CANDIDATE NAME

CLASS

CENTRE NUMBER


## H2 CHEMISTRY

INDEX NUMBER


Paper 1 Multiple Choice

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 $\mathbf{1 2}$ 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 $1.82 \mathrm{~g} \mathrm{dm}^{-3}$.
What is the identity of the other gas in the mixture?
[Density of argon $=1.78 \mathrm{~g} \mathrm{dm}^{-3}$ at s.t.p.]
A neon
B nitrogen
C oxygen
D carbon dioxide

2 Sodium thiosulfate $\left(\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}\right)$ is used in the textile industry to remove an excess of chlorine from bleaching processes by reducing it to chloride ions.
If $10 \mathrm{~cm}^{3}$ of $0.20 \mathrm{~mol} \mathrm{dm}^{-3}$ of sodium thiosulfate requires $192 \mathrm{~cm}^{3}$ of chlorine for complete reaction at r.t.p., which of the following is a possible formula of the sulfurcontaining product?
A S
B $\mathrm{SO}_{2}$
C $\mathrm{HSO}_{4}{ }^{-}$
D $\mathrm{H}_{2} \mathrm{~S}$

3 Which of the following ions would undergo the smallest deflection in an electric field?
A ${ }^{16} \mathrm{O}_{2}{ }^{+}$
B ${ }^{16} \mathrm{O}^{18} \mathrm{O}^{+}$
C ${ }^{16} \mathrm{O}^{18} \mathrm{O}^{2+}$
D ${ }^{18} \mathrm{O}^{2+}$

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

| Element | V | W | X | Y | Z |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Fourth ionisation <br> energy $/ \mathrm{kJ} \mathrm{mol}^{-1}$ | 10450 | 11710 | 4350 | 5030 | 4580 |

What is the formula of the bromide of V ?
A VBr
B $\mathrm{VBr}_{2}$
C $\mathrm{VBr}_{3}$
D $\mathrm{VBr}_{5}$

5 Two identical bulbs at the same temperature contain ideal gases $\mathbf{P}$ and $\mathbf{Q}$ separately. The density of gas $\mathbf{P}$ is half that of gas $\mathbf{Q}$ while the molecular mass of gas $\mathbf{P}$ is twice that of gas $\mathbf{Q}$.
What is the ratio of the pressure of gas $\mathbf{P}$ to that of gas $\mathbf{Q}$ ?
A 1:1
B 1:2
C 1:4
D 2:1

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

$$
2 \mathrm{BrF}_{3} \rightleftharpoons \mathrm{BrF}_{2^{+}}+\mathrm{BrF}_{4^{-}}
$$

Which of the following statements is correct?
A $\mathrm{BrF}_{3}$ is planar while $\mathrm{BrF}_{4}^{-}$is non-planar.
B $\quad \mathrm{BrF}_{2}{ }^{+}$is linear while $\mathrm{BrF}_{4}^{-}$is tetrahedral in shape.
C The $\mathrm{F}-\mathrm{Br}-\mathrm{F}$ bond angle in $\mathrm{BrF}_{3}$ is smaller than that in $\mathrm{BrF}_{2}{ }^{+}$.
D There are more lone pairs of electrons around the Br atom in $\mathrm{BrF}_{3}$ than that in $\mathrm{BrF}_{2}{ }^{+}$.

7 Dimerisation is described as a process in which two identical molecules combine to give a single product. Some examples include $\mathrm{Al}_{2} \mathrm{Cl}_{6}, \mathrm{~N}_{2} \mathrm{O}_{4}$ and $\left(\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}\right)_{2}$.
Which of the following statements about the above dimers are correct?
1 Hydrogen bonds hold the $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ molecules together in the dimer.
2 All the nitrogen-oxygen bonds in $\mathrm{N}_{2} \mathrm{O}_{4}$ are of equal length.
3 The bond angle around each aluminium atom in $\mathrm{Al}_{2} \mathrm{Cl}_{6}$ is $109.5^{\circ}$.
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 $+40.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$, what is the entropy change when 36.0 g of water boil to form water vapour?

A $+109 \mathrm{JK}^{-1}$
B $\quad-109 \mathrm{~J} \mathrm{~K}^{-1}$
C $+219 \mathrm{~J} \mathrm{~K}^{-1}$
D $\quad-219 \mathrm{~J} \mathrm{~K}^{-1}$
$9 \quad$ At T ${ }^{\circ} \mathrm{C}$ and a total pressure of $6.00 \mathrm{~atm}, \mathrm{~N}_{2} \mathrm{O}_{4}$ is $60.0 \%$ dissociated into $\mathrm{NO}_{2}$. What is the $K_{p}$ value at $\mathrm{T}^{\circ} \mathrm{C}$ ?
A 3.0
B 5.4
C $\quad 13.5$
D 21.6
$10 \mathrm{H}_{2} \mathrm{~A}$ is a weak acid which undergoes partial dissociation.

$$
\mathrm{H}_{2} \mathrm{~A}(\mathrm{aq}) \rightleftharpoons 2 \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{2-}(\mathrm{aq})
$$

Given that the pH of $1.00 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{H}_{2} \mathrm{~A}(\mathrm{aq})$ solution is 2.3 , what is the degree of dissociation of $\mathrm{H}_{2}$ A?
A $\quad 2.50 \times 10^{-3}$
B $5.01 \times 10^{-3}$
C $1.26 \times 10^{-5}$
D $1.26 \times 10^{-7}$

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

$$
\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \Delta H=+6.5 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Which of the following statements are correct?
$1 \quad K_{w}$ 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, $\mathrm{Al}(\mathrm{OH})_{3}$, if its solubility product is $2.53 \times 10^{-18} \mathrm{~mol}^{4} \mathrm{dm}^{-12}$ ?
A 4.28
B 5.44
C 9.60
D 9.72

13 The energy profile diagram of the reversible reaction between $\mathbf{M}$ and $\mathbf{N}$ is shown below.


Which of the following statements are correct?
1 The activation energy of the reverse reaction is $\mathrm{E}_{1}+\mathrm{E}_{2}$.
2 Rate equation of the reaction is rate $=k[\mathrm{M}][\mathrm{N}]^{2}$.
3 The equilibrium [ $\mathrm{MN}_{2}$ ] increases as temperature increases.
A 1 and 2 only
B 1 and 3 only
C 2 and 3 only
D 1, 2 and 3

14 The acid-catalysed reaction between $X$ and $Y_{2}$ in aqueous solution has been investigated.

$$
X+Y_{2}(\mathrm{aq}) \xrightarrow{\mathrm{H}^{+}} X Y(\mathrm{aq})+\mathrm{HY}(\mathrm{aq})
$$

It has been found that rate equation is rate $=k[\mathrm{X}]\left[\mathrm{Y}_{2}\right]^{\mathrm{m}}\left[\mathrm{H}^{+}\right]^{\mathrm{n}}$.
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 $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$.


What is the overall order of reaction?
A 0
B 1
C 2
D 3

15 W and X are 2 different elements in Period 3. The following are some of their properties:

- The oxide of $\mathbf{W}$ is insoluble in water, but is soluble in both $\mathrm{NaOH}(\mathrm{aq})$ and $\mathrm{HCl}(\mathrm{aq})$.
- The chloride of $\mathbf{X}$ dissolves completely in water to give a colourless solution of $\mathrm{pH}=2$.
Which of the following is the likely identity of element $\mathbf{W}$ and $\mathbf{X}$ ?
W X
A Al P
B $\quad \mathrm{Al} \quad \mathrm{Si}$
C $\mathrm{Mg} \quad \mathrm{P}$
D $\quad \mathrm{Mg} \quad \mathrm{Si}$

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 $\mathbf{Y}$ is less endothermic compared to $\mathbf{Z}$.
B The oxide of $\mathbf{Y}$ is less soluble in water compared to the oxide of $\mathbf{Z}$.
C The magnitude of the lattice energy of chloride of $\mathbf{Y}$ is higher compared to the chloride of $\mathbf{Z}$.

D The carbonate of $\mathbf{Y}$ decomposes at a lower temperature compared to the carbonate of $\mathbf{Z}$.

17 Purification of copper involves placing the impure copper at the anode of an electrolytic cell of $\mathrm{CuSO}_{4}(\mathrm{aq})$ 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 [ $\mathrm{CuSO}_{4}$ ] 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 $\mathrm{Zn}^{2+}$ 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 $\mathrm{Fe}^{2+}(\mathrm{aq})$
B $\mathrm{Fe}^{3+}(\mathrm{aq})$
C $\mathrm{Mn}^{3+}(\mathrm{aq})$
D acidified $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}(\mathrm{aq})$

19 Which of the following galvanic cell information is incorrect?
You may assume that all ions stated are at $1.00 \mathrm{~mol} \mathrm{dm}^{-3}$ and all measurements are made at standard conditions.

|  | Half-cell 1 |  | Half-cell 2 |  | $E \ominus_{\text {cell }} / \mathrm{V}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Electrolyte | Electrode <br> (Anode) | Electrolyte | Electrode (Cathode) |  |
| A | $\begin{gathered} \mathrm{H}^{+} \\ \mathrm{Mn}^{2+} \\ \mathrm{MnO}_{4}^{-} \end{gathered}$ | Pt | $\begin{aligned} & \mathrm{Fe}^{2+} \\ & \mathrm{Fe}^{3+} \end{aligned}$ | Pt | +0.75 |
| B | $\mathrm{Mn}^{2+}$ | Mn | $\begin{aligned} & \mathrm{Fe}^{2+} \\ & \mathrm{Fe}^{3+} \end{aligned}$ | Pt | +1.95 |
| C | $\mathrm{Mn}^{2+}$ | Mn | $\mathrm{Fe}^{2+}$ | Fe | +0.74 |
| D | $\mathrm{Fe}^{2+}$ | Fe | $\begin{aligned} & \mathrm{Mn}^{2+} \\ & \mathrm{Mn}^{3+} \end{aligned}$ | 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 $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{O}^{-} \mathrm{Na}^{+}\right)$?
$1 \mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$
$2 \mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}$
$3 \quad \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{2} \mathrm{OCH}_{2} \mathrm{CH}_{3}$
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:


Which of the following molecules is a possible identity of $\mathbf{I}$ ?

A
B

C
D

27 A compound $X$, with molecular formula $\mathrm{C}_{9} \mathrm{H}_{10} \mathrm{O}_{2}$, is heated under reflux with $\mathrm{NaOH}(\mathrm{aq})$ and the resulting mixture then cooled and acidified with $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$. The final products include a compound that turns blue litmus solution red, and another which gives a violet colouration when tested with neutral $\mathrm{FeCl}_{3}(\mathrm{aq})$.
What is a possible identity of $\mathbf{X}$ ?
A $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OCOCH}_{2} \mathrm{CH}_{3}$
B $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{OCOCH}_{3}$
C $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOCH}_{2} \mathrm{CH}_{3}$
D $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{COOCH}_{3}$

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 $\mathbf{Y}$ below?


11 mol of Y reacts with excess $\operatorname{HBr}(\mathrm{g})$ to yield a major product with 7 chiral centres.
21 mol of Y reacts with hot acidified $\mathrm{KMnO}_{4}(\mathrm{aq})$ to give a tribasic carboxylic acid as one of the products.
3 When heated, 1 mol of Y reacts with 4 mol of $\mathrm{H}_{2}(\mathrm{~g})$ 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

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

RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME

CLASS $\square$
CENTRE NUMBER

| $S$ | 3 | 0 | 4 | 4 |
| :--- | :--- | :--- | :--- | :--- |

INDEX NUMBER $\square$

## H2 CHEMISTRY

## 9729/02

Paper 2 Structured Questions
12 Sep 2018
2 hours
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 index number in the spaces at the top of this page.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
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.
A Data Booklet is provided.
The number of marks is given in brackets [ ] at the end of each question or part question.

| PAPER 2 |  |  |  |
| :---: | :---: | :---: | :---: |
| QUESTION 1 |  |  | 9 |
| QUESTION 2 9 |  |  |  |
| QUESTION 3 8 |  |  |  |
| QUESTION 4 14 |  |  |  |
| QUESTION 5 12 |  |  |  |
| QUESTION 6 10 |  |  |  |
| QUESTION 7 13 |  |  |  |
| Units |  |  |  |
| s.f. |  |  |  |
| R 3 | TOTAL | PAPER 4 | GRADE |
| 80 | $185$ | $55$ |  |


| PAPER 1 | PAPER 2 | PAPER 3 | TOTAL | PAPER 4 | GRADE |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 30 |  | 75 | 80 | 185 |  |

This paper consists of $\mathbf{2 0}$ printed pages.

Answer all questions in the spaces provided.

1 Magnesium, aluminium, $\mathbf{W}$ and $\mathbf{X}$ are 4 different elements in the $3^{\text {rd }}$ Period. The following are some of their properties:

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

The chloride of $\mathbf{X}$ reacts with ethanoic acid to form ethanoyl chloride as one of the products.
(a) Identify the elements, $\mathbf{W}$ and $\mathbf{X}$, and write the balanced equations for the reactions described above.

W: $\qquad$
Chloride of $\mathbf{W}$ dissolved in water (equation):
$\qquad$

X: $\qquad$
Chloride of $\mathbf{X}$ reacting with ethanoic acid (equation):
$\qquad$
(b) Aluminium oxide is a white solid that is soluble in $\mathrm{NaOH}(\mathrm{aq})$ to give a colourless solution.
(i) Write a balanced equation, with state symbols, to describe the reaction of aluminium oxide with $\mathrm{NaOH}(\mathrm{aq})$.
(ii) Describe the observations made when $\mathrm{HCl}(\mathrm{aq})$ is carefully added to this colourless solution, until $\mathrm{HCl}(\mathrm{aq})$ is in excess.
$\qquad$
$\qquad$
$\qquad$
(c) State and explain how the decomposition temperature of $\mathrm{BaCO}_{3}$ compares with that of $\mathrm{MgCO}_{3}$.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(d) Explain why the $1^{\text {st }}$ ionisation energy of aluminium is of lower magnitude compared to that of magnesium.
$\qquad$
$\qquad$
$\qquad$

2 Pyridine $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$ 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.

pyridine

pyridinium

Pyridinium chloride has a $\mathrm{p} K_{\mathrm{a}}$ value of 5.25 .
(a) Calculate the mass of $98.0 \%$ pyridinium chloride that must be added to $1.00 \mathrm{dm}^{3}$ 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 $5.00 \mathrm{~cm}^{3}$ of $0.0125 \mathrm{~mol} \mathrm{dm}^{-3}$ hydrochloric acid is added to $25.00 \mathrm{~cm}^{3}$ of $0.100 \mathrm{~mol} \mathrm{dm}^{-3}$ of pyridine.
(c) With the aid of two equations, explain how a solution of pyridinium chloride and pyridine can control pH .
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

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

$$
\mathrm{NO}_{2} \mathrm{Cl}(\mathrm{~g})+\mathrm{NO}(\mathrm{~g}) \rightleftharpoons \mathrm{NOCl}(\mathrm{~g})+\mathrm{NO}_{2}(\mathrm{~g}) \quad \Delta H \text { is negative }
$$

(a) A 3:1 molar ratio mixture of $\mathrm{NO}_{2} \mathrm{Cl}(\mathrm{g})$ and $\mathrm{NO}(\mathrm{g})$, 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 $\boldsymbol{t}_{1}$, the partial pressure of $\mathrm{NO}_{2} \mathrm{Cl}$ was found to be 2.90 atm .

Calculate the value of the equilibrium constant, $K_{\mathrm{p}}$, of the reaction at 800 K .
(b) At time $\boldsymbol{t}_{2}$, more $\mathrm{NO}_{2} \mathrm{Cl}$ gas was introduced into the vessel at 800 K , causing the partial pressure of $\mathrm{NO}_{2} \mathrm{Cl}$ to increase to 3.25 atm . The system was allowed to reach equilibrium before the temperature was increased to 1000 K at $\boldsymbol{t}_{3}$. A new equilibrium was established at $\boldsymbol{t}_{4}$.
In the pressure-time axes below, sketch the graph that would be observed from time $=0$ to time $=\boldsymbol{t}_{4}$, clearly indicating the values of the partial pressure of $\mathrm{NO}_{2} \mathrm{Cl}$ at time $=0, \boldsymbol{t}_{1}$ and $\boldsymbol{t}_{\mathbf{2}}$.

(c) Given that nitrogen is the central atom, draw the dot-and-cross diagram for NOCl.
(d) NOCl reacts with $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH}_{2}$ to give a product as predicted by Markovnikov's rule. When the organic product is heated with $\mathrm{NaOH}(\mathrm{aq})$, followed by acidification and addition of $\mathrm{AgNO}_{3}(\mathrm{aq})$, 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 $\mathrm{CH}_{3} \mathrm{CH}=\mathrm{CH}_{2}$.

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.

$$
\underset{\substack{\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11} \\ \text { (sucrose) }}}{ }+\mathrm{H}_{2} \mathrm{O} \xrightarrow{\mathrm{H}^{+}(\mathrm{aq})} \mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\underset{\substack{\text { (fructose) }}}{\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}}
$$

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

| Expt | Volume of <br> sucrose / <br> $\mathrm{cm}^{3}$ | Volume of <br> $\mathrm{HCl} / \mathrm{cm}^{3}$ | Volume of <br> water $/ \mathrm{cm}^{3}$ | Initial rate of reaction <br> $/ \mathrm{mol} \mathrm{dm}^{-3} \mathrm{~min}^{-1}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 20 | 30 | 0 | $1.77 \times 10^{-3}$ |
| 2 | 20 | 20 | 10 | $1.18 \times 10^{-3}$ |
| 3 | 10 | 30 | 10 | $8.85 \times 10^{-4}$ |
| 4 | 40 | 20 | 10 | $?$ |

(i) Using the data given above, determine the order of reaction with respect to sucrose and HCl .
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(ii) Hence, write the rate equation and deduce the rate constant of the reaction, stating its units.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(iii) Using your answer in (a)(ii), calculate the initial rate of reaction for Experiment 4.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(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.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(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.
(ii) Hence, explain why aspartame is soluble in water.
$\qquad$
$\qquad$
(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.

5 Manganese exhibits the widest range of oxidation states among the $1^{\text {st }}$ set of transition elements from titanium to copper.
In deaerated aqueous solution and in the presence of excess $\mathrm{CN}^{-}$ions, pale pink $\mathrm{Mn}^{2+}(\mathrm{aq})$ forms blue $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{4-}$ ion. $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{4-}$ ion reacts with $3 \%$ solution of hydrogen peroxide to form red $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ ion.

In the visible spectrum, red is the lowest energy light while violet is the highest energy light.
(a) Explain why transition elements exhibit variable oxidation states.
$\qquad$
$\qquad$
(b) Explain why there is a difference in the colour observed for $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{4-}$ and $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ ions.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(c) Given that:

$$
\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}+\mathrm{e} \rightleftharpoons\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{4-} \quad E^{\ominus}=-0.24 \mathrm{~V}
$$

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 $E^{\ominus}$.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(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 highspin.
(i) Using this information, and compare the colour of the cyanidocomplexes of manganese, deduce and draw the electronic configuration of the $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ on the splitting diagram.

(ii) Explain the spin-state of $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ in (d)(i) in terms of the energy gap between the d-orbitals in both manganese cyanido-complexes and pairing energy.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(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 $\left[\mathrm{H}^{+}\right]=1 \mathrm{~mol} \mathrm{dm}^{-3}$.

(i) Given that $\mathrm{HMnO}_{4}^{-}$undergoes disproportionation, construct a balanced equation for the reaction.
$\qquad$
$\qquad$
$\qquad$
(ii) Calculate $\Delta G^{\ominus}$ for the reaction.
$\qquad$
$\qquad$
(f) It is necessary to carry out reactions involving Mn (II) in deaerated solution as Mn (II) may react with aerated solutions.
Consider the data given below and appropriate values from the Data Booklet, calculate the $E^{\ominus}$ cell values for the oxidation of Mn (II) to Mn (III) in aerated solutions at $\mathrm{pH}=0$ and $\mathrm{pH}=14$.
Comment on what the signs of $E^{\ominus}$ cell indicate about the stability of Mn (II) in acidic and alkaline aerated solutions.

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

$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

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 $\left(\mathrm{H}_{2} \mathrm{~S}\right)$, 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 | $\Delta H_{\mathrm{c}} / \mathrm{kJ} \mathrm{mol}^{-1}$ |
| :--- | :---: | :---: |
| 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
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(ii) Write balanced equations to show the reaction for 1 mole of each component of biogas that reacted under standard conditions.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(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 $=1.00 \mathrm{dm}^{3}$
Density of biogas is $6.44 \times 10^{-4} \mathrm{~g} \mathrm{~cm}^{-3}$
Volume of water heated $=200 \mathrm{~cm}^{3}$
Density of water $=1.00 \mathrm{~g} \mathrm{~cm}^{-3}$
Initial temperature of water $=29.6^{\circ} \mathrm{C}$
Maximum temperature of water reached $=64.7^{\circ} \mathrm{C}$

## [2]

(iv) Use the information provided, calculate the amount of each gas that combusted. Hence, determine the enthalpy change of combustion of methane.
(c) To determine the fuel values of biogas, the apparatus in Figure 6.1 can simply be replaced with a beaker of water with lid and a thermometer.
Suggest how the design of the apparatus in Figure 6.1 improves the efficiency of heat transfer to the water.
$\qquad$
$\qquad$
$\qquad$
(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


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

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: $\qquad$

Reaction II:
(ii) Draw the structures of $\mathbf{E}$ and $\mathbf{G}$.

| E | G |
| :--- | :--- |
|  |  |
|  |  |
|  |  |
|  |  |

(iii) Describe the mechanism for reaction III, and provide the name of the mechanism.
(b) Suggest simple laboratory tests to distinguish between compounds B, C and F. State the expected observations for each compound.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(c) Describe what the student will observe when 3-oxo-3-phenylpropanal is warmed with Fehling's solution. Write an equation for this reaction.

## - End of Paper -

## MARK SCHEME

| 1 | (a) | W: Si $\begin{aligned} & \mathrm{SiCl} l_{4}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{SiO}_{2}+4 \mathrm{HCl} \\ & \mathrm{X}: \mathrm{P} \\ & \mathrm{PCl}_{5}+\mathrm{CH}_{3} \mathrm{COOH} \rightarrow \mathrm{POCl}_{3}+\mathrm{CH}_{3} \mathrm{COCl} \\ & \mathrm{OR} \\ & 3 \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{PC}_{3} \longrightarrow 3 \mathrm{CH}_{3} \mathrm{COCl}+\mathrm{H}_{3} \mathrm{PO}_{3} \end{aligned}$ | [4] |
| :---: | :---: | :---: | :---: |
|  | (b) <br> (i) | $\mathrm{Al}_{2} \mathrm{O}_{3}(\mathrm{~s})+2 \mathrm{NaOH}(\mathrm{aq}) \rightarrow 2 \mathrm{Na}\left[\mathrm{Al}(\mathrm{OH})_{4}\right](\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ <br> OR $\mathrm{Al}_{2} \mathrm{O}_{3}(\mathrm{~s})+2 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow 2\left[\mathrm{Al}(\mathrm{OH})_{4}\right]^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ | [3] |
|  | (b) <br> (ii) | On addition of $\mathrm{HCl}(\mathrm{aq})$, a white ppt is formed. Ppt would dissolve in excess $\mathrm{HCl}(\mathrm{aq})$ to give a colourless solution. |  |
|  | (c) | $\mathrm{BaCO}_{3}$ has a higher thermal decomposition temperature. <br> $\mathrm{Ba}^{2+}$ has a larger ionic radius compared to $\mathrm{Z}^{2+} / \mathrm{Mg}^{2+}$. $\mathrm{Ba}^{2+}$ hence has a lower charge density, and polarise the $\mathrm{CO}_{3}{ }^{2-}$ anion to a lower extent (compared to $\mathrm{Z}^{2+} / \mathrm{Mg}^{2+}$ ), and the $\mathrm{C}-\mathrm{O}$ bonds are weakened to a smaller extent, resulting in a higher thermal decomposition temperature. |  |
|  | (d) | The $3 p$ electron to be removed from Al is at a higher energy level compared 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] |
|  |  | [Total: 9] |  |


| 2 | (a) | For $\mathrm{pH}=3.5$ $\left[\mathrm{H}^{+}\right]=10^{-3.5}=\underline{3.16 \times 10^{-4} \mathrm{moldm}^{-3}}$ <br> Let the number of moles of $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NHCl}$ be Y mol $\text { Since } p K_{a}=5.25, K_{a}=10^{-5.25}=\underline{5.62 \times 10^{-6}}$ $\begin{aligned} & \left(3.16 \times 10^{-4}\right)^{2} / Y-\left(3.16 \times 10^{-4}\right)=5.62 \times 10^{-6} \\ & Y=\left[\left(3.16 \times 10^{-4}\right)^{2} / 5.62 \times 10^{-6}\right]+\left(3.16 \times 10^{-4}\right) \\ & =\underline{0.0181 \mathrm{~mol}} \end{aligned}$ <br> Or $\begin{aligned} & \left(3.16 \times 10^{-4}\right)^{2} / Y=5.62 \times 10^{-6} \\ & Y=\left[\left(3.16 \times 10^{-4}\right)^{2} / 5.62 \times 10^{-6}\right] \\ & =\underline{0.0178 \mathrm{~mol}} \end{aligned}$ $\begin{aligned} & \text { Mass to be added }=(0.0181 \times(12.0 \times 5+1.0 \times 6+14.0+35.5)) \div 0.98 \\ & =\underline{2.13 \mathrm{~g}(\text { or } 2.10 \mathrm{~g})} \end{aligned}$ | [3] |
| :---: | :---: | :---: | :---: |
|  | (b) | $\begin{aligned} & {\left[\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}\right]=[(0.100 \times 0.025)-(0.0125 \times 0.005)] / 0.03=\underline{0.0813 \mathrm{~mol} \mathrm{dm}^{-3}}} \\ & {[\mathrm{pyridinium} \mathrm{chloride}]=(0.0125 \times 0.005) / 0.03=\underline{2.08 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}}} \\ & \mathrm{p} K_{\mathrm{b}}=14-\mathrm{pK} \mathrm{a}_{\mathrm{a}}=\underline{8.75} \\ & \mathrm{pOH}=\mathrm{p} K_{\mathrm{b}}+\lg [\text { salt }] /[\text { base }] \\ & \mathrm{pOH}=8.75+\lg \left(2.08 \times 10^{-3} / 0.0813\right)=7.16 \\ & \mathrm{pH}=14-7.16=\underline{6.84} \end{aligned}$ | [3] |
|  | (c) | On addition of a small amount of acid $\left(\mathrm{H}^{+}\right)$to the buffer solution, nearly all the added $\mathrm{H}^{+}$ions are neutralised by the large amount of $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}$. Hence $\left[\mathrm{H}^{+}\right]$ does not increase appreciably and the pH is kept approximately constant. $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{~N}(\mathrm{aq})+\mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}(\mathrm{aq})$ <br> On addition of a small amount of base $\left(\mathrm{OH}^{-}\right)$to the buffer solution, nearly all the added $\mathrm{OH}^{-}$ions are neutralised by the large amount of $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}$. Hence [ $\mathrm{OH}^{-}$] does not increase appreciably and the pH is kept approximately constant. $\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{C}_{5} \mathrm{H}_{5} \mathrm{NH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ | [3] |
|  |  | [Total: 9] |  |



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


|  | (ii) | When [sucrose] is low, reaction is first order with respect to sucrose due to the availability of active sites on the enzyme molecules for binding. <br> When [sucrose] is high, all active sites on the enzyme molecules are occupied. The rate of reaction then is independent of [sucrose] and the reaction is zero order with respect to sucrose. | [2] |
| :---: | :---: | :---: | :---: |
| (c) | (i) |  | [1] |
|  | (ii) | The zwitterions of aspartame form ion-dipole interactions with water. | [1] |
|  | (iii) |   | [3] |
|  | [Total: 14] |  |  |


| 5 | (a) | Due to the similar energy/ close proximity of the 3d and 4s electrons in the transition elements, transtion element can form ions of approximately the similar stability by losing different number of electrons. | [1] |
| :---: | :---: | :---: | :---: |
|  | (b) | In the presence of octahedral ligand field, the degenerate d-orbitals in the metal complex were spilt into two energy levels. The colour observed is due to the difference in energy levels, $\Delta \mathrm{E}$. The difference in electronic configuration due to different oxidation state affect $\Delta \mathrm{E}$. Light of different energies/ different wavelengths are absorbed for the promoion of electrons from the lower energy orbital to the vacant/partially filled higher energy orbital/d-d transition, different complementary colour is observed. | [2] |
|  | (c) | $\mathrm{E}^{\ominus}\left(\mathrm{Mn}^{3+} / \mathrm{Mn}^{2+}\right)$ is more positive than $\mathrm{E}^{\ominus}\left(\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-/}\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{4-}\right)$, which shows that $\mathrm{Mn}^{3+}$ is more readily reduced, hence a weaker oxidising agent in cynaide solution than in water. More energy is required to add an electron to the negatively charged $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ due to repulsion. | [2] |
|  | (d) | (i) <br> Figure 1.1 energy | [1] |
|  |  | (ii) Since $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ ions are red, the energy gap between the 2 sets of d-orbitals in $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ is bigger. This suggests that $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ is the low spin complex, as its energy gap, $\Delta \mathrm{E}$, is greater than the pairing energy/ Coulombic repulsion/ repulsion energy, electrons in $\left[\mathrm{Mn}(\mathrm{CN})_{6}\right]^{3-}$ would pair up. | [1] |
|  | (e) | (i) $[\mathrm{O}] \mathrm{HMnO}_{4}^{-} \rightarrow \mathrm{MnO}_{4}^{-}+\mathrm{H}^{+}+\mathrm{e}$ <br> $[\mathrm{R}] 3 \mathrm{H}^{+}+2 \mathrm{e}+\mathrm{HMnO}_{4}^{-} \rightarrow \mathrm{MnO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$ <br> Overall equation: $3 \mathrm{HMnO}_{4}^{-}+\mathrm{H}^{+} \rightarrow \mathrm{MnO}_{2}+2 \mathrm{MnO}_{4}^{-}+2 \mathrm{H}_{2} \mathrm{O}$ | [1] |
|  |  | (ii) $\begin{aligned} & \mathrm{E}_{\text {cell }}=+2.10-(+0.90)=+1.20 \mathrm{~V} \\ & \Delta \mathrm{G}=-\mathrm{nFE} \text { cell }=-(2)(96500)(1.20)=\underline{-232 \mathrm{~kJ} \mathrm{~mol}^{-1}}\end{aligned}$ | [2] |
|  | (f) | In acidic condition, $\begin{array}{ll} \mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e} \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O} & \mathrm{E}^{\ominus}=+1.23 \mathrm{~V} \\ \mathrm{Mn}^{3+}+\mathrm{e} \rightleftharpoons \mathrm{Mn}^{2+} & \mathrm{E}^{\ominus}=+1.54 \mathrm{~V} \\ \mathrm{E}^{\ominus} \text { cell }=+1.23-(+1.54)=-0.31 \mathrm{~V} & \end{array}$ |  |


|  | In alkaline solution, <br> $\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{e} \rightleftharpoons 4 \mathrm{OH}^{-}$ <br> $\mathrm{E}^{\ominus}$ cell $=+0.40-(+0.18)=+0.22 \mathrm{~V}$ <br> Since the $\mathrm{E}^{\ominus}$ cell $>0$ in alkaline environment and $\mathrm{E}^{\ominus}$ cell $<0$ in acidic <br> environment, $\mathrm{Mn}(\mathrm{II})$ is more stable in acidic environment than in alkaline <br> environment. <br>  <br>  <br> [Total: 12] |
| :--- | :--- | :--- | :--- |


| 6 | (a) | (i) | $\mathrm{CO}_{2}$ : Carbon in $\mathrm{CO}_{2}$ has attained maximum oxidation state. <br> $\mathrm{N}_{2}$ : $\mathrm{N} \equiv \mathrm{N}$ is very strong resulting high activation energy. | [2] |
| :---: | :---: | :---: | :---: | :---: |
|  |  | (ii) | Methane: $\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ <br> Hydrogen sulfide: $\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+11 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ <br> Hydrogen: $\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | [2] |
|  |  | (iii) | $\begin{aligned} & \text { Energy evolved }=200 \times 4.18 \times(64.7-29.6)=29.34 \mathrm{~kJ} \\ & \text { mass of biogas used }=1000 \times 6.44 \times 10^{-4}=0.644 \mathrm{~g} \\ & \text { Fuel value of biogas }=29.34 \div 0.644=45.6 \mathrm{~kJ} \mathrm{~g}^{-1} \end{aligned}$ | [2] |
|  |  | (iv) | ```Amount of methane in \(1 \mathrm{dm}^{3}\) biogas \(=0.644 \times 0.722 \div(12.0+4.0)\) \(=0.0291 \mathrm{~mol}\) Amount of \(\mathrm{H}_{2} \mathrm{~S}\) in \(1 \mathrm{dm}^{3}\) biogas \(=0.644 \times 0.012 \div(2.0+32.1)\) \(=0.000227 \mathrm{~mol}\) Amount of \(\mathrm{H}_{2}\) in \(1 \mathrm{dm}^{3}\) biogas \(=0.644 \times 0.027 \div 2.0\) \(=0.00869 \mathrm{~mol}\) Energy evolved \(=29.34 \mathrm{~kJ}\) \(=\left(0.0291 \times\left\|\Delta H_{c}\left(\mathrm{CH}_{4}\right)\right|\right)+(0.000227 \times 482)+(0.00869 \times 386)\) \(\Delta H_{\mathrm{c}}\left(\mathrm{CH}_{4}\right)=-890 \mathrm{~kJ} \mathrm{~mol}^{-1}\)``` | [2] |
|  | (c) |  | nger time for hot flue gas to pass through spiral copper coil iral copper coil increase the surface area for energy transfer per is a good conductor of heat combustion takes place inside the apparatus, not affected by ught. | [1] |
|  | (d) |  | move sulfur dioxide gas as low concentration of this gas can also es the respiratory system. | [1] |
|  |  | [Total: 10] |  |  |

(a)

## RIVER VALLEY HIGH SCHOOL YEAR 6 PRELIMINARY EXAMINATION

CANDIDATE NAME

CLASS

| 6 |  |
| :--- | :--- |

CENTRE
NUMBER

| S |  |  |  |  |
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INDEX
NUMBER


## H2 CHEMISTRY

Paper 3 Free Response
18 September 2018
2 hours
Candidates answer on separate paper.
Additional Materials: 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 $\mathbf{1 5}$ printed pages and $\mathbf{1}$ blank page.

## Section A

Answer all the questions in this section.
1 (a) (i) Phosphorus reacts with

- $\mathrm{F}_{2}$ to produce $\mathrm{PF}_{5}$ as the only product.
- $\mathrm{Cl}_{2}$ to give both $\mathrm{PCl}_{5}$ and $\mathrm{PCl}_{3}$.
- $\mathrm{Br}_{2}$ and $\mathrm{I}_{2}$ to give $\mathrm{PBr}_{3}$ and $\mathrm{PI}_{3}$ respectively.

With reference to the Data Booklet, explain the difference in oxidation states of phosphorus in the phosphorus-containing compounds formed.
(ii) The table below gives the $\mathrm{p} K_{\mathrm{a}}$ values of the hydrogen halides.

| hydrogen halide | pKa |
| :---: | :---: |
| HF | 3.17 |
| HCl | -7 |
| HBr | -9 |
| HI | -10 |

Explain the trend in the $\mathrm{p} K_{a}$ values.
(b) The following reaction scheme shows the formation of an alcohol via the Grignard reaction.

(i) Suggest the type of reaction undergone in Step II.
(ii) Suggest the identities of a suitable carbonyl compound and Grignard reagent to form 1-methylcyclohexan-1-ol.
(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 ( $\mathrm{R}-\mathrm{MgBr}$ ) produces the $: \mathrm{R}^{-}$, as the reacting species to form 1-methylcyclohexan-1-ol.
(c) Calcium phosphate, $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$, is a sparingly soluble salt. ..
(i) Write the expression for the solubility product of calcium phosphate.
(ii) Given that the solubility of calcium phosphate in water is $1.14 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3}$, calculate the solubility product of calcium phosphate, stating its units.
(iii) Calculate the solubility of calcium phosphate in the presence of $0.150 \mathrm{~mol} \mathrm{dm}^{-3}$ of potassium phosphate.
(iv) A saturated solution was prepared by dissolving two sparingly soluble salts, calcium phosphate and calcium sulfate, $\mathrm{CaSO}_{4}$, in tap water. The tap water used was found to be contaminated with trace amounts of $\mathrm{SO}_{4}{ }^{2-}$.
Explain the impact of the contamination on the solubilities of calcium phosphate and calcium sulfate.
[Total: 18]

2 Strepsils ${ }^{\circledR}$ 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 |  |
| :---: | :---: | :---: |
|  | amylmetacresol |  |
| non-active ingredients | (-)-menthol |  |
|  | tartaric acid |  |
|  | propylene glycol |  |

(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.

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

Draw the structure of the possible by-product that may result.
(iv) Describe a simple chemical test that can distinguish between 2,4-dichlorobenzyl alcohol and amylmetacresol.
State the expected observations for each compound.
(b) Arrange amylmetacresol, menthol and tartaric acid in increasing order of acidity.

Explain your answer.
You only need to consider the first acid dissociation of tartaric acid.
(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.
(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.
(iii) Draw the structure of the by-product formed.
(d) (i) $\mathrm{A} 25.0 \mathrm{~cm}^{3}$ solution of $0.0100 \mathrm{~mol} \mathrm{dm}^{-3}$ tartaric acid in a conical flask is titrated with $0.0100 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}(\mathrm{aq})$ from a burette.

Given that $\mathrm{p} K_{\mathrm{a} 1}=2.89$ and $\mathrm{p} K_{\mathrm{a} 2}=4.40$, and ignoring the autoionisation of water, determine the pH of the solution when the following volumes of $\mathrm{NaOH}(\mathrm{aq})$ are added:

- $0.00 \mathrm{~cm}^{3}$
- $12.50 \mathrm{~cm}^{3}$
- $50.00 \mathrm{~cm}^{3}$
(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.
(e) Propylene glycol can be produced from gaseous propene.
(i) State the reagent and condition required for propene to form propylene glycol.
(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 $30^{\circ} \mathrm{C}$. It is found that the mass of the $500 \mathrm{~cm}^{3}$ glass bulb increased by 0.36 g .
Identify the inorganic gas and determine the pressure of the gas collected.

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 $\left(\mathrm{V}_{2} \mathrm{O}_{5}\right)$ 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 |
| :---: | :---: | :---: |
| $\mathrm{V}^{2+}$ | +2 | violet |
| $\mathrm{V}^{3+}$ | +3 | green |
| $\mathrm{VO}^{2+}$ | +4 | blue |
| $\mathrm{VO}_{3}{ }^{-}$ | +5 | yellow |

When a sample of yellow $\mathrm{VO}_{3}^{-}$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.
(c) A similar process as (b) was carried out as follows:
$100 \mathrm{~cm}^{3}$ of $0.0500 \mathrm{~mol} \mathrm{dm}^{-3}$ of $\mathrm{NaVO}_{3}$ is reacted completely with zinc powder. The final colour of the solution is blue-green.
$25.0 \mathrm{~cm}^{3}$ of this blue-green solution requires $20.63 \mathrm{~cm}^{3}$ of $0.0200 \mathrm{~mol} \mathrm{dm}^{-3}$ of $\mathrm{KMnO}_{4}$ 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 $\mathrm{VO}^{2+}$.

State the identity of the other ion.
(ii) Write a balanced chemical equation between $\mathrm{VO}^{2+}$ and $\mathrm{MnO}_{4}^{-}$under acidic conditions.
(iii) Calculate the amount of $\mathrm{KMnO}_{4}$ that has undergone reaction.
(iv) Given that:

- 5 mol of the ion identified in (c)(i) reacts exactly with 2 mol of $\mathrm{KMnO}_{4}$
- $x$ mol of $\mathrm{VO}^{2+}$ is present in $25.0 \mathrm{~cm}^{3}$ of the blue-green solution Show that the total amount of $\mathrm{KMnO}_{4}$ 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:

$$
\mathrm{R}_{1}-\mathrm{CHO}+\mathrm{HO}-\mathrm{R}_{2} \rightarrow \mathrm{R}_{1}-\mathrm{COO}-\mathrm{R}_{2}+2[\mathrm{H}]
$$

Compound $A, \mathrm{C}_{8} \mathrm{H}_{8} \mathrm{O}_{2}$ undergoes oxidative esterification in the presence of $\mathrm{V}_{2} \mathrm{O}_{5}$ catalyst to form a neutral compound $\mathbf{B}, \mathrm{C}_{8} \mathrm{H}_{6} \mathrm{O}_{2}$. On heating $\mathbf{B}$ under reflux with $\mathrm{NaOH}(\mathrm{aq})$, the sodium salt of compound $\mathrm{C}, \mathrm{C}_{8} \mathrm{H}_{8} \mathrm{O}_{3}$, was formed. Compounds A, B and $\mathbf{C}$ reacts with $\mathrm{LiAlH}_{4}$ in dry ether to form compound $\mathbf{D}$, $\mathrm{C}_{8} \mathrm{H}_{10} \mathrm{O}_{2}$, while compounds $\mathbf{A}, \mathrm{C}$ and D are able to decolourise aqueous bromine.
Draw the structures of $\mathbf{A}, \mathbf{B}, \mathbf{C}$ and $\mathbf{D}$, and explain your reasoning.

## Section B

Answer one question from this section.

4 (a) Compound $\mathbf{Y}$ can be obtained from ethyne using the following synthesis pathway:

Step 1



Step 2

2. A, $\mathrm{H}_{2} \mathrm{O}$ Step $3 \downarrow \mathrm{Na}, \mathrm{NH}_{3}$ 1. HCN, with a small amt of $\mathrm{NaCN}(\mathrm{aq})$
2. $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$, heat


(i) Given that $\mathrm{HC} \equiv \mathrm{C}^{-}$is formed, state the role of $\mathrm{NaNH}_{2}$ 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.
(iii)

phenylamine
Suggest why phenylamine is unable to carry out the role of sodium amide, $\mathrm{NaNH}_{2}$, in Step 1.
(iv) Suggest the reagent $\mathbf{A}$ in Step 2, and reagents and conditions for Step 4.
(v) Draw the structure of Compound $\mathbf{Y}$.

Explain why HCN reacts with $\mathrm{C}=\mathrm{O}$ but not with $\mathrm{C}=\mathrm{C}$ in the same compound.
(b) Sodium borohydride, $\mathrm{NaBH}_{4}$, 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.

$$
\mathrm{NaBH}_{4}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{NaBO}_{2}(\mathrm{~s})+4 \mathrm{H}_{2}(\mathrm{~g}) \quad \Delta H^{\ominus}=-210 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

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 $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | $-241 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| :--- | :--- |
| standard enthalpy change of atomisation of Na | $+107 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| standard enthalpy change of formation of <br> $\mathrm{BH}_{4}^{-}(\mathrm{g})$ | $-78.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| standard enthalpy change of vapourisation of <br> $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | $+40.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| standard enthalpy change of formation of <br> $\mathrm{NaBO}_{2}(\mathrm{~s})$ | $-1059 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |

(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.

$$
3 \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}+2 \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+16 \mathrm{H}^{+} \rightarrow 3 \mathrm{CH}_{3} \mathrm{COOH}+4 \mathrm{Cr}^{3+}+11 \mathrm{H}_{2} \mathrm{O}
$$

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 $2100 \mathrm{~cm}^{3}$ of breath contains the same amount of ethanol as $1 \mathrm{~cm}^{3}$ of blood.

Given that the volume of exhaled air in (c)(i) is $65 \mathrm{~cm}^{3}$, calculate the amount of ethanol per $\mathrm{cm}^{3}$ of blood.
[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) $\mathrm{RVCM}{ }^{\circledR}$ 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.
(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.
(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.

Figure 5.1

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

## [2]

(d) Pu'erh (Chinese: 普洱) is a variety of fermented tea produced in Yunnan province, China. Black Pu'erh tea is known to contain more gallic acid than green Pu'erh tea. Gallic acid and its derivatives have been reported to elicit antioxidant, anti-cancer and anti-diabetic activities.
The structures of gallic acid and its derivatives are given below:

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

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

In an experiment, 1.00 g sample of pure gallic acid was dissolved in $100 \mathrm{~cm}^{3}$ of water. This aqueous solution of gallic acid and $50.0 \mathrm{~cm}^{3}$ 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 $20.0 \mathrm{~cm}^{3}$ of the aqueous layer required $20.25 \mathrm{~cm}^{3}$ of $0.180 \mathrm{~mol} \mathrm{dm}^{-3}$ 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 $50 \mathrm{~cm}^{3}$ of diethyl ether.
Describe and explain how would you modify the solvent extraction method in d(i) such that mainly $3,4,5$-trimethylgallic acid is left in the diethyl ether layer.
(iii) Suggest a chemical test to distinguish methyl gallate from gallic acid.

## - End of Paper -

## [BLANK PAGE]

## Section A

| 1 | (a) | (i) | Element <br> $1 / 2 \mathrm{~F}_{2}+\mathrm{e}^{-} \rightleftharpoons \mathrm{F}^{-}$ <br> $1 / 2 \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightleftharpoons \mathrm{Cl}^{-}$ <br> $1 / 2 \mathrm{Br}_{2}+\mathrm{e}^{-} \rightleftharpoons \mathrm{Br}^{-}$ <br> $1 / 2 \mathrm{I}_{2}+\mathrm{e}^{-} \rightleftharpoons \mathrm{I}^{-}$ <br> The order of oxidising st the $E^{\ominus}$ values above, dec <br> Due to the strong oxidis Phosphorus +5 in $\mathrm{PF}_{5,}+5$ $\mathrm{PI}_{3}$ respectively. | $\begin{gathered} E^{\ominus} / \mathrm{V} \\ \hline+2.87 \\ \hline+1.36 \\ +1.07 \\ \hline+0.54 \\ \hline \end{gathered}$ <br> ngth of <br> ases do <br> powe <br> and +3 | [3] |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | (ii) | The smaller the $\mathrm{p} K_{\mathrm{a}}$, th strongest acid, followed F to Cl to Br to I , atomic overlap between H and increasingly weaker, mak | strong $\mathrm{HBr}, \mathrm{H}$ adius i X decre <br> $g$ it eas | [2] |
|  | (b) | (i) | (Acidic) hydrolysis |  | [1] |
|  |  | (ii) |  <br> and $\mathrm{CH}_{3} \mathrm{MgBr}$ |  | [2] |


|  | (iii) |  | [3] |
| :---: | :---: | :---: | :---: |
| (c) | (i) | $K_{\text {sp }}=\left[\mathrm{Ca}^{2+}\right]^{3}\left[\mathrm{PO}_{4}{ }^{3-}\right]^{2}$ | [1] |
|  | (ii) | $\begin{aligned} & {\left[\mathrm{Ca}^{2+}\right]=1.14 \times 10^{-7} \times 3=3.42 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3}} \\ & {\left[\mathrm{PO}_{4}{ }^{3-}\right]=1.14 \times 10^{-7} \times 2=2.28 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3}} \\ & K_{\text {sp }}=\left(3.42 \times 10^{-7}\right)^{3}\left(2.28 \times 10^{-7}\right)^{2}=2.08 \times 10^{-33} \mathrm{~mol}^{5} \mathrm{dm}^{-15} \end{aligned}$ | [2] |
|  | (iii) | Let the solubility of calcium phosphate in the presence of potassium phosphate be $y$. $2.08 \times 10^{-33}=(3 y)^{3}(0.15+y)^{2}$ <br> Assume that $y$ is small such that $0.15+y \approx 0.15$ $\begin{aligned} & 2.08 \times 10^{-33}=(3 y)^{3}(0.15)^{2} \\ & y=1.51 \times 10^{-11} \mathrm{~mol} \mathrm{dm}^{-3} \end{aligned}$ | [2] |
|  | (iv) | An increase in $\left[\mathrm{SO}_{4}{ }^{2-}\right.$ ] causes the equilibrium position of $\mathrm{CaSO}_{4} \rightleftharpoons \mathrm{Ca}^{2+}+\mathrm{SO}_{4}{ }^{2-}$ to shift left, decreasing the solubility of $\mathrm{CaSO}_{4}$. <br> Since the solubility of $\mathrm{CaSO}_{4}$ is lowered, there will be less $\mathrm{Ca}^{2+}$ from dissolution of $\mathrm{CaSO}_{4}$. Equilibrium position of $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2} \rightleftharpoons 3 \mathrm{Ca}^{2+}+2 \mathrm{PO}_{4}^{3-}$ shifts right, increasing the solubility of $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$. | [2] |
|  |  | [Tota | 18] |


| 2 | (a) | (i) | $\mathrm{NaOH}(\mathrm{aq})$, heat under reflux | [1] |
| :---: | :---: | :---: | :---: | :---: |
|  |  | (ii) | The $\mathrm{C}-\mathrm{Cl}$ 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 $\pi$ electron cloud of the benzene ring. This strengthens the $\mathrm{C}-\mathrm{Cl}$ bond, making it more difficult to break. | [1] |
|  |  | (iii) |  | [1] |
|  |  | (iv) | Add $\mathrm{PCl}_{5} / \mathrm{SOCl}_{2}$ <br> 2,4-dichlorobenzyl alcohol: white fumes (of HCl ) observed amylmetacresol: no white fumes observed or <br> Add $\mathrm{Br}_{2}(\mathrm{aq})$ <br> 2,4-dichlorobenzyl alcohol: $\mathrm{Br}_{2}(\mathrm{aq})$ remains orange amylmetacresol: orange $\mathrm{Br}_{2}(\mathrm{aq})$ decolourises or <br> Add neutral $\mathrm{FeCl}_{3}$ <br> 2,4-dichlorobenzyl alcohol: no violet complex formed amylmetacresol: violet complex formed | [2] |



|  | (iii) | (Accept: benzoate salt) | ] |
| :---: | :---: | :---: | :---: |
| (d) | (i) | When $0.00 \mathrm{~cm}^{3}$ of NaOH is added, solution contains only tartaric acid. $\begin{aligned} & {\left[\mathrm{H}^{+}\right]=\sqrt{(0.0100)\left(10^{-2.89}\right)}=3.59 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}} \\ & \mathrm{pH}=-\lg \left(3.59 \times 10^{-3}\right)=\underline{2.45} \end{aligned}$ <br> When $12.50 \mathrm{~cm}^{3}$ of NaOH is added, solution contains equal concentration of unreacted tartaric acid and tartrate mono-anion, giving rise to a buffer at its maximum buffering capacity. <br> Hence, $\mathrm{pH}=\mathrm{pK} K_{\mathrm{a} 1}=\underline{2.89}$. <br> When $50.00 \mathrm{~cm}^{3}$ of NaOH is added, solution only contains tartrate di-anion which undergoes hydrolysis to form $\mathrm{OH}^{-}$. <br> [Tartrate di-anion] $=\left(\frac{25.00}{1000} \times 0.0100\right) \div \frac{75.00}{1000}=0.00333 \mathrm{~mol} \mathrm{dm}^{-3}$ $\begin{aligned} & {\left[\mathrm{OH}^{-}\right]=\sqrt{(0.00333)\left(\frac{1.00 \times 10^{-14}}{10^{-4.40}}\right)}=9.15 \times 10^{-7} \mathrm{~mol} \mathrm{dm}^{-3}} \\ & \mathrm{pOH}=-\lg \left(9.15 \times 10^{-7}\right)=6.04 \\ & \mathrm{pH}=14-6.04=\underline{7.96} \end{aligned}$ | [4] |
|  | (ii) | The solid has a giant ionic lattice structure while tartaric acid has a simple covalent structure. More energy 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 $\mathrm{KMnO}_{4}(\mathrm{aq})$ | [1] |
|  | (ii) |  | [1] |


|  | (iii) | The gas is $\mathrm{CO}_{2}$. <br> $\mathrm{pV}=\mathrm{nRT}$ <br> $\mathrm{p}\left(500 \times 10^{-6}\right)=\left(\frac{0.36}{44.0}\right)(8.31)(30+273)$ <br> $p=4.12 \times 10^{4} \mathrm{~Pa}$ | [2] |  |  |
| :--- | :--- | :--- | :--- | :--- | :---: |
|  |  | [Total: 23] |  |  |  |


| 3 | (a) | It is a substance that is at a different phase as the reactants, and it speeds up the rate of the reaction by providing an alternative reaction pathway with a lower activation energy. |  | [2] |
| :---: | :---: | :---: | :---: | :---: |
|  | (b) | $\begin{aligned} & \mathrm{Zn} / \mathrm{Zn}^{2+} \text { half-cell } \mathrm{E} \ominus=-0.76 \mathrm{~V} \\ & \mathrm{VO}_{3}-/ \mathrm{VO}^{2+} \text { half-cell } \mathrm{E} \ominus=+1.00 \mathrm{~V} \\ & \mathrm{VO}^{2+} / \mathrm{V}^{3+} \text { half-cell } \mathrm{E} \ominus=+0.34 \mathrm{~V} \\ & \mathrm{~V}^{3+} / \mathrm{V}^{2+} \text { half-cell } \mathrm{E} \ominus=-0.26 \\ & \left(\mathrm{VO}_{3}-/ \mathrm{VO}^{2+} / / \mathrm{Zn} / \mathrm{Zn}^{2+}\right) \mathrm{E} \ominus_{\text {cell }}=+1.76 \mathrm{~V} \end{aligned}$ <br> Zn is able to reduce $\mathrm{VO}_{3}^{-}$to $\mathrm{VO}^{2+} /$ reduction of $\mathrm{VO}_{3}^{-}$to $\mathrm{VO}^{2+}$ by Zn is spontaneous. $\left(\mathrm{VO}^{2+} / \mathrm{V}^{3+} / / \mathrm{Zn} / \mathrm{Zn}^{2+}\right) \mathrm{E}^{\ominus} \text { cell }=+1.10 \mathrm{~V}$ <br> Zn is able to reduce $\mathrm{VO}^{2+}$ to $\mathrm{V}^{3+} /$ reduction of $\mathrm{VO}^{2+}$ to $\mathrm{V}^{3+}$ by Zn is spontaneous. $\left(\mathrm{V}^{3+} / \mathrm{V}^{2+} / / \mathrm{Zn} / \mathrm{Zn}^{2+}\right) \mathrm{E}_{\text {cell }}=+0.50 \mathrm{~V}$ <br> Zn is able to reduce $\mathrm{V}^{3+}$ to $\mathrm{V}^{2+} /$ reduction of $\mathrm{V}^{3+}$ to $\mathrm{V}^{2+}$ by Zn is spontaneous. Hence, the solution changes from yellow to blue to green to violet. |  | [3] |
|  | (c) | (i) | $\mathrm{V}^{3+}(\mathrm{aq})$ | 1] |
|  |  | (ii) | $5 \mathrm{VO}^{2+}+\mathrm{MnO}_{4}^{-}+6 \mathrm{H}_{2} \mathrm{O} \rightarrow 5 \mathrm{VO}_{3}^{-}+\mathrm{Mn}^{2+}+12 \mathrm{H}^{+}$ <br> OR $5 \mathrm{VO}^{2+}+\mathrm{MnO}_{4}^{-}+\mathrm{H}_{2} \mathrm{O} \rightarrow 5 \mathrm{VO}_{2}^{+}+\mathrm{Mn}^{2+}+2 \mathrm{H}^{+}$ | 1] |
|  |  | (iii) | $n_{K M n O_{4}}=\frac{20.63}{1000} \times 0.02=0.000413 \mathrm{~mol}$ | 1] |


cesmes)

## Section B

Answer one question from this section.

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


|  | (ii) | By Hess' Law, $\begin{aligned} & \text { - L.E. }-(+494)-(+107)-(-78.2)-2(-241)+2(+40.8)-1059=-210 \\ & \text { L.E. }=-808 \mathrm{~kJ} \mathrm{~mol}^{-1} \end{aligned}$ | [5] |
| :---: | :---: | :---: | :---: |
| (c) | (i) | $\begin{aligned} & Q=I t=n F \\ & n=\frac{I t}{F}=\frac{0.12 \times 60}{96500}=7.4611 \times 10^{-5} \mathrm{~mol} \\ & n_{\text {ethanol }}=\frac{1}{4} \times 7.4611 \times 10^{-5}=1.87 \times 10^{-5} \mathrm{~mol} \end{aligned}$ <br> Mass of alcohol per breath $=1.87 \times 10^{-5} \times 46.0=8.58 \times 10^{-4} \mathrm{~g}$ | [3] |
|  | (ii) | $\begin{aligned} \text { Amount of ethanol per } \mathrm{cm}^{3} \text { of blood } & =\frac{2100}{65} \times 1.87 \times 10^{-5} \\ & =6.04 \times 10^{-4} \mathrm{~mol} \end{aligned}$ | [1] |
|  |  | [Total: 20] |  |


| 5 | (a) | Mg <br> Mg <br> $\mathrm{P}_{4}$ <br> wa <br> $\mathrm{P}_{4}$ <br> $\mathrm{P}_{4}$ <br> $\mathrm{P}_{4}$ roo alk | (s) reacts with acid to form neutral salt and water. $\mathrm{O}(\mathrm{~s})+2 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{Mg}^{2+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ <br> (s) (or $\mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})$ ) react violently/vigorously with alkali to form salt and er. $\begin{aligned} & 10(\mathrm{~s})+12 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow 4 \mathrm{PO}_{4}^{3-}(\mathrm{aq})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \\ & \mathrm{m}_{6}(\mathrm{~s})+8 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow 4 \mathrm{HPO}_{3}^{2-}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \end{aligned}$ <br> $\mathrm{O}_{6}(\mathrm{~s})$ (or $\mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})$ ) 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) | $\begin{aligned} & \mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{~s}) \rightarrow \mathrm{MgO}(\mathrm{~s})+2 \mathrm{NO}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \\ & \mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{~s}) \rightarrow \mathrm{CaO}(\mathrm{~s})+2 \mathrm{NO}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \end{aligned}$ | [1] |
|  |  | (ii) | $\mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ decomposed at 575 K but not $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$. <br> Both $\mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ and $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ decomposed at 949 K . <br> $\mathrm{Mg}^{2+}$ has a smaller ionic radius than $\mathrm{Ca}^{2+}$ while their ionic charges are the same. Charge density of $\mathrm{Mg}^{2+}$ is higher and hence has higher polarising power than $\mathrm{Ca}^{2+} . \mathrm{Mg}^{2+}$ is able to polarise / distort the electron cloud of $\mathrm{NO}_{3}{ }^{2-}$ and weaken the covalent bonds in $\mathrm{NO}_{3}{ }^{2-}$ to larger extent. <br> Since the mole ratio of $\mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ and $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ in the samples is $2: 1$, <br> Sample at 575 K lost $x \mathrm{~g}$ from $\mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ <br> Sample at 949 K lost $x \mathrm{~g}$ from $\mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ and $2 x \mathrm{~g}$ from $\mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}(3 x \mathrm{~g}$ in total). | [3] |
|  | (c) | (i) | To condense the product formed so that it can be collected. | [1] |
|  |  | (ii) | Hydrolysis: | [2] |
|  |  | (iii) | 3-methylbutanal (lowest b.p. compared to the isoamyl cinnamate, cinnamic acid and 3-methylbutanol, deduce using chem bonding knowledge) | [1] |


|  | (iv) |   | [2] |
| :---: | :---: | :---: | :---: |
| (d) | (i) | Total amount of gallic acid $(G A)=\frac{1.00}{170}=0.005882 \mathrm{~mol}$ $\mathrm{GA} \equiv 4 \mathrm{NaOH}$ $\begin{aligned} \text { Amount of GA in } 100 \mathrm{~cm}^{3} \text { aqueous layer } & =\frac{20.25}{1000} \times 0.180 \times \frac{1}{4} \times 5 \\ & =4.556 \times 10^{-3} \mathrm{~mol} \end{aligned}$ $\begin{aligned} \text { Amount of GA in } 50 \mathrm{~cm}^{3} \text { organic layer } & =0.005882-4.556 \times 10^{-3} \\ & =1.326 \times 10^{-3} \mathrm{~mol} \end{aligned}$ $K_{\text {partition }}=\frac{\left(\frac{4.556 \times 10^{-3}}{0.100}\right)}{\left(\frac{1.326 \times 10^{-3}}{0.050}\right)}=1.72$ | [3] |
|  | (ii) | Add ( $100 \mathrm{~cm}^{3}$ of / an excess of) aqueous NaOH and the ( $50 \mathrm{~cm}^{3}$ 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. <br> modification: use of aqueous NaOH to neutralise the gallic acid and its derivatives <br> explanation: explain why mainly 3,4,5-trimethoxygallic acid is left in diethyl ether layer <br> gallic acid forms anion with more charge (+4) than anion from 3,4,5trimethoxygallic acid, therefore more ion-dipole interaction <br> 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 $\mathrm{KMnO}_{4}$, heat. Bubble gaseous product into limewater. <br> For methyl gallate, purple $\mathrm{KMnO}_{4}$ is decolourised and a colourless, odourless gas evolved gives white ppt in limewater. <br> For gallic acid, $\mathrm{KMnO}_{4}$ remained purple. | [2] |
|  | [Total: 20] |  |  |

