PERTH MODERN SCHOOL

Semester Two Examination, 2013

Question/Answer Booklet

CHEMISTRY
Stage 3

Student name: _____

Teacher name: _____

Time allowed for this paper

Reading time before commencing work:	ten minutes
Working time for paper:	three hours

Q32 (b) 25mL
Q38 (e) 0.2493

If 12.5mL of the nitric acid was added to 25mL of the ammonia solution

when a 0.2493 g sample

Material required/recommended for this paper

To be provided by the supervisor
This Question/Answer booklet
Multiple-choice Answer sheet
Chemistry Data sheet

To be provided by the candidate
Standard items: pens (blue/black preferred), pencils (including coloured), sharpener, correction fluid/tape, eraser, ruler, highlighters

Special items: non-programmable calculators approved for use in the WACE examinations

Important note to candidates

No other items may be taken into the examination room. It is **your** responsibility to ensure that you do not have any unauthorised notes or other items of a non-personal nature in the examination room. If you have any unauthorised material with you, hand it to the supervisor **before** reading any further.

Structure of this paper

Section	Number of questions available	Number of questions to be answered	Suggested working time (minutes)	Marks available	Percentage of exam
Section One: Multiple-choice	25	25	50	25	25
Section Two: Short answer	8	8	60	70	35
Section Three: Extended answer	5	5	70	80	40
				Total	100

Instructions to candidates

1. The rules for the conduct of Western Australian external examinations are detailed in the *Year 12 Information Handbook 2013*. Sitting this examination implies that you agree to abide by these rules.

2. Answer the questions according to the following instructions.

   Section One: Answer all questions on the separate Multiple-choice Answer sheet provided. For each question shade the box to indicate your answer. Use only a blue or black pen to shade the boxes. If you make a mistake, place a cross through that square then shade your new answer. Do not erase or use correction fluid/tape. Marks will not be deducted for incorrect answers. No marks will be given if more than one answer is completed for any question.

   Sections Two and Three: Write your answers in this Question/Answer Booklet.

3. When calculating numerical answers, show your working or reasoning clearly. Express numerical answers to three significant figures and include appropriate units where applicable.

4. You must be careful to confine your responses to the specific questions asked and to follow any instructions that are specific to a particular question.

5. Spare pages are included at the end of this booklet. They can be used for planning your responses and/or as additional space if required to continue an answer.
   - Planning: If you use the spare pages for planning, indicate this clearly at the top of the page.
   - Continuing an answer: If you need to use the space to continue an answer, indicate in the original answer space where the answer is continued, i.e. give the page number. Fill in the number of question(s) that you are continuing to answer at the top of the page.

6. The Chemistry Data Sheet is **not** handed in with your Question/Answer Booklet.

Section One: Multiple-choice 25% (50 marks)

This section has **25** questions. Answer **all** questions on the separate Multiple-choice Answer Sheet provided. For each question shade the box to indicate your answer. Use only a blue or black pen to shade the boxes. If you make a mistake, place a cross through that square then shade your new answer. Do not erase or use correction fluid/tape. Marks will not be deducted for incorrect answers. No marks will be given if more than one answer is completed for any question.

Suggested working time: 45 minutes.

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1. An element, X, was found to have the following successive ionisation energies:

Ionisation	1st	2nd	3rd	4th	5th	6th	7th	8th
Ionisation energy/kJ mol^{-1}	736	1450	7740	10500	13600	18000	21700	25600

Which of the following represents the **most** likely formula for the sulfate of X?

(a) XSO_4
(b) X_2SO_4
(c) $X_2(SO_4)_3$
(d) $X(SO_4)_2$

2. Which of the following bonds would be expected to have the **greatest** polarity?

(a) S–Cl
(b) Si–Cl
(c) C–F
(d) O–F

3. Carbon, silicon, germanium, tin, and lead are all placed together in the same group of the periodic table because:

(a) They have the same number of valence electrons.
(b) Each has a structural form with delocalized electrons.
(c) Atoms of each element have the same number of electrons.
(d) There is a gradual increase in their atomic masses.

4. Arsenic has 23 isotopes, one of them is ^{65}As. Which of the following correctly lists the number of subatomic particles in the arsenide ($^{65}As^{3-}$) ion?

(a) 65 protons, 33 neutrons and 68 electrons
(b) 33 protons, 32 neutrons and 30 electrons
(c) 65 protons, 32 neutrons and 65 electrons
(d) 33 protons, 32 neutrons and 36 electrons

5. Place the following substances in order of melting point, starting with the **lowest:**

$SiO_2(s)$, $SO_2(s)$, $O_2(s)$, $AgNO_3(s)$

(a)	$SO_2(s)$	$O_2(s)$	$AgNO_3$ (s)	SiO_2 (s)
(b)	$SO_2(s)$	$O_2(s)$	SiO_2 (s)	$AgNO_3(s)$
(c)	$O_2(s)$	$SO_2(s)$	$AgNO_3$ (s)	SiO_2 (s)
(d)	$O_2(s)$	$SO_2(s)$	SiO_2 (s)	$AgNO_3$ (s)

6. Which of the following molecules is trigonal planar in shape?

(a) Arsenic tribromide
(b) Sulfur dichloride
(c) methanal
(d) ammonia

7. Which of the following has the **greatest** solubility in water.

(a) Propanoic acid
(b) Propan-1-ol
(c) Propanone
(d) Propane

8. Which one of the following aqueous solutions is the **best** conductor of electricity.

(a) 1.00 $molL^{-1}$ ethanoic acid
(b) 1.00 $molL^{-1}$ ammonia
(c) 1.00 $molL^{-1}$ calcium chloride
(d) 1.00 $molL^{-1}$ nitric acid

9. The sign of ΔH for the reverse of the reaction shown below is :

$H_2O(\ell) \rightarrow H_2O(s) + heat$

(a) is positive and the reaction is endothermic.
(b) Is positive and the reaction is exothermic.
(c) is negative and the reaction is endothermic.
(d) is negative and the reaction is exothermic.

10. Which of the following statements about the effect of a catalyst is **false**?

(a) A catalyst increases the proportion of particles possessing sufficient energy to react.
(b) A catalyst boosts the energy of reactants, enabling to collide with enough energy to react.
(c) A catalyst provides an alternative reaction pathway.
(d) A catalyst is not consumed in a reaction.

11 .Which one of the following pairs of substances forms a buffer in aqueous solution?

(a) HCO_3^- and CO_3^{2-}
(b) H_3O^+ and OH^-
(c) $HC\ell$ and $C\ell^-$
(d) HNO_3 and NH_4NO_3

12. Which of the following lists the 1 mol L^{-1} solutions in of **increasing** pH?

(a)	$CH_3COOH(aq)$	$NH_4C\ell(aq)$	$NaC\ell(aq)$	$CH_3CH_2NH_2(aq)$
(b)	$CH_3COOH(aq)$	$NaC\ell(aq)$	$NH_4C\ell(aq)$	$CH_3CH_2NH_2(aq)$
(c)	$CH_3CH_2NH_2(aq)$	$NaC\ell(aq)$	$NH_4C\ell(aq)$	$CH_3COOH(aq)$
(d)	$NH_4C\ell(aq)$	$CH_3COOH(aq)$	$CH_3CH_2NH_2(aq)$	$NaC\ell(aq)$

13. During an experiment to establish the concentration of an oxalic acid solution, a student carried out the following steps.

- Rinsed a burette with distilled water.
- Rinsed a conical flask with distilled water.
- Filled the burette with a standardised sodium hydroxide solution.
- Rinsed a pipette with the solution of oxalic acid.
- Dispensed 25 mL of oxalic acid into the conical flask using the pipette.

What effect would her procedure have had on the accuracy of her results?

(a) An artificially large volume of sodium hydroxide is needed to reach the end point, and the calculated concentration of oxalic acid would have been too low.
(b) An artificially small volume of sodium hydroxide is needed to reach the end point, and the calculated concentration of oxalic acid would have been too low.
(c) An artificially large volume of sodium hydroxide is needed to reach the end point, and the calculated concentration of oxalic acid would have been too high.
(d) An artificially small volume of sodium hydroxide is needed to reach the end point, and the calculated concentration of oxalic acid would have been too high.

14. Pure water undergoes self-ionisation according to the equation

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

The equilibrium constant (K_W) for the reaction as written is 1.0×10^{-14} at 25 °C and 1.0×10^{-13} at 60 °C.

At 50 °C, pure water has a pH value that is

(a) less than 7 and the water is still neutral
(b) less than 7 and therefore the water is now acidic
(c) greater than 7 and therefore the water is now basic
(d) not able to be estimated since there is no value for K_W at 50 °C .

15. What would be the **most** likely pH of a 0.010 mol L^{-1} solution of sulfuric acid?

(a) Less than 0.5
(b) Between 0.5 and 1
(c) Exactly 2
(d) Between 1.5 and 2.0

The next two questions (16 & 17) refers to the following reaction between phosphorus trichloride and chlorine to form phosphorus pentachloride:

$$PC\ell_3(g) + C\ell_2(g) \rightleftharpoons PC\ell_5(g) \qquad \Delta H = -124 \text{ kJ mol}^{-1}$$

16. If phosphorus trichloride and chlorine were placed in a sealed insulated vessel together with a catalyst, which of the following would **not** cause an increase in the rate at which equilibrium would be attained?

    (a) Increasing the volume of the vessel
    (b) Increasing the temperature
    (c) The addition of chlorine to the reaction mixture
    (d) Increasing the state of sub-division of the catalyst

17. Which of the following changes would **not** be observed if a little phosphorus trichloride were added at constant temperature to the sealed insulated vessel containing the three gases in the equation and equilibrium was allowed to re-establish?

    (a) The reverse reaction would speed up.
    (b) The concentration of phosphorus trichloride would increase.
    (c) The mass of chlorine in the vessel would fall.
    (d) The value of the equilibrium constant, K, would fall.

18. The formation of bromoethane from ethene and hydrogen bromide can be represented by the following equation:

    $$CH_2CH_2 + HBr \rightleftharpoons CH_3CH_2Br$$

    The equilibrium expression for the reaction is:

    $$K = \frac{[CH_3CH_2Br]}{[CH_2CH_2]\,[HBr]} = 7.5 \times 10^7$$

    If more hydrogen bromide is added to the reaction mixture after equilibrium has been established, the value of the equilibrium constant will be

    (a) Less then 7.5×10^7
    (b) Equal to 7.5×10^7
    (c) Greater than 7.5×10^7
    (d) Unknown as the amount of HBr added is not given.

19. The metals Hg, Cd, Ga and Pd react as follows:

    $3\ Pd^{2+} + 2\ Ga \rightarrow 2\ Ga^{3+} + 3\ Pd$

    $Cd + Ga^{3+}$ no reaction

    $Hg^{2+} + Pd \rightarrow Pd^{2+} + Hg$

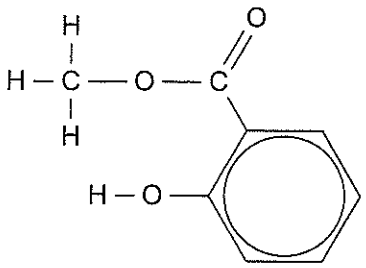
    Which of the following metals is the strongest reducing agent?

    (a) Pd
    (b) Ga
    (c) Cd
    (d) Hg

20. Which one of the reactions shown below is an oxidation reduction reaction.

(a) $HCOOH(aq) + NH_3(aq) \rightarrow HCONH_2(aq) + H_2O(\ell)$
(b) $NaOH(aq) + CO(g) \rightarrow HCOONa(aq)$
(c) $2\ H_2(g) + CO(g) \rightarrow CH_3OH$
(d) $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(\ell)$

21. Consider the following molecule, commonly known as oil of wintergreen:



oil of wintergreen

Which of the following statements about oil of wintergreen is **false**?

(a) It can be synthesised using methanol as one of the starting materials.
(b) It is an aldehyde.
(c) It is unsaturated.
(d) It is an ester.

22. In one part of an organic molecule, there is a carbon-oxygen double bond (C=0) while in another part, there is a nitrogen-hydrogen single bond (N-H).

If these two parts of the molecule were sufficiently close together, there would be

(a) two hydrogen bonds formed involving all four atoms.
(b) an attraction of the nitrogen atom in one bond to the oxygen atom in the other.
(c) an attraction of the hydrogen atom in one bond to the oxygen atom in the other.
(d) a repulsion between the carbon atom in one bond and the nitrogen atom in the other

23. Ethanol is removed from the body by reaction with the enzyme *alcohol dehydrogenase* (ADH).In fact, ADH can oxidise any alcohol .ADH, like all enzymes, is very specific and will not catalyse any other reaction. However, the product of the ADH reaction with an alcohol may undergo further reaction with other enzymes

The reaction of butan-2-ol with ADH would produce

(a) butanal
(b) butanoic acid
(c) butan-2-one
(d) 2-methylpropan-2-one

Question 24 is refers to the compounds I – IV shown below.

$C_4H_{10}O$

I $CH_3CH_2CH_2CH_2OH$

C_4H_8O

II $CH_3CH_2CH_2C(=O)H$

III $CH_3CH_2CH_2C(=O)OH$

C_4H_8O

IV $CH_3CH_2C(=O)CH_3$

24. Which two compounds may be described as structural isomers?

(a) I and II
(b) II and III
(c) I and III
(d) II and IV

25. The following formula represents the structure of a compound commonly used as a detergent:

$$CH_3(CH_2)_{10}CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-ONa$$

Which of the following statements about detergents is **false**?

(a) They are often preferred to soaps because of their low tendency to form scums with hard water.
(b) Part of the molecule is highly water-soluble.
(c) They are the sodium salts of carboxylic acids.
(d) The molecules contain large non-polar regions that can form strong intermolecular forces with fats.

End of section one

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Section Two: Short answer **35% (70 Marks)**

This section has **eight (8)** questions. Answer **all** questions. Write your answers in the space provided.

When calculating numerical answers, show your working or reasoning clearly. Express numerical answers to three significant figures and include appropriate units where applicable.

Do not use abbreviations, such as 'nr' for 'no reaction', without first defining them.

Spare pages are included at the end of this booklet. They can be used for planning your responses and/or as additional space if required to continue an answer.

- Planning: If you use the spare pages for planning, indicate this clearly at the top of the page.

Suggested working time: 60 minutes.

Question 26 **(6 marks)**

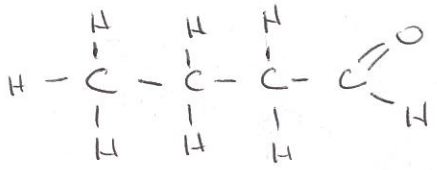
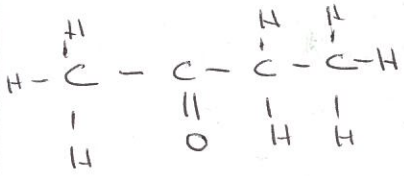
For each of the following pairs of substances, provide details of a **chemical** test that would allow the two substances to be distinguished from one another. Equations are **not** required.

substances	chemical test	observations
Ni(s) and Mg(s)	Add dilute acid	**Ni(s)** bubbles of gas and solution Turns green
		Mg(s) bubbles of gas and colourless solution
$NaCH_3COO(s)$ and $NaC\ell(s)$	• Dissolve Add solution of silver nitrate	**$NaCH_3COO(s)$** No visible reaction
		$NaC\ell(s)$ White precipitate forms

1 Each.

Question 27 **(8 marks)**

(a) 2-methylpropanal, whose formula is $(CH_3)_2CHCHO$, has two other structural isomers. In the spaces provided below, draw the structural formula and the IUPAC names of these two isomers. (4 marks)

structure	IUPAC name
 (All H drawn) (-1) overall.	Butanal
	Butenone

1 each

2-methylpropanal can be converted into substance Y by heating it with acidified potassium dichromate.

(b) State an observation that can be made as this reaction proceeds. (1 mark)

Orange solution turns green

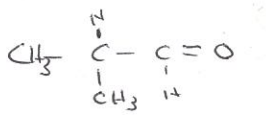
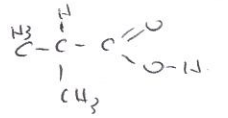
(c) Name the functional group present in substance Y that is **not** present in 2-methylpropanal. (1 mark)

Carboxylic acid or carboxolate

(d) Write a balanced half-equation showing the conversion of 2-methylpropanal into substance Y (2 marks)

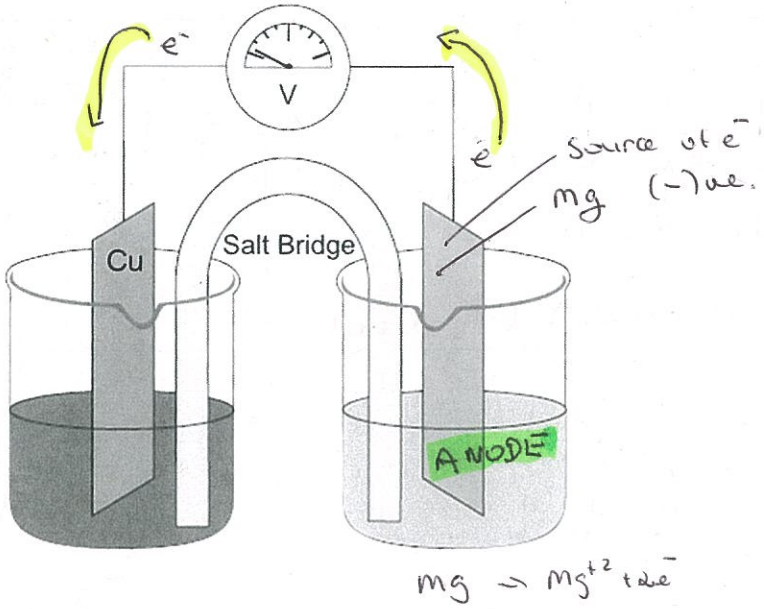
$C_4H_8O + H_2O \rightarrow C_4H_8O_2 + 2H^+ + 2e^-$

All or None ?

 C_4H_8O →  $C_4H_8O_2$

Question 28 **(12 marks)**

A student wishing to investigate the strength as reducing agents of various metals, set up an electrochemical cell made up of a copper rod immersed in a solution of copper(II) sulfate and a magnesium rod immersed in a solution of magnesium nitrate. The apparatus used is shown in the diagram below.



a) Add a label to the diagram to show the anode. (1 mark)

b) By adding an arrow to the diagram, show the direction of electron flow in the external circuit. (1 mark)

c) Give the half equation for the reaction occurring at the positive electrode. (1 mark)

$Cu^{+2} + 2e^- \rightarrow Cu$

d) Give the name or formula of a suitable substance that the salt bridge might contain. (1 mark)

Potassium nitrate | Ammonium nitrate |

e) Identify the reducing agent (reductant) in the cell. (1 mark)

Mg

[5]

f) The initial voltage measured in the cell was higher than the expected value using the table of Standard Reduction Potentials. Give **one** possible reason for this observation. (1 mark)

- Concentration of solution not $1 mol L^{-1}$
- Temperature not 25°C

g) Describe an observation that would be expected to be made in the copper half-cell whilst the experiment was taking place. (1 mark)

Salmon pink solid forming and intensity of blue solution diminishes

h) The student weighed both electrodes before and after the experiment, would the gain in mass in one half-cell be the same as the loss in mass in the other half-cell? Explain your answer, calculations are not required. (3 marks)

(1)
No. The same number of moles of each are involved (1)
but equal N° of moles of Cu and Mg have
different masses (1)

Rusting can be described as the initial formation of iron (II) ions from iron in the presence of water and oxygen and their subsequent conversion to iron(III) hydroxide(rust) . Rusting can be prevented by attaching magnesium to the object that is to be protected.

i) With reference to the table of Standard Reduction Potentials found on your data sheet, explain why tin would not be a suitable material for this purpose. (2 marks)

$Sn \rightarrow Sn^{+2} + 2e^-$

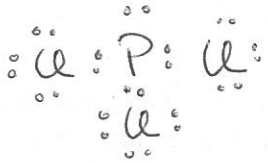
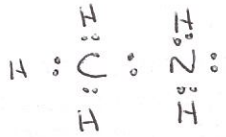
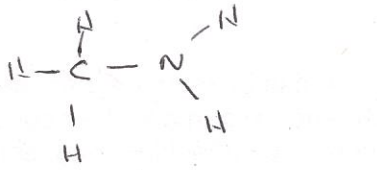
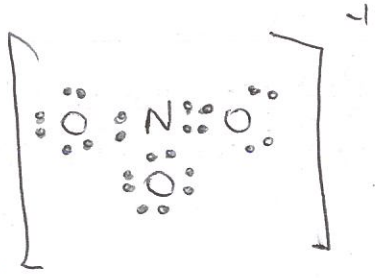
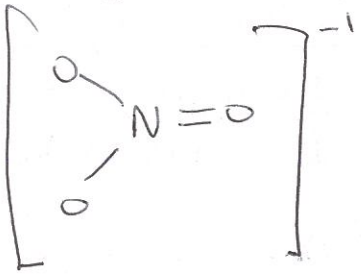
$Fe \rightarrow Fe^{+2} + 2e^-$

Iron is a stronger Reducing agent than Tin (1)
Iron would be oxidized before Tin (1)

Question 29 **(9 marks)**

For each species listed in the table below, draw the Lewis structure, representing all valence shell electron pairs either as : or as — **and** state or sketch the shape of the species.

(for example, water $H:\ddot{O}:H$ or $H-\ddot{O}-H$ or $H-\bar{\underline{O}}-H$ bent, polar)

Species	Lewis structure (showing all valence electrons)	Shape (sketch or name)
phosphorus trichloride PCl_3	 2	Pyramidal  1
methylamine CH_3NH_2	 2	pyramidal at N Tetrahedral at C  1
nitrate ion NO_3^- $5 + (3\times 6) + 1$ 24	 2	Trigonal Planar  1

- not showing all valence e^- (−1) overall
- no bracket and charge NO_3^- (−1) only once

(9)

Question 30 **(9 marks)**

By referring to the atomic structure and/or position on the Periodic table, account for the following:

(a) Carbon's electronegativity is lower than that of oxygen.

- Oxygen has smaller atomic radius (1)
- Oxygen has 2 more proton increase attraction valence e⁻ / shared electrons (1)
- increases electronegativity (1)

(3 marks)

(b) Aluminum's atomic radius is smaller than magnesium's atomic radius.

- valence electrons are in the same energy level (1)
- Aluminium has 1 more proton
- Increase charge in nucleus increases attraction valence electron reducing atomic radius (1)

(2 marks)

(c) Silicon dioxide (SiO_2) is a solid with an extremely high melting point, whilst carbon dioxide (CO_2) sublimes at -78°C

- SiO_2 forms covalent network solid (1)
- Silicon shares it 4 valence electrons with 4 other oxygens - strong covalent bonds extensive (1)
- Carbon shares electrons 2 oxygens forms covalent molecule (1)
- Carbon dioxide non-polar molecule dispersion forces (1)

(4 marks)

Question 31 **(7 marks)**

(a) But-1-ene and but-2-ene are isomers of one another. What is the name given to this type of isomerism?

Structural or positional isomerism

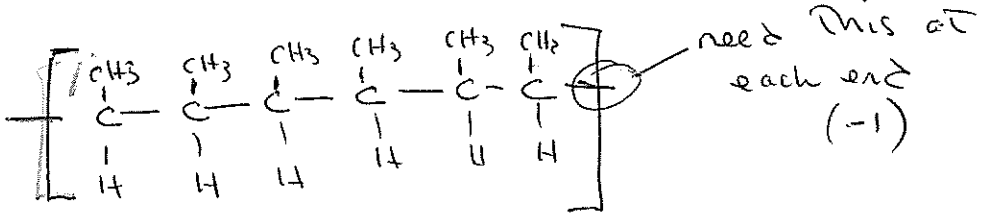
(1 mark)

(b) In addition to the type of isomerism displayed by the molecules in part (a), but-2-ene unlike but-1-ene is able to exhibit another type of isomerism. State the name given to this type of isomerism, and identify the features of but-2-ene that make this type of isomerism possible.

- geometric isomerism (1)
- presence of = bond between C_2 and C_3 (1)
- forms rigid structure with different groups attached to end of = bond (1)

(3 marks)

(c) In the space provided, draw a length of polymer chain that could be formed from 2-butene, showing **three** repeating units.

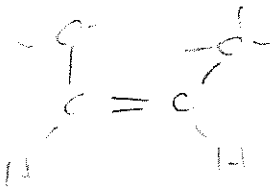


(2 marks)

(d) State the name given to the type of polymerisation described in part (c).

Addition

(1 mark)



Question 32 **(8 marks)**

(a) Nitrous acid (HNO_2) is a weak acid. Use relevant equations to explain how you would expect the pH of a 0.01 mol L^{-1} solution of nitrous acid to compare with that of a 0.01 mol L^{-1} solution of nitric acid. (3 marks)

$HNO_3 + H_2O \xrightarrow{100\%} H_3O^+ + NO_3^-$ $[H_3O^+] = 0.01\ mol\ L^{-1}$ (1)

$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$ $[H_3O^+] < 0.01\ mol\ L^{-1}$ (1)

pH of HNO_2 would be higher than the pH of HNO_3 (1)

A titration is carried out using 25.0 mL of approximately 0.900 mol L^{-1} ammonia solution placed in a conical flask. A few drops of indicator are added, and 0.900 mol L^{-1} nitric acid is added from a burette. weak base + strong acid → salt of weak base → end point acidic

The table below shows some indicators, together with their pH ranges, and their colours.

indicator name	pH range	colour in acid	colour in base
methyl yellow	2.9 – 4.0	red	yellow
bromothymol blue	6.9 – 7.6	yellow	blue
nile blue	10.1 – 11.1	blue	red
nitramine	11.0 – 13.0	colourless	orange

(b) From the indicators shown in the table, choose one that would be suitable to detect the end-point for the titration, and state the colour change that would be expected to occur.

Indicator: methyl yellow (1)

Colour change: yellow to red. base → Acid (1) change (2 mark)

If approximately 12.5 mL of nitric acid was added to (25) the ammonia solution, the resulting solution in the flask can be used as a buffer solution.

(c) With the aid of equations, explain how the solution is able to act as a buffer.

$HNO_3 + NH_3 \rightleftharpoons NH_4^+ + NO_3^-$

NH_4^+ ions and NH_3 present (1)

Add^N base $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ (1)

Addition Acid $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$ (1)

(3 marks)

Question 33 **(10 marks)**

When pure ethanol and pure ethanoic acid are mixed together with a small amount of concentrated sulfuric acid which acts as a catalyst, the following reversible reaction occurs:

$$CH_3CH_2OH(\ell) + CH_3COOH(\ell) \rightleftharpoons CH_3COOCH_2CH_3(\ell) + H_2O(\ell)$$

(a) Identify the type of reaction taking place in the forward direction, and give the IUPAC name of the organic product. (2 marks)

Type of reaction: Condensation / Elimination / Esterfication

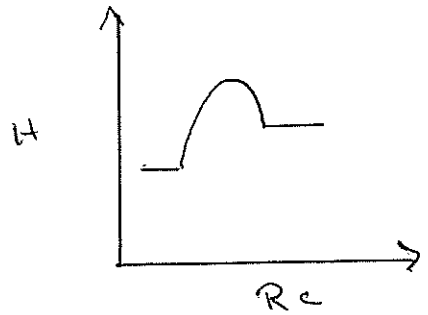
Name of product: ethyl ethanoate

(b) Write an expression for the equilibrium constant, K, for the reaction in the space provided. (1 mark)

$$K = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3CH_2OH][H_2SO_4]}$$

(c) The reaction is usually carried out at high temperatures in order to increase the yield. State and explain what this tells us about the enthalpy of the products compared to the enthalpy of the reactants. (3 marks)

- Enthalphy products higher than reactant (1)
- Reactants + heat ⇌ Products (reaction endothermic) (1)
- Addition of heat favours forward reaction increasing yield. (1)



A titration can be used to determine the proportions of reactants and products present at equilibrium. Sodium hydroxide solution is added quantitatively to the reaction mixture, reacting first with the sulfuric acid and then with any remaining ethanoic acid. The amount of ethanoic acid present at equilibrium can be easily determined since the sulfuric acid is present in the same quantity as at the start of the experiment.

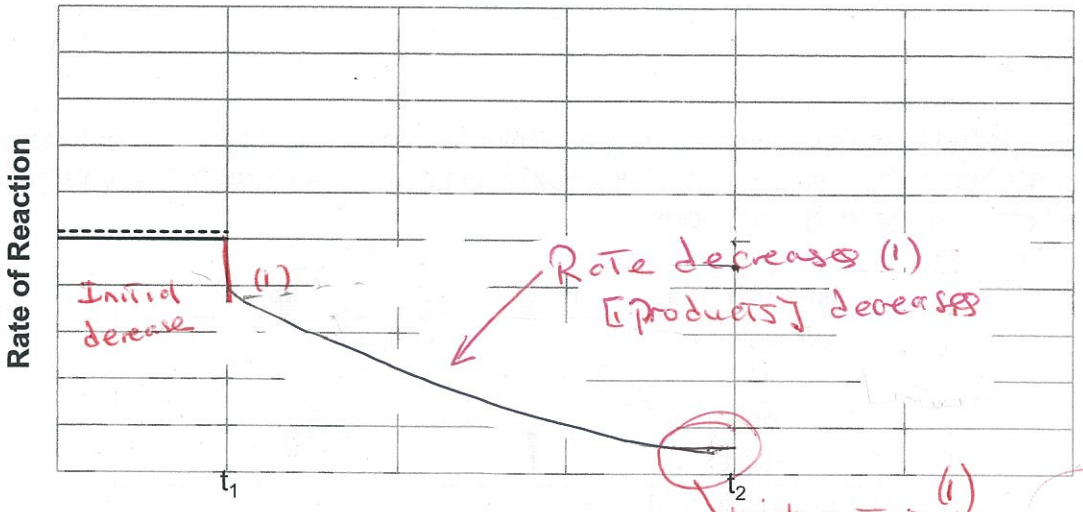
Although the addition of sodium hydroxide does disturb the equilibrium, the inaccuracy introduced is small if the reaction mixture is cooled immediately prior to titration.

(d) State the effect of addition of sodium hydroxide on the value of the **equilibrium constant**, K, by circling the correct answer below. (1 mark)

Effect on K (circle one) INCREASE DECREASE NO CHANGE

(e) On the axes shown below, sketch the initial effect of cooling the reaction mixture (at t_1) on the rate of the reverse reaction. The show the change in the rate of the reverse reaction until the system returns to a new equilibrium (at t_2). (3 marks)

Reactants + heat ⇌ Products



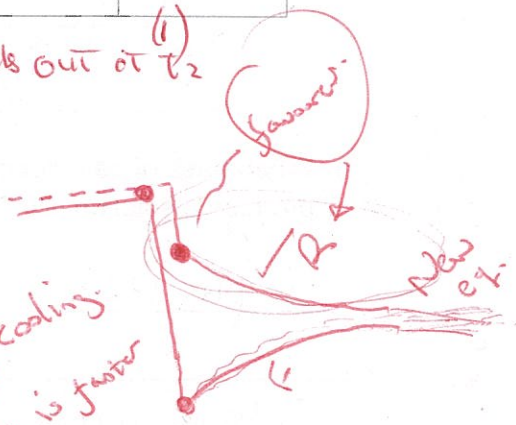
① L.C. says reverse is favoured

Rate decreases as temp decreases.

Both rates decrease at time of cooling.

Reverse rate decreases less - it is faster

(forward rate is slower)



End of section two

Section Three: Extended answer 40% (80 marks)

This section contains **five (5)** questions. Answer **all** questions. Write your answers in the spaces provided.

Where questions require an explanation and/or description, marks are awarded for the relevant chemical content and also for coherence and clarity of expression.

Final answers to calculations should be expressed to three (3) significant figures.

Spare pages are included at the end of this booklet. They can be used for planning your responses and/or as additional space if required to continue an answer.

- Planning: If you use the spare pages for planning, indicate this clearly at the top of the page.
- Continuing an answer: If you need to use the space to continue an answer, indicate in the original answer space where the answer is continued, i.e. give the page number. Fill in the number of the question(s) that you are continuing to answer at the top of the page.

Suggested working time: 70 minutes.

Question 34 (13 marks)

Chlorine is found in acids of various strengths. Chlorine can exist in different oxidations states. Three acids formed by chlorine in its different oxidation states are shown in the table below. Parts (a) and (b) refer to different acids.

Name and formula of acid	Strong/Weak
hydrochloric acid $HC\ell$	strong
chloric acid $HC\ell O_3$	strong
perchloric acid $HC\ell O_4$	strong

(a) What mass of perchloric acid would need to be dissolved in 250 mL of distilled water to produce a solution with a pH of 3.59? (3 marks)

pH 3.59 $[H^+]$ = inv log − 3.59

$[H^+] = 2.57 \times 10^{-4}$ mol L^{-1} = $[HClO_4]$ (1)

Moles $HClO_4$ = $\frac{C \times V}{1000}$ = $\frac{2.57 \times 10^{-4} \times 250}{1000}$ $HClO_4$ = 100.46

= 6.426×10^{-5} moles (1)

Mass $HClO_4$ = $100.46 \times 6.426 \times 10^{-5}$

= 6.46×10^{-3} g (1) (3)

A 1.20 g sample of solid calcium hydroxide was added to a beaker containing 250 mL of a 0.161 mol L^{-1} aqueous solution of chloric acid, and the solution stirred until all the solid had dissolved. (Any change in volume due to the addition of the calcium hydroxide can be ignored).

(b) Write a balanced equation to show the reaction taking place in the beaker. (2 marks)

1 for molecular.

$Ca(OH)_{2(s)} + 2H^+ \rightarrow Ca^{+2} + 2H_2O$

(c) Determine the limiting reagent by calculation. (4 marks)

Moles of chloric acid $= \frac{C \times V}{1000} = \frac{0.161 \times 250}{1000}$

$= 4.025 \times 10^{-2}$ moles (1)

Moles $Ca(OH)_2 = \frac{1.20}{74.096} = 1.619 \times 10^{-2}$ (1)

40.08
32.00
2×1.008
74.096

1 mole $Ca(OH)_2$ reacts 2 moles $HClO_3$

1.619×10^{-2} : x

$x = 3.24 \times 10^{-2}$ – we have 4.025×10^{-2} mols chloric acid (1)

∴ $Ca(OH)_2$ is LR. (1)

only (3) without clearly identifying LR – not ÷ by coefficient (4)

(d) Calculate the pH of the resulting solution. (4 marks)

Moles of H^+ in excess $= 4.025 \times 10^{-2} - 3.24 \times 10^{-2}$ (1)

$= 7.859 \times 10^{-3}$ moles (1)

$n = \frac{C \times V}{1000}$

Conc $H^+ = \frac{n \times 1000}{V} = \frac{7.859 \times 10^{-3} \times 1000}{250}$

$= 3.143 \times 10^{-2}$ (1)

$pH = -\log [H^+]$

$= -\log 3.143 \times 10^{-2}$

$= 1.50$ (1) (4)

Question 35 **(17 marks)**

Solutions of iron(II) salts are often used in redox titrations, but can be problematic as the Fe^{2+} ions can be oxidised by dissolved oxygen in the solution, forming various hydrated forms of iron(III) oxide, according to the following equation:

$$Fe^{2+}(aq) + O_2(g) + (2x + 4)\,H_2O(\ell) \rightleftharpoons 2\,Fe_2O_3.xH_2O(s) + 8H^+(aq)$$

Ammonium iron(II) sulfate, or Mohr's salt, is often preferred over iron(II) sulfate for redox titration purposes since the unwanted oxidation of Fe^{2+} is prevented by the ammonium ions present, which reduce the pH of the solution. Mohr's salt is commonly found in hydrated form, as any of a number of salts with the formula $(NH_4)_2Fe(SO_4)_2.\,xH_2O$.

(a) Write an equation to show how the ammonium ions are able to lower the pH of a solution. (2 marks)

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ (2)

(b) Use the equation given above to explain why the oxidation of Fe^{2+} is prevented in solutions of low pH. (2 marks)

- Low pH $[H^+]$ increased (1)
- Shift position of equil to left reducing rate of oxidation Fe^{+2} (1)

10.1 g of hydrated ammonium iron(II) sulfate crystals were dissolved in distilled water and made up to 250 mL in a volumetric flask. 25.0 mL aliquots of this solution were titrated against 0.0240 mol L^{-1} potassium permanganate solution until consistent results were obtained. The table below shows the results of the experiment.

	Rough	1	2	3	4
Final volume (mL)	23.01	22.25	22.27	23.65	23.65
Initial volume (mL)	0.01	1.05	1.02	1.10	1.80
Titre (mL)	23.00	21.20	21.25	22.55 (22.3, 22.75)	21.85 (22.5)

(c) Complete the table and calculate the average titre volume.

Average titre: $= \dfrac{21.20 + 21.25}{2}$ only 2 values within 0.2mL

$= 21.23$ mL (21.225) (1)

(1 mark)

(d) Write the balanced redox equation for the reaction taking place.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O$

$Fe^{+2} \rightarrow Fe^{+3} + e^-$

$MnO_4^- + 5\,Fe^{+2} + 8H^+ \rightarrow Mn^{+2} + 5\,Fe^{+3} + 4H_2O$

(2 marks)

(e) Calculate the mass of $(NH_4)_2Fe(SO_4)_2$ in 250 mL of solution.

Moles $MnO_4^- = \frac{c \times V}{1000} = \frac{0.024 \times 21.23}{1000}$

$= 5.094 \times 10^{-4}$ moles (1)

Moles $Fe^{+2} = 5 \times 5.09 \times 10^{-4}$

$= 2.547 \times 10^{-3}$ moles in 25mL (1)

Moles in 250 mL $= 2.547 \times 10^{-3} \times 10$ (1)

$= 2.547 \times 10^{-2}$ moles

$(NH_4)_2Fe(SO_4)_2$

Mass $(NH_4)_2Fe(SO_4)_2 = 2.547 \times 10^{-2} \times 284.054 = 284.054$ g (1)

$= 7.23$ g (1)

+2 ? +1 sig fig (7)

3.62 g if 2:5 ratio.

(7 marks) 6

(f) Calculate the value of x in the formula $(NH_4)_2Fe(SO_4)_2 . xH_2O$

Mass H_2O in 10.1 g sample $(NH_4)_2(FeSO_4)_2 . xH_2O$

$= (10.1 - 7.23)$ g $= 2.87$ g (1)

Moles $H_2O = \frac{2.87}{18.016} = 0.1593$ moles (B) (1)

Ratio $(NH_4)_2Fe(SO_4)_2 : H_2O$

$2.547 \times 10^{-2} \quad 0.1593$ (1)

$6.25 \quad 1$

$x = 6$

(3 marks)

Question 36 **(22 marks)**

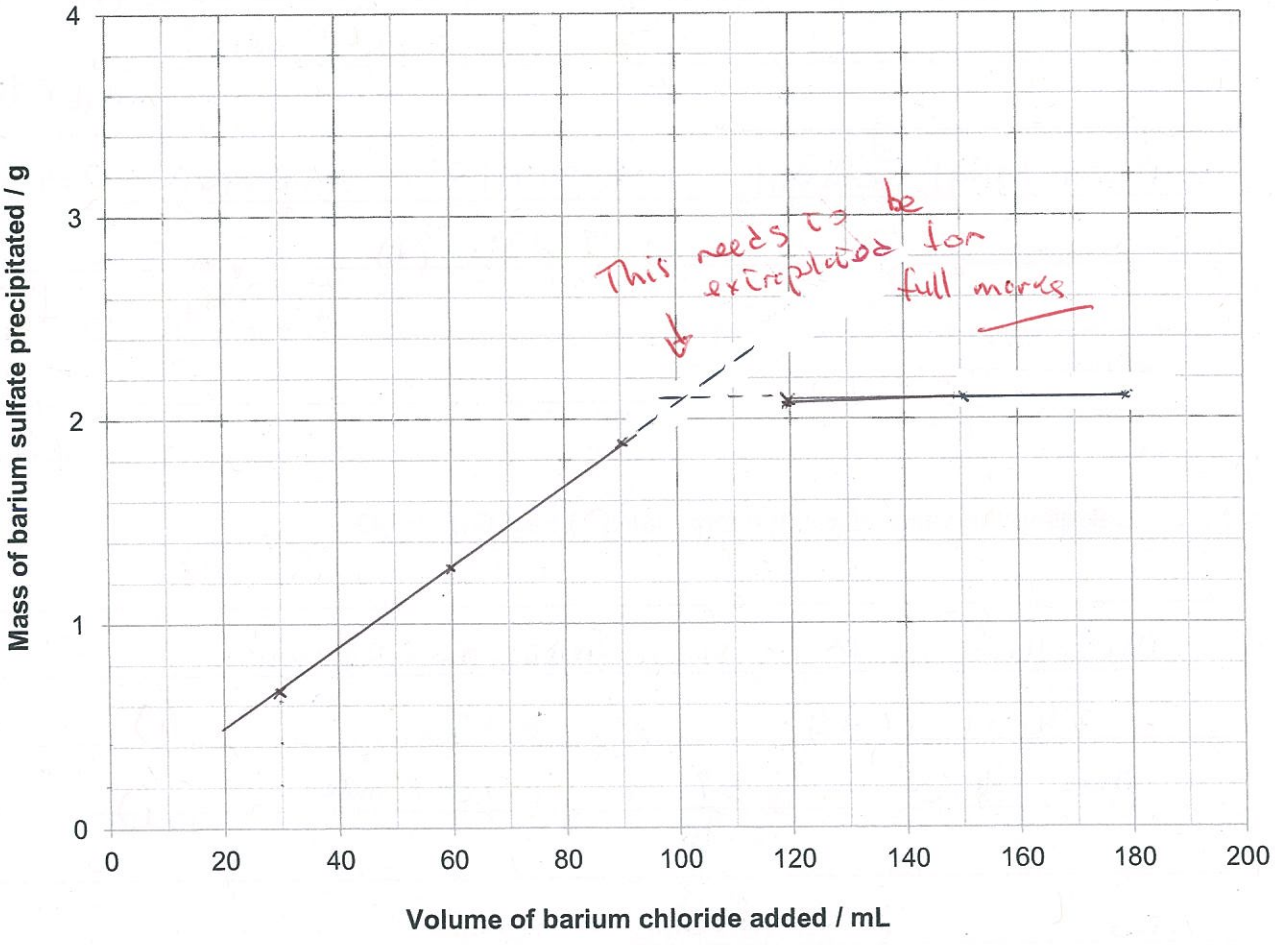
A sample of powdered magnesium sulfate is known to have been contaminated with sodium chloride. The percentage purity of the magnesium sulfate can be determined by the following method:

- 32.50 g of the impure magnesium sulfate is dissolved in water and the solution is made up to 500.0 mL in a volumetric flask.
- Six 20.0 mL aliquots of this solution are placed in separate conical flasks.
- Different volumes of 0.100 mol L^{-1} $BaC\ell_2(aq)$ are added to each flask, causing any sulfate ions present to precipitate out of the solution.
- The precipitate from each sample is filtered, rinsed with distilled water and then dried to constant mass.

The results of this analysis are shown in the table below.

Sample	1	2	3	4	5	6
Volume of $BaC\ell_2(aq)$ added (mL)	30.0	60.0	90.0	120.0	150.0	180.0
Mass of $BaSO_4(s)$ precipitated (g)	0.61	1.23	1.83	2.04	2.04	2.04

(a) Display the results in a suitable format using the axes provided. (2 marks)



(b) Write a balanced ionic equation for the reaction taking place. (1 mark)

$Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4$

(c) Explain why the mass of precipitate remained constant for the last three samples, in spite of the fact that more barium chloride was being added. (1 mark)

SO_4^{-2} (s) ions are the Limiting Reagent

(d) Use the mass of precipitate to calculate the percentage purity of the magnesium sulfate. (5 marks)

Max mass precipitate = 2.04g

$BaSO_4$ = 137.30 + 32.06 + 64.00 = 233.36

Moles $BaSO_4$ = $\frac{2.04}{233.36}$ = 8.742×10^{-3} (1)

Moles SO_4^{-2} = 8.742×10^{-2} in 20mL

Moles SO_4^{-2} in 500mL = $8.742 \times 10^{-2} \times \frac{500}{20}$

= 2.185×10^{-1} moles (1)

Moles $MgSO_4$ = 2.185×10^{-1} moles (1)

$MgSO_4$ = 24.3 + 32.06 + 64.00 = 120.36

mass $MgSO_4$ = $2.185 \times 10^{-1} \times 120.36$

= 26.3 g (1)

% Purity by mass = $\frac{26.3}{32.50} \times \frac{100}{1}$ = 80.9% (1)

(5)

(e) Use the graph you have drawn in part (a) to estimate the minimum volume of barium chloride needed to precipitate all the sulfate ions from solution. (1 mark)

Range (97 – 102) mL

Question 36 (continued)

(f) Calculate the final concentration (in mol L^{-1}) of chloride ions in the filtrate collected from **sample four**. You may assume that sodium chloride was the only impurity present in the impure magnesium sulfate. (7 marks)

If we use 120 mL of $BaCl_2$ Sample 4 2.04 g $BaSO_4$

Moles $BaCl_2$ = $\frac{0.1 \times 120}{1000}$ = 1.20×10^{-2} mole (1)

Moles Cl^- from $BaCl_2$ = 2.40×10^{-2} moles (1)

(100 − 80.9) = 19.1% NaCl

Mass NaCl in 32.5 g $MgSO_4$ = $\frac{19.1}{100} \times \frac{32.5}{1}$

% Purity

= 6.21 g in 500 mL (1)

Mass NaCl in 20 mL = $\frac{6.21 \times 20}{500}$ = 0.248 g (1)

Moles NaCl = $\frac{0.248}{58.44}$ = 4.243×10^{-3}

22.99
35.45
58.44

Total N° moles Cl^- = $2.40 \times 10^{-2} + 4.243 \times 10^{-3}$ (1)

= 2.824×10^{-2}

Total Volume = (120 + 20) mL (1) $n = \frac{c \times v}{1000}$

$c = \frac{2.824 \times 10^{-2} \times 1000}{140}$ = 2.02×10^{-1}

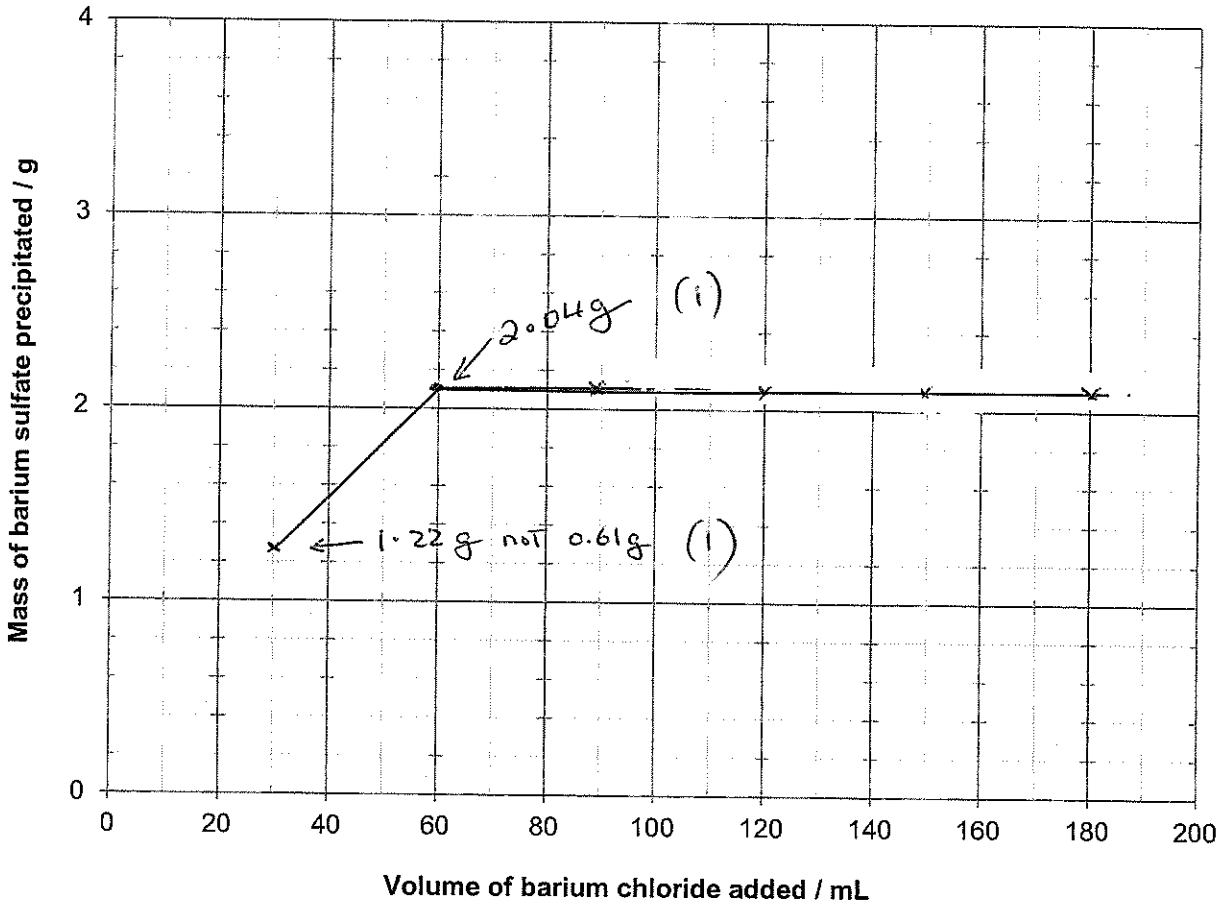
$[Cl^-]$ = 0.202 mol L^{-1} (1)

(g) Another student carried out a similar analysis, but neglected to rinse the precipitates before drying them. Explain what effect this would have on the student's calculated value of the percentage purity. (3 marks)

- Mass precipitates larger
- Mass $MgSO_4$ higher
- Calculated percentage purity higher

The analysis was repeated using six further 20 mL aliquots of the impure magnesium sulfate solution and the same volumes of barium chloride. However, the concentration of the barium chloride solution used was 0.200 mol L^{-1}.

(h) Using the axes below, draw the graph of the expected results when plotting the mass of barium sulfate precipitated against volume of barium chloride added. (2 marks)



No Contamination

Moles $BaCl_2$ = 1.20×10^{-2}

Moles Cl^- = 2.40×10^{-2}

Total volume = (120 + 20)mL

$n = \frac{c \times v}{1000}$

$$\text{Conc of } Cl^- = \frac{2.40 \times 10^{-2} \times 1000}{140}$$

$$= 0.171 \text{ mol } L^{-1}$$

Question 37 **(11 marks)**

The functional groups present in organic molecules can, by definition, have a strong influence on the chemical properties of those molecules, but they can also play a role in determining the physical properties of substances.

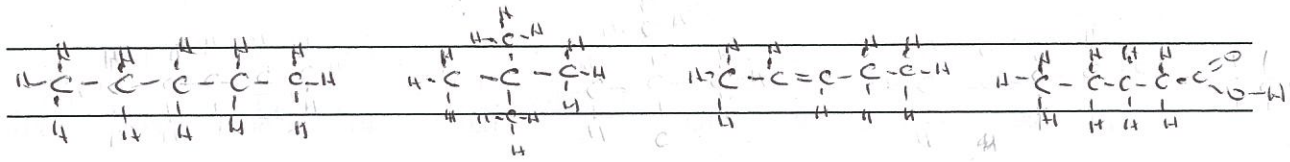
The table below outlines some of the physical properties of four organic substances; pentane, 2,2-dimethylpropane, 2-pentene, and propanoic acid.

	boiling point (°C)	solubility in water	solubility in ethanol
pentane	36.1	low	high
2,2-dimethylpropane	9.5	low	high
pent-2-ene	37.0	low	high
propanoic acid	144.1	high	high

With clear reference to the structure and bonding present, compare and contrast the **physical properties** of the four substances. You should focus on the physical data provided in the table, and use your knowledge of the functional group chemistry of the compounds.

Your answer should include clearly labelled diagrams where appropriate. How many

Marks are awarded for clarity of communication. Answers may be written as a series of dot points and diagrams may be used, but care should be taken to ensure that there is a logical sequence of ideas and that any abbreviations or diagrams are explained clearly.



Boiling Point -3

- Pentane, 2,2-dimethylpropane, pent-2-ene all have dispersion forces as intermolecular forces
- Propanoic acid has H-bonding and dipole-dipole interaction as main intermolecular forces (+ disp)
- H-bonding + Dipole-dipole much stronger than dispersion forces
- Propanoic acid has highest bp
- 2-2 dimethyl propane has lowest bp because of its shape/branching preventing molecules getting close together
- strength of dispersion forces related to distance

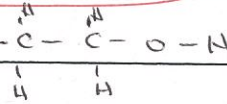
3

Solubility in water

- water has strong H-bonding between molecules
- pentane 2-2 dimethylpropane and pent-2ene have weak dispersion forces between molecules
- These species are not able to disrupt H-bonding between water molecules and form new intermolecular forces of attraction
- propanoic acid has intermolecular forces similar in nature and strength and is able to disrupt H-bonds between water molecules and form new intermolecular bonds

Solubility in ethanol

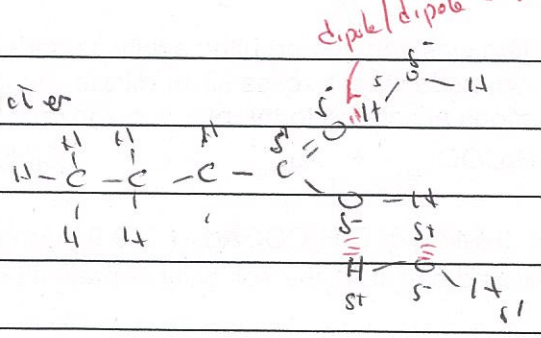
3

- Ethanol  - non polar tail + polar head
- The pentane --- pent-2-ene are able to form new intermolecular bonds using dispersion forces between their molecules and the hydrocarbon end of the ethanol
- This enables them to dissolve in ethanol

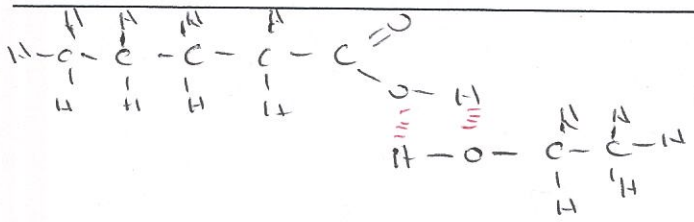
- Propanoic acid has the capacity to have dipole-dipole interaction and H-bonding between it and the ethanol molecule

AT Least

- Diagrams Solubility water



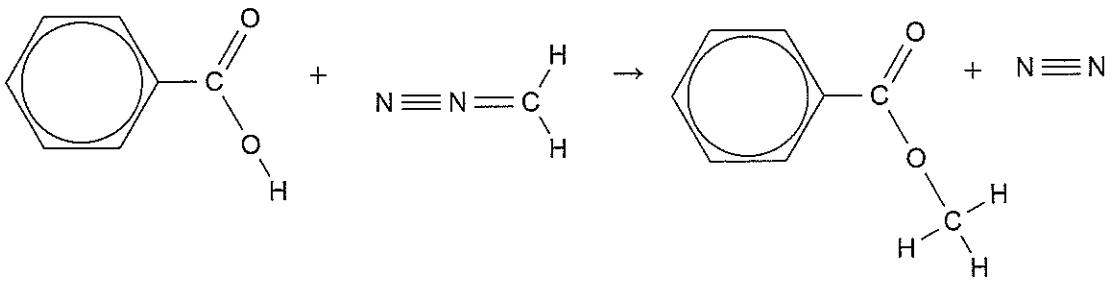
Solubility in Ethanol



+2

Question 38 **(17 marks)**

Methyl benzoate (136.15 g mol^{-1}) is a colourless pleasant smelling liquid that is poorly soluble in water, but miscible with organic solvents. Methyl benzoate is used in perfumery and also finds use as a solvent and as a pesticide used to attract insects such as orchid bees.
Methyl benzoate can be produced by the reaction between benzoic acid and diazomethane according to the reaction shown below.



When 4.598 g of benzoic acid (122.12 g mol^{-1}) was mixed with an excess of diazomethane the nitrogen that was produced in the reaction recovered. The volume of nitrogen recovered was 829 mL at 105 kPa when the temperature was 19.2 °C.

Use the information to determine:

(a) The moles of nitrogen actually produced

(1marks)

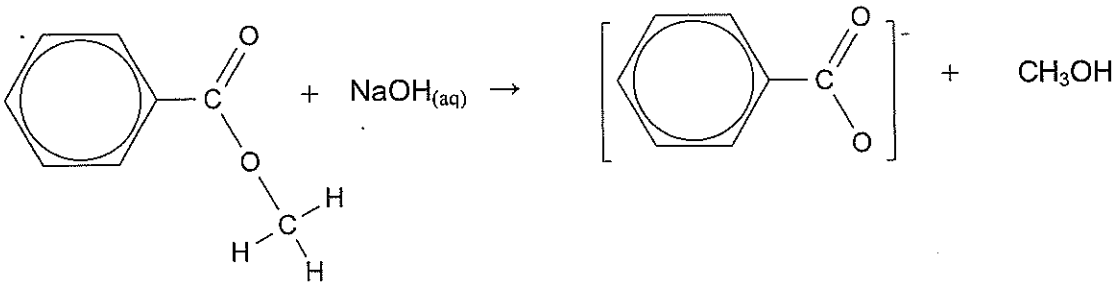
(b) The percentage yield of the reaction

(4 marks)

(c) The mass of methyl benzoate that was produced.

(2 marks)

In order to determine the solubility of methyl benzoate in ppm in water a 500 g sample of a saturated solution was heated with sodium hydroxide to produce the methyl benzoate ion and methanol. The equation for the reaction is given below



The solution was cooled and nitric acid was added to neutralise the solution, by removing any excess hydroxide ions. Excess silver nitrate was added to precipitate out all of the methyl benzoate ions according to the reaction shown below.

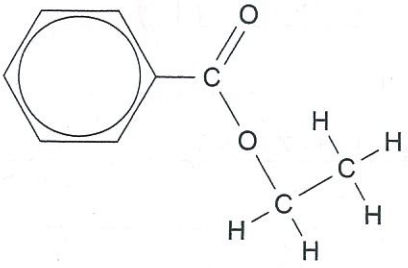
$$C_6H_5COO^-_{(aq)} + Ag^+_{(aq)} \rightarrow C_6H_5COOAg_{(s)}$$

(d) If 0.147 g of $C_6H_5COOAg_{(s)}$ (229.01 g mol^{-}) was recovered after the solution was filtered calculate the solubility of methyl benzoate in ppm.

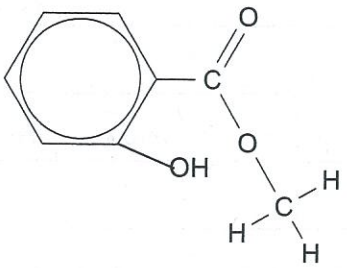
(5 marks)

Another aromatic ester ethyl benzoate has an aroma similar to methyl salicylate commonly known as oil of wintergreen. The structures of the two esters are shown below.

ethyl benzoate
$C_9H_{10}O_2$



methyl salicylate
$C_8H_8O_3$



A chemist found a bottle that contained an oily liquid that had an odour that smelt similar to that of oil of wintergreen. The chemist concluded that the sample could either have been ethyl benzoate or methyl salicylate.
The respective formula masses for ethyl benzoate and methyl salicylate are 150.17 g mol^{-1} and 152.15 g mol^{-1}.

(e) When a 02493 g sample of the unknown ester was burnt in excess oxygen 0.1181 g of water was recovered.
Use this information to determine the identity of the ester.

(5 marks)

$T = (273.15 + 19.2)$

(a) $PV = nRT$ $= 292.35$

$105 \times 0.829 = n \times 8.314 \times 292.35$ $V = 0.829L$

$n = 3.581 \times 10^{-2}$ moles (1) [1]

(b) Moles of benzoic acid $= \frac{4.598}{122.12} = 3.765 \times 10^{-2}$ (1)

1 mole benzoic acid produces 1 mole N_2 (1)

% yield $= \frac{3.581 \times 10^{-2}}{3.765 \times 10^{-2}} \times \frac{100}{1} = 95.1\%$ (1)

(+2) [4]

Moles of methyl benzoate $= 3.581 \times 10^{-2}$ (1)

(c) mass methyl benzoate $= 3.581 \times 10^{-2} \times 136.15$

$= 4.88$ g (1) [2]

END OF QUESTIONS

(d) Moles of $C_6H_5COOAg = \frac{0.147}{229.01}$

$= 6.419 \times 10^{-4}$ (1)

Moles benzoate ion = moles methyl benzoate in 500g

Mass methyl benzoate $= 6.419 \times 10^{-4} \times 136.15$

$= 8.739 \times 10^{-2}$ g (1)

$= 87.39$ mg (1)

Conc ppm $= \frac{\text{mass solute mg}}{\text{mass solvent in kg}}$ (1)

$= \frac{87.39}{0.5} = 175$ ppm. (1) (5)

e) 0.2493 g sample

$C_9H_{10}O_2 \rightarrow 9CO_2 + 5H_2O$

$C_8H_8O_3 \rightarrow 8CO_2 + 4H_2O$

Moles $H_2O = \frac{0.1181}{18.016} = 6.555 \times 10^{-3}$ (1)

If sample was $C_9H_{10}O_2$ moles sample $= \frac{6.555 \times 10^{-3}}{5}$

$= 1.311 \times 10^{-3}$ (1)

Spare answer page

Question number: _____

$n = \frac{\text{mass}}{FW}$

$FW = \frac{0.2493}{1.311 \times 10^{-3}}$ $= 190.1\ g$ (1)

If sample was $C_8H_8O_3$ moles $H_2O = \frac{6.777 \times 10^{-3}}{4}$

$= 1.638 \times 10^{-3}$ (1)

$FW = \frac{0.2493}{1.638 \times 10^{-3}}$ $= 152.17\ g$ (1)

∴ Sample is methyl salicylate. (5)

Spare answer page

Question number: _____

Spare answer page

Question number: _____

Spare answer page

Question number: _____