scales should allow you to extrapolate this line to volume of **FA 1** = 0 cm^3 .

You should also identify any points you consider anomalous by drawing a circle around it.



✓ Therefore, the reaction is first order with respect to Fe³⁺.

| 10 | |
|----|--|

| (e) | (i) | Use your graph to calculate the time that the reaction would have taken if 4.0 cm ³ of FA 1 had been used. Show your working clearly. | | |
|--|---|--|----|--|
| | | If 4.0 cm ³ of FA 1 is used, rate = xxx mol dm ⁻³ s ⁻¹ Time = Δ [Fe ³⁺] × 10 ⁶ / rate = xxx s (to 3 sf or nearest seconds). | | |
| | | time = | 11 | |
| | (ii) | Calculate the initial concentration of iron(III) ions and the initial concentration of iodide ions if 4.0 cm^3 of FA 1 had been used. | | |
| | | [Fe ³⁺] = $\frac{0.030 \times 4.0}{60.0}$ = 0.00200 mol dm ⁻³ | | |
| | | $[I^{-}] = \frac{0.060 \times 10.0}{60.0} = 0.0100 \text{ mol } \text{dm}^{-3}$ | | |
| | | initial [Fe ³⁺] = | | |
| | | initial [I ⁻] = | 12 | |
| | (iii) | Given that the reaction is second order with respect to iodide, calculate the rate constant. | | |
| | | <mark>rate = k[Fe³⁺][I[−]]²</mark> | | |
| | | $k = \frac{rate}{[Fe^{3+}][I^-]^2} = xxx \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$ | | |
| | | rate constant = | 13 | |
| (f) | The c | omplex [Fe(S₂O₃)] ⁺ formed in reaction 1 is purple. | | |
| Consider the colour change observed when FA 1 was added to the solution prepared in Step 1 before the blue-black colour appeared. Suggest an explanation for the sequence of colour change in terms of the chemistry involved. | | | | |
| | The brown solution is due to a <u>mixture of purple complex [Fe(S₂O₃)]</u> ⁺ and orange-brown Fe³+(aq). | | | |
| | Since the I ₂ formed reacted immediately with thiosulfate, [S ₂ O ₃ ^{2–} (aq)] decreased, and the position of equilibrium in (1) shifts left. | | | |
| | Thus, solutio | <u>concentration of [Fe(S₂O₃)]⁺decreased. Hence, the <u>colour of the</u> on gradually fades/ until the <u>solution became pale yellow due to</u></u> | | |
| | <u>⊢e³⁺.</u> | | 14 | |
| | | | | |
| | | [Total: 15] | | |

| 2 | Dete | rmining the percentage purity of calcium carbonate. | For Examiner's |
|---|--|--|-------------------|
| | In this question, you will determine the percentage purity of an industrial grade calcium carbonate, CaCO ₃ , by two different methods. | | Use |
| | (a) | Method 1 | |
| | | The percentage purity of calcium carbonate can be determined by measuring the change in mass when the sample of calcium carbonate reacts with hydrochloric acid. | |
| | | $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(I) + CO_2(g)$ | |
| | | FA 4 is industrial grade calcium carbonate, CaCO₃. FA 5 is 2.00 mol dm⁻³ dilute hydrochloric acid. | |
| | | You do not need to carry out Method 1 . | |
| | | Procedure: | |
| | | 1. Weigh accurately about 2.0 g of FA 4 in a small weighing bottle. | |
| | | 2. Weigh accurately about 25 cm ³ of FA 5 in a small conical flask. | |
| | | 3. Add FA 4 to FA 5 and swirl the mixture continuously until no more bubbles is observed. | |
| | | 4. Reweigh the weighing bottle with its residual FA 4 . | |
| | | 5. Reweigh the conical flask and its content. | |
| | | A student performed a series of experiments by repeating the above procedure with different masses of FA 4 . | |
| | | | |

The results from her series of experiment are plotted on the grid in Fig 2.1.

Identify the anomalous data point by drawing a circle around it. Draw the most appropriate best-fit line taking into account all of the plotted points, except for the anomaly. Extrapolate (extend) this line to the mass of **FA 4** used = 0.00 g.

For Examiner's Use





- 8. Fill the burette with **FA 6**.
- 9. Wash and rinse the pipette then use it to transfer 25.0 cm³ of **FA 7** into a conical flask.
- 10. Add about 5 drops of thymolphthalein indicator.
- 11. Titrate FA 7 with FA 6.
- 12. Repeat the titration as many times as you think necessary to obtain consistent results.
- 13. Record in the space below, all of your mass readings, burette readings and the volume of **FA 6** added.

Results

| Mass of weighing bottle and FA 4 / g | <mark>4.433</mark> | | |
|---|--------------------|--|--|
| Mass of weighing bottle and residual FA 4 /g | <mark>3.823</mark> | | |
| Or | | | |
| Mass of weighing bottle and residue/g | | | |
| Mass of FA 4 used/ g | <mark>0.610</mark> | | |

| Titration number | <mark>1</mark> | <mark>2</mark> |
|---|--------------------|--------------------|
| Final burette reading /cm ³ | <mark>29.30</mark> | <mark>29.30</mark> |
| Initial burette reading /cm ³ | <mark>0.00</mark> | <mark>0.00</mark> |
| Volume of FA 6 (used) /cm ³ | <mark>29.30</mark> | <mark>29.25</mark> |

| 20 | |
|----|--|
| 21 | |
| 22 | |
| 23 | |
| 24 | |
| 25 | |



(d) From your accurate titration results, obtain a suitable value for the volume of **FA 6** to be used in your calculations. Show clearly how you obtained this value.



Volume of **FA 6** used =



Calculations





Reaction of calcium oxide with hydrochloric acid does not result in loss in mass/ does not produce any gases.

(f)

For

Use

| | Method 2: Percentage purity of FA 4 calculated is higher than expected. | | |
|-----|---|----------|--|
| | <u>Less HC/ is left</u> after reaction with sample. Based on the <u>lower titre</u> obtained/ less NaOH is needed to react with the remaining HC/, a greater amount of CaCO ₃ is calculated to be present. | 31 32 | |
| (g) | Explain why sulfuric acid cannot be used in both methods. | | |
| | The insoluble CaSO ₄ / salt formed coats the calcium carbonate particles, which results in incomplete reaction/ owtte. | 33 | |

(h) Planning

Unlike the acid-base titration in **Part (c)** that uses acid-base indicator to determine the end-point, thermometric titration uses heat evolved or temperature change of solution to determine the end-point of the reaction. In thermometric titration, the titre value can be determined from the graph of energy evolved against volume of titrant (solution from the burette) added.

Since a neutralisation reaction is exothermic, thermometric titration can be used to determine the amount of excess hydrochloric acid in flask X from **Part (c)**.

(i) Given that the concentration of undiluted excess hydrochloric acid in flask X is about 1.7 mol dm⁻³, and the desired titre is around 24 cm³, calculate the concentration of sodium hydroxide required for the thermometric titration.

[NaOH] = $\frac{0.025 \times 1.7}{0.024}$ = 1.77 mol dm⁻³

(ii) You are to plan a thermometric titration to determine the concentration of hydrochloric acid. The experimental results obtained should allow the titre value to be determined graphically.

You may assume that you are provided with

- 50 cm³ of hydrochloric acid, HC*l*, of concentration around 1.7 mol dm⁻³
- standard solution of sodium hydroxide solution, NaOH, of the same concentration calculated in (h)(i)
- apparatus commonly found in a school or college laboratory

In your plan you should include the following:

- a diagram of the apparatus set-up that may be used
- the procedure that you would follow and the measurement you would take
- the precautions and measures that you would take to minimise heat loss to the surroundings

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3 Inorganic qualitative analysis

In this experiment you are to explore the chemistry of some compounds of an unknown transition element **W**. You are provided with 4 samples, **FA 8**, **FA 9**, **FA 10** and **FA 11**.

- **FA 8** is a solid sample of a common dioxide of the unknown transition element **W**.
- **FA 9** is a dilute sulfuric acid, H_2SO_4 .
- **FA 10** is a solid sample of sodium ethanedioate, $Na_2C_2O_4$.
- **FA 11** is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

Carry out the following experiments. Carefully record your observations. Test any gases produced.

| | test | observations |
|--------|---|--|
| (a)(i) | Transfer all of the solid sample of FA 10 into a 100 cm ³ beaker. Add 25 cm ³ of FA 9 to this beaker. | White solid (Na ₂ C ₂ O ₄) <u>dissolves</u> to give a colourless solution. [accept: partially dissolves] |
| | Gently heat the beaker until the temperature of the mixture reaches about 60°C. | |
| | Stir the mixture carefully. Place the beaker on the white tile. | |
| | Add 2 – 3 spatula of FA 8 to the mixture, stir the mixture carefully with thermometer and observe any changes in the temperature of the mixture. | Effervescence/ bubbles after addition (not gas evolved) Colourless, odourless gas gave white ppt with limewater |
| | Filter the mixture into a boiling tube when you think that the reaction is completed. Leave the filtrate to stand. The filtrate contains compound X . | (even though no heat is applied) Temperature rise stops/ temperature falls/ mixture starts to cool as the effervescence much less vigorous |
| | Retain this filtrate for use (a)(II) . | (Pale_pink)_filtrate_turns_yellow- green/pale_yellow/pale_orange |

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(a) (ii) You are to investigate the effect of the addition of aqueous sodium hydroxide, and the addition of aqueous ammonia, to separate portions of the filtrate from (a)(i) and FA 11.

In the space below, record the details of the tests performed and the observations made in a suitable table.

| | Add sodium hydroxide, dropwise with shaking, followed by in excess, to separate samples. | Add aqueous ammonia, dropwise with shaking, followed by in excess, to separate samples. | |
|-----------------------------|--|--|--|
| Filtrate from (a)(ii) | (Light <u>) brown</u> precipitates <u>insoluble in</u> <u>excess</u> *ppt darken (on | (Light <u>) brown</u> precipitates <u>insoluble in</u> <u>excess</u> *ppt darken (on | |
| FA 11 | Off-white/ very light brown precipitates insoluble in excess *ppt darken (on standing) | Off-white/ very light brown precipitates insoluble in excess *ppt darken (on standing) | |

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(b) Explain how you determined when the reaction is completed in **4(a)(i)**. You should support your answer by referring to your observations.



| | (ii) | In (a)(i), the reaction between FA 8 and FA 10 occurs under acidic conditions. | | |
|-----|---|---|----|--|
| | | Write a balanced equation for this reaction. | | |
| | | $MnO_2 + 4H^+ + C_2O_4^{2-} \rightarrow Mn^{2+} + 2H_2O + 2CO_2$ | 53 | |
| | (iii) | State the role of FA 8 in the reaction and support your answer by referring to your observations. | | |
| | | FA 8 is an oxidising agent. Colourless, odourless <u>gas evolved</u> gave white ppt in limewater showed that <u>CO₂ was evolved</u> because CoOt ²⁺ was oxidised. Dark grey/ black MpO ₂ solid is | | |
| | | reduced to pale pink Mn ²⁺ ions. | 54 | |
| (d) | Deduc in (c) , | ce the nature of reaction, other than the type of reaction identified occurring in (a)(i) . | | |
| | Justify by referring to your observations. | | | |
| | The reaction is <u>exothermic</u> . The <u>temperature increased, without further</u> <u>heating</u> , as FA 8 was added. | | | |
| | Accept neutralisation between MnO ₂ and H ₂ SO ₄ with correct evidence and conclusion. | | | |
| | | | 55 | |

END OF PAPER

Qualitative Analysis Notes [ppt. = precipitate] 9

9(a) Reactions of aqueous cations

| estion | reaction with | | |
|--|---|---|--|
| cauon | NaOH(aq) | NH₃(aq) | |
| aluminium, Al ^{ð*} (aq) | white ppt. white ppt. insoluble in excess | | |
| ammonium, NH₄⁺ (aq) | ammonia produced on heating | a-a | |
| barium, Ba ²⁺ (aq) | no ppt. (if reagents are pure) | no ppt. | |
| calcium, Ca ²⁺ (aq) | white. ppt. with high [Ca ²⁺ (aq)] | no ppt. | |
| chromium(III), Cr ³⁺ (aq)grey-green ppt. soluble in excess giving dark green solutiongrey-green ppt. insoluble in excess | | grey-green ppt. insoluble in excess | |
| copper(II), Cu ²⁺ (aq), | pale blue ppt. insoluble in excess | blue ppt. soluble in excess giving dark blue solution | |
| iron(II), Fe ²⁺ (aq) | green ppt., turning brown on contact with air insoluble in excess | green ppt., turning brown on contact with air insoluble in excess | |
| iron(III), Fe ^{3⁺} (aq) | red-brown ppt. insoluble in excess | red-brown ppt. insoluble in excess | |
| magnesium, Mg ^{2⁺} (aq) | white ppt. insoluble in excess | white ppt. insoluble in excess | |
| manganese(II), Mn2+(aq)off-white ppt., rapidly turning brown on contact with air insoluble in excessoff-white ppt., ra brown on contact insoluble in excess | | off-white ppt., rapidly turning brown on contact with air insoluble in excess | |
| zinc, Zn ²⁺ (aq) | white ppt. soluble in excess | white ppt. soluble in excess | |

9(b) Reactions of anions

| anion | reaction | |
|---|--|--|
| carbonate, CO ₃ ²⁻ | CO ₂ liberated by dilute acids | |
| chloride, C <i>l</i> ⁻ (aq) | gives white ppt. with Ag⁺(aq) (soluble in NH₃(aq)) | |
| bromide, Br ⁻ (aq) | gives pale cream ppt. with $Ag^{*}(aq)$ (partially soluble in $NH_{3}(aq)$) | |
| iodide, I⁻(aq) | gives yellow ppt. with Ag ⁺ (aq) (insoluble in NH ₃ (aq)) | |
| nitrate, NO₃ [−] (aq) | NH_3 liberated on heating with $OH^-(aq)$ and Al foil | |
| nitrite, NO ₂ ⁻ (aq) | NH_3 liberated on heating with $OH^-(aq)$ and Al foil; NO liberated by dilute acids (colourless $NO \rightarrow$ (pale) brown NO_2 in air) | |
| sulfate, SO_4^{2-} (aq) | gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids) | |
| sulfite, SO_3^{2-} (aq) | SO ₂ liberated with dilute acids; gives white ppt. with Ba ²⁺ (aq) (soluble in dilute strong acids) | |

9(c) Tests for gases

| gas | test and test result | | |
|---------------------------------|--|--|--|
| ammonia, NH ₃ | turns damp red litmus paper blue | | |
| carbon dioxide, CO ₂ | gives a white ppt. with limewater (ppt. dissolves with excess CO ₂) | | |
| chlorine, Cl ₂ | bleaches damp litmus paper | | |
| hydrogen, H ₂ | "pops" with a lighted splint | | |
| oxygen, O ₂ | relights a glowing splint | | |
| sulfur dioxide, SO ₂ | turns aqueous acidified potassium manganate(VII) from purple to colourless | | |

9(d) Colour of halogens

| halogen | colour of element | colour in aqueous solution | colour in hexane |
|---------------------------|----------------------------|----------------------------|------------------|
| chlorine, Cl ₂ | greenish yellow gas | pale yellow | pale yellow |
| bromine, Br ₂ | reddish brown gas / liquid | orange | orange-red |
| iodine, I2 | black solid / purple gas | brown | purple |