

2020

NESA Number

HIGHER SCHOOL CERTIFICATE EXAMINATION

Chemistry

General Instructions	 Reading time – 5 minutes Working time – 3 hours Write using black or blue pen Draw diagrams using pencil Calculators approved by NESA may be used Write your NESA number where required
Total marks: 100	 Section I – 20 marks (pages 2-9) Attempt Questions 1-20 Allow about 35 minutes for this section Section II – 80 marks (pages 10-27) Attempt Questions 21-37 Allow about 2 hours and 25 minutes for this section

Section I: Multiple Choice Questions (20 marks) Attempt Questions 1-20Allow about 35 minutes for this section

Use the multiple choice answer sheet for Questions 1 - 20.



1. Phosgene (COCl₂) can be prepared from a reaction between carbon monoxide and chlorine:

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)} \quad \Delta H < 0$$

Which of the following will increase the yield of phosgene at equilibrium?

- (A) Increasing the temperature of the system
- (B) Removing carbon monoxide from the system
- (C) Decreasing the volume of the system
- (D) Adding argon gas into the system to increase the pressure
- 2. Which of the following is a conjugate acid/base pair that can act as a buffer?
 - (A) HNO_3/NO_3^-
 - (B) H_3PO_4/PO_4^{3-}
 - (C) $\rm NH_4^+/NH_3$
 - (D) SO_4^{2-}/SO_3^{2-}
- 3. Consider the following organic compound where two of the carbon atoms have been labelled as C^a and C^b:

$${\rm CH}_3 \!-\! {\rm C}^{\rm a} {\rm H}_2 \!-\! {\rm C} {\rm H}_2 \!-\! {\rm C}^{\rm b} \!\equiv\! {\rm N}$$

Which row of the following table correctly shows the type of shape formed by the bonds around the C^{a} and C^{b} atoms?

	$\mathbf{C}^{\mathbf{a}}$	C^{b}	
(A)	Tetrahedral	Linear	
(B)	Trigonal planar	Linear	
(C)	Tetrahedral	Tetrahedral	
(D)	Linear	Trigonal planar	

- 4. Which of the following species is NOT amphiprotic?
 - (A) H₂O
 - (B) CH_3COO^-
 - (C) HPO_4^{2-}
 - (D) HCO_3^-
- 5. Which of the following options contains a pair of structural isomers where the boiling point of the first compound is lower than that of the second compound?
 - (A) Pentanoic acid and hexanoic acid
 - (B) Butanoic acid and ethyl ethanoate
 - (C) Propan-1-ol and propan-2-ol
 - (D) 2-methylpropane and butane

6. Consider the following reaction:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

In an experiment, 6.0 moles of N_2O_4 and 1.0 mole of NO_2 was injected into a 0.50 L container at 100°C and allowed to react until equilibrium was attained. The equilibrium constant for this reaction is 0.212 at 100°C.

Which row of the following table correctly identifies the direction in which the reaction will proceed to reach equilibrium and the reason for this shift?

	Direction favoured	Reason
(A)	Left	Q > K
(B)	Left	Q < K
(C)	Right	Q > K
(D)	Right	Q < K

7. A laboratory contains solutions of a weak monoprotic acid (HA) and a strong monoprotic acid (HB), both at the same volume and concentration.

Which of the following statements regarding these two solutions is correct?

- (A) HA has a lower pH than HB
- (B) HA has a higher hydronium ion concentration than HB
- (C) The concentration of A^- in HA is higher than the concentration of B^- in HB
- (D) Both solutions would be neutralised by the same volume of $0.10 \text{ mol } \text{L}^{-1}$ NaOH
- 8. Benzoic acid (C_6H_5COOH) is a weak monoprotic acid that can be used as a primary standard for titrations. A 0.15 mol L⁻¹ solution of benzoic acid has a pH of 2.51.

What is the pK_b of the benzoate ($C_6H_5COO^-$) ion?

- (A) 3.60
- (B) 4.19
- (C) 9.81
- (D) 10.40
- 9. A sample of magnesium hydroxide was added to $0.0500 \text{ mol L}^{-1}$ sodium hydroxide solution and only some of the magnesium hydroxide dissolved.

What is the solubility of magnesium hydroxide in this solution?

- (A) $2.24 \times 10^{-9} \text{ mol } \text{L}^{-1}$
- (B) $3.38 \times 10^{-9} \text{ mol } \text{L}^{-1}$
- (C) $4.52 \times 10^{-9} \text{ mol } \text{L}^{-1}$
- (D) $5.26 \times 10^{-9} \text{ mol } \text{L}^{-1}$

10. In a particular titration, a base from a burette was delivered into a conical flask containing an acid. The conductivity curve below was produced from monitoring the conductivity of the conical flask solution during the titration.



Which of the following titrations would produce the conductivity curve above?

- (A) HCl + KOH
- (B) $HCl + NH_3$
- (C) $CH_3COOH + KOH$
- (D) $CH_3COOH + NH_3$
- 11. Consider the following organic compound:



What is the systematic name of this compound?

- (A) 1-bromo-5,5-diffuoro-3-methylpentan-2-amine
- (B) 1-bromo-5,5-difluoro-3-methylpentan-2-amide
- (C) 5-bromo-1,1-difluoro-3-methylpentan-4-amine
- (D) 5-bromo-1,1-difluoro-3-methylpentan-4-amide

12. Consider the following titration curves that are produced from two different titrations:



Which row of the following table contains an indicator that would be suitable for BOTH titrations?

	Indicator	pH range	Colour (Low pH)	Colour (High pH)
(A)	Congo red	3.0 - 5.0	Blue	Red
(B)	Methyl red	4.4 - 6.2	Red	Yellow
(C)	Thymol blue	8.0 - 9.6	Yellow	Blue
(D)	Indigo carmine	11.4 - 13.0	Yellow	Blue

13. In a calorimetry experiment, but an-1-ol was completely combusted to heat 150.0 mL of water from 20.0°C to 70.0°C. The molar heat of combustion of but an-1-ol is 2670 kJ mol⁻¹.

If only 65.0% of the heat released by the combustion was absorbed by the water, what volume of carbon dioxide gas was produced at 25° C and 100 kPa?

- (A) 1.06 L
- (B) 1.16 L
- (C) 1.64 L
- (D) 1.79 L
- 14. A 25.0 mL solution of 0.15 mol L^{-1} hydrochloric acid was mixed with a 20.0 mL solution of 0.20 mol L^{-1} potassium hydroxide.

What is the pH of the resultant solution?

- (A) 2.26
- (B) 3.60
- (C) 10.40
- (D) 11.74

15. Consider the following series of reactions where \mathbf{A} to \mathbf{D} are different organic compounds.



The infrared (IR) spectrum of compound \mathbf{D} is given below.



Based on the above information, the identity of compound \mathbf{C} is:

- (A) 1-bromopropane
- (B) <mark>2-bromopropane</mark>
- (C) 1-bromopropan-1-ol
- (D) 2-bromopropan-2-ol
- 16. A white solid was added to nitric acid and bubbling was observed. When the resultant mixture was tested with a flame test, a brick red flame colour was observed.

What is the most likely identity of the white solid?

- (A) Barium sulfate
- (B) Barium carbonate
- (C) Calcium carbonate
- (D) Calcium sulfate

17. In an experiment, 0.570 g of an unknown sample was analysed for its phosphate content. Excess calcium nitrate was added to an aqueous solution of the unknown sample to precipitate out the phosphate ions. The precipitate that formed had a mass of 0.125 g.

What is the theoretical percentage by mass of phosphate in the unknown sample?

- (A) 6.75%
- (B) **13.4%**
- (C) 15.4%
- (D) 30.8%
- 18. Which of the following substances is a liquid that readily decolourises bromine water under standard conditions?
 - (A) Ethene
 - (B) Cyclohexane
 - (C) Benzene
 - (D) Hex-2-ene
- 19. The ultraviolet-visible (UV-vis) spectrum below shows how the absorbance varies over a range of wavelengths for a solution containing a particular inorganic compound.



In an experiment to determine the concentration of the inorganic compound in this solution, light from a lamp was passed through the solution to a detector and the following intensities of light were then measured:

- I(x nm) = Intensity of light at a wavelength of x nm from the lamp
- $I_{d}(x \text{ nm}) =$ Intensity of light at a wavelength of x nm at the detector

Which of the following pairs of intensities should be used to determine the concentration of the inorganic compound in this solution using UV-vis spectroscopy?

- (A) $I(510~{\rm nm})$ and $I_{\rm d}(510~{\rm nm})$
- (B) I(625 nm) and $I_{d}(625 \text{ nm})$
- (C) I(510 nm) and $I_{d}(625 \text{ nm})$
- (D) $I_{\rm d}(510 \text{ nm})$ and $I_{\rm d}(625 \text{ nm})$

20. A section of a polymer containing three monomer units is shown below.



When this polymer is formed from its monomer, water is produced as a by-product.

The monomer used to directly produce the polymer above was analysed with nuclear magnetic resonance (NMR) spectroscopy.

Excluding the signal given by the tetramethylsilane (TMS) reference, the monomer would give:

- (A) 1 signal on a 1 H NMR spectrum and 3 signals on a 13 C NMR spectrum
- (B) 3 signals on a ¹H NMR spectrum and 3 signals on a ¹³C NMR spectrum
- (C) 3 signals on a ¹H NMR spectrum and 4 signals on a ¹³C NMR spectrum \sim
- (D) 4 signals on a 1 H NMR spectrum and 4 signals on a 13 C NMR spectrum

Section II: Short Answer Questions (80 marks)

Question 21 (4 marks)

Hydrochloric acid and acetic acid are both common acids with very different properties.

(a) Calculate the pH of a 0.10 mol L^{-1} acetic acid solution given that the p K_a of acetic acid is 4.76.

(b) Account for the differences in pH between an acetic acid solution and a hydrochloric acid 1 solution of the same concentration.

HCl is a strong acid that completely ionises in water to produce H^+ ions, whereas acetic acid is a weak acid that only partially ionises in water to produce H^+ ions. Therefore, HCl will have a higher $[H^+]$ and thus a lower pH compared to acetic acid. 1 mark – Accounts for why HCl has a lower pH than acetic acid in terms of acid

Question 22 (3 marks)

strength and $[H^+]$

Addition polymers such as polyethylene are versatile materials that are used for many household **3** applications. Two such uses of polyethylene are shown in the photos below.



Explain, in terms of its structure and properties, why polyethylene can be used for the two applications shown above.

Polyethylene can be produced in two forms, LDPE and HDPE.

LDPE is an amorphous polymer with a high degree of chain branching that prevents the polymer chains from packing closely together, so the dispersion forces between the polymer chains will be quite weak. This makes LDPE a soft and flexible polymer which can be used as glad wrap.

HDPE is a crystalline polymer with very minimal chain branching within its structure, so the polymer chains can pack closely together, resulting in stronger dispersion forces. This makes HDPE a very hard and rigid polymer which can be used as buckets.

3 marks – Explains the above uses of polyethylene in terms of its molecular structure, dispersion forces and physical properties (1 mark each)

Question 23 (3 marks)

When sodium acetate is dissolved in water, the resultant solution has a pH greater than 7.

Explain why the Brönsted-Lowry theory can account for this result whereas the Arrhenius theory cannot. Include a relevant chemical equation in your answer.

Arrhenius defined acids as substances that ionise to produce H^+ ions and bases as substances that produce OH^- ions in aqueous solution. When NaCH₃COO is dissolved in water, it dissociates into Na⁺ and CH₃COO⁻ ions. Since NaCH₃COO contains no OH⁻ ions that can be released when it is dissolved in water, Arrhenius would not have classified it as a base, and thus he cannot account for this result.

Bronsted/Löwry defined acids as proton donors and bases as proton acceptors. In this case, the Na⁺ ion has no tendency to react with water, but the CH_3COO^- ion is the weak conjugate base of a weak acid (CH_3COOH), and thus it can accept a proton from water:

 $CH_3COO^-_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$

The OH^- ions produced from this hydrolysis reaction causes the solution to have a pH > 7, and thus the Bronsted-Löwry theory can account for this result.

- 2 marks Explains how a solution of $NaCH_3COO$ would be viewed differently by both theories
- 1 mark Provides a chemical equation for the hydrolysis of the CH₃COO⁻ ion

Note: Students must link the OH⁻ ions produced from the hydrolysis reaction to the pH of the solution.

Question 24 (7 marks)

2.69 moles of hydrogen sulfide gas was mixed with 0.300 moles of sulfur dioxide gas in a 3.50 L container and allowed to react at 100° C according to the following equation:

$$2\,H_2S_{(g)} + SO_{2(g)} \rightleftharpoons 3\,S_{(s)} + 2\,H_2O_{(g)}$$

At equilibrium, the concentration of water vapour was found to be $0.120 \text{ mol } \text{L}^{-1}$.

(a) Using the information above, calculate the equilibrium constant for this reaction at 100°C.

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(b) Outline how the equilibrium system and the equilibrium constant will be affected if the volume of the container is increased.

Increasing the volume of the system is equivalent to decreasing the pressure by Boyle's law. Le Chatelier's principle predicts that the system will counteract this change by shifting towards the left, where there are more moles of gas in an attempt to increase the gas pressure. However, the value of K will be unaffected because temperature is the only factor that can affect K.

- 1 mark Outlines how the equilibrium behaves when volume is increased, using Le Chatelier's principle
- 1 mark Outlines that K will be unaffected by the volume change

(c) The equilibrium constant for this reaction decreases when the system is heated.

Predict whether the reaction is endothermic or exothermic and justify your answer.

At higher temperatures, Le Chatelier's principle predicts that the equilibrium will favour the heat absorbing endothermic reaction in an attempt to decrease the temperature. Since K decreases when the system is heated, this indicates the equilibrium shifts left (more reactants and less products at equilibrium) at higher temperatures. Therefore, the reverse reaction is endothermic and so the forward reaction is exothermic.

1 mark – Identifies that the reaction is exothermic

1 mark - Justifies why with reference to the K values and Le Chatelier's principle



Question 25 (4 marks)

The graph below shows how the boiling points of two different homologous series varies with molecular mass.



(a) Explain the trends shown in the graph above.

The alkanes have low BPs because they are non-polar molecules that are held together by weak dispersion forces which requires little energy to overcome. Alcohols, however, have higher BPs since they are polar molecules due to their polar hydroxyl (-OH)group, and are capable of forming strong hydrogen bonds which requires significant energy to overcome.

It can also be seen that when molecular mass increases, the BP of substances in each homologous series increases. This occurs because larger molecules have stronger dispersion forces, since they contain more electrons and there is a higher probability of temporary dipoles forming.

- 1 mark Explains why the BPs of the alkanes are the low with reference to polarity and dispersion forces
- $1~{\rm mark}$ Explains why the alcohols have higher BPs with reference to polarity and hydrogen bonds
- $1~{\rm mark}-{\rm Explains}$ why the BP increases with molecular mass in each series with reference to dispersion forces
- (b) On the graph above, draw a line to roughly show how the boiling points of carboxylic acids 1 will compare with the alcohols and justify your answer.

Carboxylic acids have even higher BPs than the alcohols because they contain a polar hydroxyl (-OH) group and an additional polar carbonyl (C=O) group that makes them capable of more extensive hydrogen bonding.

 $1~{\rm mark}$ – Draws a line showing that carboxylic acids have higher BPs than alcohols and justifies why

Question 26 (4 marks)

An aqueous solution is known to contain a red molecule (HInd) and a blue anion (Ind⁻).

(a) Explain, in terms of Le Chatelier's principle, why this solution can be used as an acid-base 3 indicator. Include a relevant chemical equation in your answer.

The following equilibrium will be present in this solution: $HInd_{(aq)} + H_2O_{(l)} \rightleftharpoons Ind_{(aq)}^- + H_3O_{(aq)}^+$

When an acid is added to this solution, $[H_3O^+]$ will increase. Le Chatelier's principle predicts that the equilibrium will shift left to decrease $[H_3O^+]$. This causes more red HInd molecules to form, causing the solution to turn red.

When a base is added to this solution, $[OH^-]$ will increase. The added OH^- ions will react with the H_3O^+ ions to form water, effectively removing some H_3O^+ from the system. Le Chatelier's principle predicts that the equilibrium will shift right to increase $[H_3O^+]$. This causes more blue Ind^- ions to form, causing the solution to turn blue.

Therefore, this solution can be used as an indicator because it can take on two distinctly different colours when it is mixed with an acid and a base.

- 2 marks Explains why the solution can be used as an indicator with reference to Le Chatelier's principle and its behaviour when mixed with an acid and a base (1 mark each)
- 1 mark Includes a relevant chemical equation
- (b) A dilute aqueous solution of acetic acid causes dry, blue litmus paper to turn red. However, when glacial (pure) acetic acid is added to dry, blue litmus paper, no colour change is observed.

Propose a reason for this observation.

In an aqueous solution of acetic acid, some acetic acid molecules have been ionised in water to form H_3O^+ ions that can change the colour of blue litmus. However, in glacial acetic acid, there is no water present so the acetic acid molecules are unionised; there are no H_3O^+ ions present that can change the colour of blue litmus.

1 mark – Proposes a reason for why glacial acetic acid does not cause a colour change in dry, blue litmus paper

Question 27 (8 marks)

In an organic chemistry laboratory, a student was asked to synthesise ethyl propanoate.

(a) Describe a reaction pathway that can be used to theoretically synthesise ethyl propanoate using ethene and 1-chloropropane as the ONLY starting organic reagents. Include relevant chemical equations using structural formulae in your answer.

Ethene can be hydrated with water using a dilute H_2SO_4 catalyst to form ethanol.



1-chloropropane can undergo a nucleophilic substitution reaction with NaOH to form propan-1-ol.

$$\begin{array}{ccccccccccc} H & H & H & H & H & H & H \\ | & | & | & | \\ H - C - C - C - C - C - C + OH^{-} & \longrightarrow & H - C - C - C - O - H + CI^{-} \\ | & | & | & | \\ H & H & H & & H & H \end{array}$$

Propan-1-ol can then be oxidised with acidified KMnO_4 to produce propanal which gets further oxidisied to propanoic acid as the final product.

The ethanol and propanoic acid produced from the steps above can then be heated together under reflux with a concentrated H_2SO_4 catalyst to produce ethyl propanoate via an esterification reaction.

structural formulae and identifies all reagents required for the synthesis (1 mark each)

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Esterification reactions are slow, so the reaction mixture is heated to increase the reaction rate. However, since the reactants and ester product are volatile, they will vaporise when heated. Refluxing is useful here as it prevents the loss of these volatile substances. Any substances that vaporise from the heat are condensed and allowed to run back into the reaction vessel. Using a reflux condenser that is open at the top is also much safer than a closed system prone to dangerous gas pressure build-up.

2 marks – Draws a labelled diagram of a reflux apparatus

2 marks - Explains why refluxing is used for the production of esters

Question 28 (3 marks)

A student was asked to standardise a solution of sodium hydroxide by titrating it against a benzoic acid primary standard solution. The procedure used by the student is outlined below.

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- 1. A conical flask was rinsed with distilled water only.
- 2. A 25.0 mL pipette was rinsed with distilled water and then with the sodium hydroxide solution.
- 3. A pipette filler was used to fill the pipette with the sodium hydroxide solution to the level shown in the diagram below.



- 4. The sodium hydroxide solution in the pipette was transferred to the conical flask. Three drops of an appropriate indicator was added to the conical flask.
- 5. A burette was rinsed with distilled water only and then filled with the benzoic acid solution. The student then carried out the remainder of the titration appropriately.

The student did not follow acceptable procedures for this titration.

Explain the effect of the mistakes made by the student on the calculation of the concentration of the sodium hydroxide solution.

In step 3, the pipette should have been filled until the base of the meniscus was on the engraved mark. By going over the mark, more moles of NaOH would have been transferred into the conical flask. In step 5, the burette should have also been rinsed with the benzoic acid solution. Since the burette was left with wet with water, the benzoic acid solution would be more dilute than expected.

During the titration, a larger volume of benzoic acid would be needed from the burette to reach the end point than expected, since the benzoic acid has been diluted, and there are more moles of NaOH in the conical flask that needs to be neutralised. This would lead to an overestimation of the moles of benzoic acid and NaOH titrated, and thus an overestimation of the NaOH concentration.

2 marks – Identifies the two mistakes made by the student and explains the effect of each mistake in terms of the moles of NaOH and the concentration of benzoic acid (1 mark each)

 $1~{\rm mark}\,-\,{\rm Explains}$ that the calculated concentration of NaOH will be overestimated

Question 29 (7 marks)

The production of new materials is driven by the recognition that traditional products may no longer be satisfactory in some aspect of their use or supply.

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Evaluate the potential of ethanol as an alternative fuel to petrol (octane) with reference to the current progress that has been made. Include relevant chemical equations in your answer.

Unlike octane, ethanol is a renewable fuel since it can be produced by fermentation of sugars from crops like sugar cane.

$$C_6H_{12}O_{6(aq)} \xrightarrow{\text{yeast}} 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$$

Ethanol has long been touted as a renewable alternative car fuel that is both 'cleaner' and more 'greenhouse neutral' than traditional petrol fuels derived from non-renewable fossil fuels. Indeed, complete combustion of ethanol requires less moles of oxygen compared to octane, so it is less likely that toxic pollutants like CO and soot will be produced, and the use of ethanol releases less CO_2 overall, even taking into account energy needed for growing and harvesting crops, fermenting the sugars and distilling the crude ethanol product.

$$\begin{split} & C_2H_5OH_{(l)} + 3\,O_{2(g)} \rightarrow 2\,CO_{2(g)} + 3\,H_2O_{(g)} \\ & C_8H_{18(l)} + \frac{25}{2}\,O_{2(g)} \rightarrow 8\,CO_{2(g)} + 9\,H_2O_{(g)} \end{split}$$

Yet, the issue of supplying sufficient ethanol for fuel has proved difficult to solve, since fermentable crops need time to grow and large tracts of arable land are required that could otherwise be used for food production. The overuse of fertile land may also lead to problems such as erosion and salinity. The combustion of ethanol also releases less energy both per gram and per mole compared to octane, so ethanol has a lower fuel economy and it provides less power. Moreover, expensive engine modifications are required when using petrol blends with >15-20% ethanol. Although E10 (10% ethanol in petrol) is now widely available, public uptake remains limited. There is concern that car manufacturers may void warranties if E10 is used, and some public suspicion about the actual composition. The lack of infrastructure and expense of continuing to subsidise the industry makes it difficult for governments and consumers in Australia to adopt ethanol blends higher than E10.

As such, although ethanol holds great potential as an alternative fuel, its use is severely limited by its disadvantages, in particular its cost. The process of translating innovations into practice has often proved more difficult than expected and much more research and development will be needed before ethanol can be used on a larger scale.

- $5~{\rm marks}$ Explains the advantages and disadvantages of ethanol as a fuel with reference to the progress that has been made
- 1 mark Provides at least TWO relevant chemical equations
- 1 mark Makes a clear evaluation on the potential of ethanol as an alternative fuel

Question 30 (4 marks)

A 25.0 mL solution of $0.0100 \text{ mol } \text{L}^{-1}$ silver nitrate is mixed with 25.0 mL of $0.0150 \text{ mol } \text{L}^{-1}$ potassium sulfate solution at 25°C.

(a) Using relevant calculations, predict if silver sulfate will form as a precipitate under these 3 conditions.

$$\begin{split} 2\,\mathrm{AgNO}_{3(\mathrm{aq})} + \mathrm{K}_2\mathrm{SO}_{4(\mathrm{aq})} &\to \mathrm{Ag}_2\mathrm{SO}_{4(\mathrm{s})} + 2\,\mathrm{KNO}_{3(\mathrm{aq})} \\ \mathrm{Ag}_2\mathrm{SO}_{4(\mathrm{s})} &\rightleftharpoons 2\,\mathrm{Ag}^+_{(\mathrm{aq})} + \mathrm{SO}_4^{2^-}_{(\mathrm{aq})} \\ \mathrm{K}_{\mathrm{sp}} &= 1.20 \times 10^{-5} \end{split}$$

$$\begin{split} n(\mathrm{Ag}^+)_{\mathrm{i}} &= n(\mathrm{AgNO}_3) \\ &= 0.0100 \ \mathrm{mol} \, \mathrm{L}^{-1} \times 0.0250 \ \mathrm{L} \\ &= 2.50 \times 10^{-4} \ \mathrm{mol} \\ [\mathrm{Ag}^+]_{\mathrm{i}} &= \frac{2.50 \times 10^{-4} \ \mathrm{mol}}{(0.0250 + 0.0250) \ \mathrm{L}} \\ &= 5.00 \times 10^{-3} \ \mathrm{mol} \, \mathrm{L}^{-1} \\ n(\mathrm{SO}_4^{2^-})_{\mathrm{i}} &= n(\mathrm{K}_2\mathrm{SO}_4) \\ &= 0.0150 \ \mathrm{mol} \, \mathrm{L}^{-1} \times 0.0250 \ \mathrm{L} \\ &= 3.75 \times 10^{-4} \ \mathrm{mol} \\ [\mathrm{SO}_4^{2^-}]_{\mathrm{i}} &= \frac{3.75 \times 10^{-4} \ \mathrm{mol}}{(0.0250 + 0.0250) \ \mathrm{L}} \\ &= 7.50 \times 10^{-3} \ \mathrm{mol} \, \mathrm{L}^{-1} \\ \end{split}$$

$$\begin{split} Q_{\mathrm{sp}} &= [\mathrm{Ag}^+]^2 [\mathrm{SO}_4^{2^-}] \\ &= (5.00 \times 10^{-3})^2 \times 7.50 \times 10^{-3} \\ &= 1.88 \times 10^{-7} \\ &< K_{\mathrm{sp}} \end{split}$$

: The equilibrium reaction will NOT proceed from right to left so Ag_2SO_4 will NOT form as a precipitate.

- 1 mark Calculates the correct initial concentrations of Ag^+ and SO_4^{2-}
- $1 \text{ mark} \text{Calculates the correct value of } Q_{sp}$
- 1 mark Predicts that a precipitate will NOT form under these conditions



(b) Draw a diagram to show the interactions between water molecules and the ions present in a potassium sulfate solution.

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Question 31 (5 marks)

Aspirin tablets are often used for pain relief. A chemist performed an investigation on a tablet to determine the proportion of aspirin $(C_9H_8O_4)$ in it.

The chemist crushed up a 1.95 g tablet and dissolved it in 250.0 mL of 0.175 mol L^{-1} sodium hydroxide solution. All of the aspirin in the tablet was neutralised according to the following equation:

$$C_9H_8O_{4(s)} + NaOH_{(aq)} \rightarrow NaC_9H_7O_{4(aq)} + H_2O_{(l)}$$

Four 25.0 mL aliquots of the resultant solution were then transferred to separate conical flasks and, in each case, the excess sodium hydroxide was titrated against a $0.100 \text{ mol } \text{L}^{-1}$ oxalic acid dihydrate primary standard solution. The results are given in the table below.

Titration	Titre volume (mL)	
1	17.20	
2	16.80	
3	16.75	
4	16.85	

(a) Given that oxalic acid dihydrate is a diprotic acid, calculate the moles of leftover sodium 2 hydroxide after the reaction with the tablet.

Oxalic acid dihydrate is a diprotic acid, so we can denote it as H_2X . $H_2X_{(aq)} + 2 \operatorname{NaOH}_{(aq)} \rightarrow \operatorname{Na}_2X_{(aq)} + 2 \operatorname{H}_2O_{(l)}$ $V(H_2X) = \frac{(0.01680 + 0.01675 + 0.01685) \text{ L}}{3}$ = 0.01680 L $n(H_2X) = 0.100 \text{ mol } \text{L}^{-1} \times 0.01680 \text{ L}$ $= 1.68 \times 10^{-3} \text{ mol}$ $n(\operatorname{NaOH}) = 2 \times 1.68 \times 10^{-3} \text{ mol}$ $= 3.36 \times 10^{-3} \text{ mol}$

These moles came from a 25.0 mL aliquot. Therefore, the moles of leftover NaOH in the original 250.0 mL solution is given by:

$$n$$
(NaOH) leftover = $10 \times 3.36 \times 10^{-3}$ mol
= 0.0336 mol

1 mark – Calculates the correct moles of oxalic acid

 $1~{\rm mark}\,-\,{\rm Calculates}$ the correct moles of leftover NaOH

(b) Calculate the percentage by mass of aspirin in the tablet that was analysed.

$$\begin{split} n(\mathrm{NaOH}) & \mathrm{added} = 0.175 \ \mathrm{mol} \ \mathrm{L}^{-1} \times 0.2500 \ \mathrm{L} \\ &= 0.0438 \ \mathrm{mol} \\ n(\mathrm{NaOH}) \ \mathrm{reacted} = n(\mathrm{NaOH}) \ \mathrm{added} - n(\mathrm{NaOH}) \ \mathrm{leftover} \\ &= 0.0438 \ \mathrm{mol} - 0.0336 \ \mathrm{mol} \\ &= 0.0102 \ \mathrm{mol} \\ n(\mathrm{C}_9\mathrm{H}_8\mathrm{O}_4) = 0.0102 \ \mathrm{mol} \\ n(\mathrm{C}_9\mathrm{H}_8\mathrm{O}_4) = 0.0102 \ \mathrm{mol} \times (9(12.01) + 8(1.008) + 4(16.00)) \ \mathrm{g} \ \mathrm{mol}^{-1} \\ &= 1.83 \ \mathrm{g} \\ \% \mathrm{C}_9\mathrm{H}_8\mathrm{O}_4 = \frac{1.83 \ \mathrm{g}}{1.95 \ \mathrm{g}} \times 100\% \\ &= 93.8\% \end{split}$$
 $1 \ \mathrm{mark} - \ \mathrm{Calculates} \ \mathrm{the \ correct} \ \mathrm{moles \ of \ NaOH} \ \mathrm{added} \\ 1 \ \mathrm{mark} - \ \mathrm{Calculates} \ \mathrm{the \ correct} \ \mathrm{percentage} \ \mathrm{by} \ \mathrm{mass} \ \mathrm{of} \ \mathrm{aspirin} \ \mathrm{in \ the \ sample \ tablet} \ \mathrm{to} \\ 3 \ \mathrm{significant \ figures} \end{split}$

Question 32 (3 marks)

Describe the molecular structure of soap and explain how soap acts as a cleaning agent.

Soap contains a long non-polar hydrocarbon tail and a negatively charged carboxylate polar head. When soap is added to water and oil, the hydrophobic tail is embedded in the oil via dispersion forces, while the hydrophilic head interacts with water through hydrogen bonds (or more strictly speaking, ion-dipole forces). With agitation, the oil particles are lifted off the surface being cleaned and micelles are formed.



The micelles are stabilised due to the repulsion between the negative polar heads and thus the oil particles cannot coalesce. This forms a stable soapy emulsion of water and oil that can washed away, leaving the surface clean.

1 mark – Describes the molecular structure of soap

 $2~{\rm marks}$ $-~{\rm Explains}$ how so ap acts as a cleaning agent by forming a stable emulsion through micelles

Question 33 (3 marks)

The diagram below shows a schematic diagram of a mass spectrometer.



An analytical chemist analysed a sample of ethanol using mass spectrometry.

(a) Describe how ethanol molecules can be converted into different ions in the ionisation **2** chamber.

When a vaporised sample of ethanol enters the ionisation chamber, it is bombarded with high energy electrons from a heated filament. This causes a radical cation (the molecular ion) to be produced by electron impact.

 $C_2H_5OH_{(g)} + e^- \rightarrow C_2H_5OH^{\bullet+}_{(g)} + 2e^-$

The molecular ion formed from electron impact has a very high energy and is unstable, so it undergoes fragmentation to form smaller ions with lower m/z ratios.

2 marks - Describes how ions can be formed by electron impact and fragmentation (1 mark each)

(b) Identify the component of the spectrometer labelled as A on the diagram and outline its **1** role.

A is a magnet that produces a magnetic field to deflect the ions into a circular path. This allows the ions be to separated based on their m/z ratios by varying the magnetic field strength.

 $1~{\rm mark}$ – Identifies that A is a magnet and outlines that the magnet can be used to deflect and/or separate the ions

Question 34 (5 marks)

A beaker is known to contain at least one of the following solutions:

- Copper(II) nitrate
- Lead nitrate
- Barium nitrate
- (a) Construct a flowchart to demonstrate a series of precipitation tests that could be used to identify the solutions in the beaker. Include any expected observations in your answer.



(b) Write a net ionic equation for the reaction that may occur in the first step of your flowchart 1 in part (a).

 $Pb^{2+}_{(aq)} + 2 Cl^{-}_{(aq)} \rightarrow PbCl_{2(s)}$ 1 mark – Writes the correct net ionic equation including the solid state (c) The precipitate that may form in part (b) is commonly mistaken for silver chloride.

Outline an additional test that can be used to distinguish the precipitate in part (b) from silver chloride, along with the expected result.

AgCl will dissolve in excess ammonia solution to form a colour less complex ion, while ${\rm PbCl}_2$ will not.

1 mark – Outlines a suitable additional test and the correct expected result

Answers may also include:

• In contrast to PbCl₂, AgCl will visibly darken in the presence of UV light as it decomposes to Ag solid.

Note: The KI test cannot be used as all the Pb^{2+} ions have been precipitated, and also because PbI_2 and AgI are both yellow precipitates.

Question 35 (7 marks)

An unknown organic compound with a molecular formula of $C_4H_8O_2$ was analysed with mass spectrometry, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The following spectra were obtained from these techniques.

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Describe the information that can be obtained from each of the analytical techniques used, and analyse the spectra above to determine the structural formula of the organic compound.

Note: ¹H NMR chemical shift data has been included on your data sheet.

The MF of the compound is C₄H₈O₂. Calculating the degrees of unsaturation (on the side of your exam paper): Modified MF: C₄H₈ Alkane: C₄H₁₀

 \implies There is a deficiency of 2H which is equivalent to 1 d.u

Mass spectrometry involves ionising a vaporised substance and determining the m/z ratio of the ions produced. In this case, the molecular ion peak in the mass spectrum is at m/z = 88, so the substance has a molecular mass of 88 amu, and this is consistent with the given MF of C₄H₈O₂. The fragmentation patterns of the molecular ion can also provide some structural information.

IR spectroscopy can provide information about the functional groups present in a molecule since many functional groups have characteristic IR absorption bands. In this case, we note that:

- There is no absorption band at $\approx 3230-3550~{\rm cm^{-1}},$ indicating that there is no O–H bond present
- There is a strong absorption at $\approx 1680-1750$ cm⁻¹, indicating that a C=O group is present

¹H and ¹³C NMR spectroscopy provides a wealth of information about the hydrogen and carbon environments in a molecule respectively, and they can be used to characterise the hydrocarbon framework of a molecule. The information obtained from the ¹H NMR spectrum is summarised below.

δ (ppm)	Integration	Multiplicity (signal splitting)	$^{1}\mathrm{H}$ Neighbours $(\mathrm{n}+1 \mathrm{rule})$	Conclusion
1.2	3H	Triplet (3)	2	A typical CH_3- group with a low δ CH_3-CH_2-
2.0	ЗН	Singlet (1)	0	A moderately deshielded CH_3 - group adjacent to the C=O group that was identified in the IR spectrum O CH_3 -C-
4.1	2H	Quartet (4)	3	A deshielded $-CH_2-$ group adjacent to an O atom CH_3-CH_2-O-

The information obtained from the ¹³C NMR spectrum is summarised below.

i (ppm)	Conclusion
	A typical alkyl carbon with a low δ
12	$\mathrm{CH}_3 \!-\! \mathrm{CH}_2 \!-\!$
	A moderately deshielded carbon adjacent to the C=O group
20	$\overset{\mathrm{O}}{\overset{\parallel}{\overset{\parallel}{}_{\mathrm{H}_3-\mathrm{C}}}}$
	A deshielded carbon adjacent to an O atom
60	$-CH_2-O-$
	A C=O group in an ester
	(cannot be a carboxylic acid due to the IR spectrum)
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From the information above, the two fragments that make up the molecule are:

$$CH_3 - CH_2 - O - CH_3 - CH_2 - O - O$$

Putting these fragments together gives the following structure which is consistent with the MF and all the spectra:



- 2 marks Describes the information that can be obtained from mass spectrometry, IR spectroscopy and NMR spectroscopy
- 4 marks $-\,$ Analyses the IR, $^1{\rm H}$ NMR and $^{13}{\rm C}$ NMR spectra to identify the major structural fragments of the organic compound
- $1~{\rm mark}\,-\,{\rm Determines}$ the correct structural formula of the organic compound

Note: If the correct structural formula is provided but no description of the information provided by each technique is given, 6 marks max.

Question 36 (6 marks)

An analytical chemist wanted to analyse a polluted waterway for its mercury content using atomic absorption spectroscopy (AAS). A sample was first prepared for analysis by diluting 10.0 mL of a water sample from the polluted waterway to 100.0 mL in a volumetric flask with distilled water. Three unknown samples were prepared in this way.

Four standard solutions of mercury were then prepared and the absorbances of the standard and unknown solutions were measured relative to a blank. The results are shown in the table below.

Solution	Mercury concentration (ppm)	Absorbance
Blank	0.00	0.000
Standard A	1.00	0.170
Standard B	2.00	0.330
Standard C	3.00	0.503
Standard D	4.00	0.680
Unknown A	?	0.823
Unknown B	?	0.820
Unknown C	?	0.817

(a) Construct a calibration curve using the information given, and estimate the average 3 concentration of mercury in the polluted waterway.



$$A_{\text{avg}} = \frac{0.823 + 0.820 + 0.817}{3}$$
$$= 0.820$$

Extrapolating from the calibration curve yields:

$$[\mathrm{Hg}^{2+}]_{\mathrm{diluted}} = 4.90 \mathrm{\,ppm}$$

However, the water sample was diluted 10-fold prior to the analysis.

$$\implies [Hg^{2+}]_{undiluted} = 10 \times 4.90 \text{ ppm}$$
$$= 49.0 \text{ ppm}$$

2 marks - Constructs an appropriate calibration curve with concentration on the x-axis and absorbance on the y-axis

1 mark - Determines the correct concentration of Hg²⁺ based on the calibration curve drawn (values may vary slightly)

(b) Calculate the average mass of mercury in 500.0 mL of water from the polluted waterway 1 in grams.

$$[\mathrm{Hg}^{2+}]_{\mathrm{undiluted}} = 49.0 \mathrm{~mg~L}^{-1}$$
$$m(\mathrm{Hg}^{2+}) = 49.0 \mathrm{~mg~L}^{-1} \times 0.5000 \mathrm{~L}$$
$$= 24.5 \mathrm{~mg}$$
$$= 0.0245 \mathrm{~g}$$

1 mark - Calculates the correct mass of Hg²⁺ in grams

(c) Comment on the validity and reliability of the estimate you obtained in part (a).

The estimate is invalid as it was obtained by extrapolating from the calibration curve. This assumes that the trend of the graph will continue to be linear which may not necessarily be the case. However, the estimate is reliable because three samples were analysed and consistent absorbance values were obtained for each.

 $1~{\rm mark}$ - Comments on the validity of the estimate with reference to the calibration curve

 $1~{\rm mark}\,-\,{\rm Comments}$ on the reliability of the estimate

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Question 37 (4 marks)

In the industrial production of a chemical Z from the reactants X and Y, the equilibrium 4 reaction involved is:

$$\mathbf{X}_{(g)} + \mathbf{Y}_{(g)} \rightleftharpoons 3 \,\mathbf{Z}_{(g)} \quad \Delta H > 0$$

Analyse how the temperature and pressure of the reaction vessel could be managed to optimise the industrial production of Z in terms of the yield and reaction rate of the process.

At higher temperatures, Le Chatelier's principle predicts that the equilibrium will favour the heat absorbing endothermic forward reaction and this increases the yield of Z. High temperatures also increases the average kinetic energy of reactant particles, allowing more collisions to overcome the E_A barrier and this increases the reaction rate. Therefore, high temperatures should be used to produce a high yield of Z at a quick rate.

Le Chatelier's principle predicts that at low pressures, the equilibrium will favour the right where there are more moles of gas, and this increases the yield of Z. However, the collision theory predicts that low pressures would decrease the reaction rate as there will be less reactant particles per unit volume that can collide successfully. As such, a moderate pressure should be used to maintain a balance between yield and kinetics so that moderate yields of Z can be produced moderately quickly.

4 marks – Analyses how the temperature and pressure could be managed with respect to the yield and reaction rate, making reference to Le Chatelier's principle (2 marks each)