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NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

QUALIFY FOR THE FUTURE WORLD
KIA NOHO TAKATŪ KI TŌ ĀMUA AO!

Scholarship 2017
Chemistry

9.30 a.m. Friday 24 November 2017
Time allowed: Three hours
Total marks: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

Pull out Resource Booklet S–CHEMR from the centre of this booklet.

You should answer ALL the questions in this booklet.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–24 in the correct order and that none of these pages is blank.

You are advised to spend approximately 45 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Question	Mark
ONE	
TWO	
THREE	
FOUR	
TOTAL	/32

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QUESTION ONE

(a) When iodine and ammonia gas react, the resulting black solid, commonly known as nitrogen triiodide, actually has the formula $NI_3{\cdot}NH_3$. The structure of the solid has a chain arrangement of NI_2 units joined by an I atom: …–NI_2–I–NI_2–I–NI_2– … . The NH_3 molecules are situated between the chains.

The compound formed, $NI_3{\cdot}NH_3$, is extremely reactive due to its thermal instability. When something as light as a feather touches the black solid, purple iodine vapour, $I_2(g)$, is observed. Gaseous ammonia, $NH_3(g)$, and nitrogen gas, $N_2(g)$, are also formed.

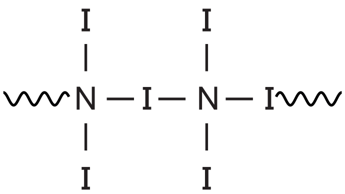
Before reaction

After reaction

(i) Draw a Lewis structure and a 3-D diagram for two repeating units of the nitrogen triiodide chain.

Include bond angles and justify your answer.

A 2-D representation for two repeating units of the chain is given below.



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(ii) Discuss the stability of $NI_3{\cdot}NH_3(s)$ using enthalpy and entropy considerations, considering the nature of the bonds broken and formed.

Table 1: Enthalpy of formation /kJ mol^{-1}

$NH_3(g)$	–46.0
$I_2(g)$	+62
$NI_3{\cdot}NH_3(s)$	+146

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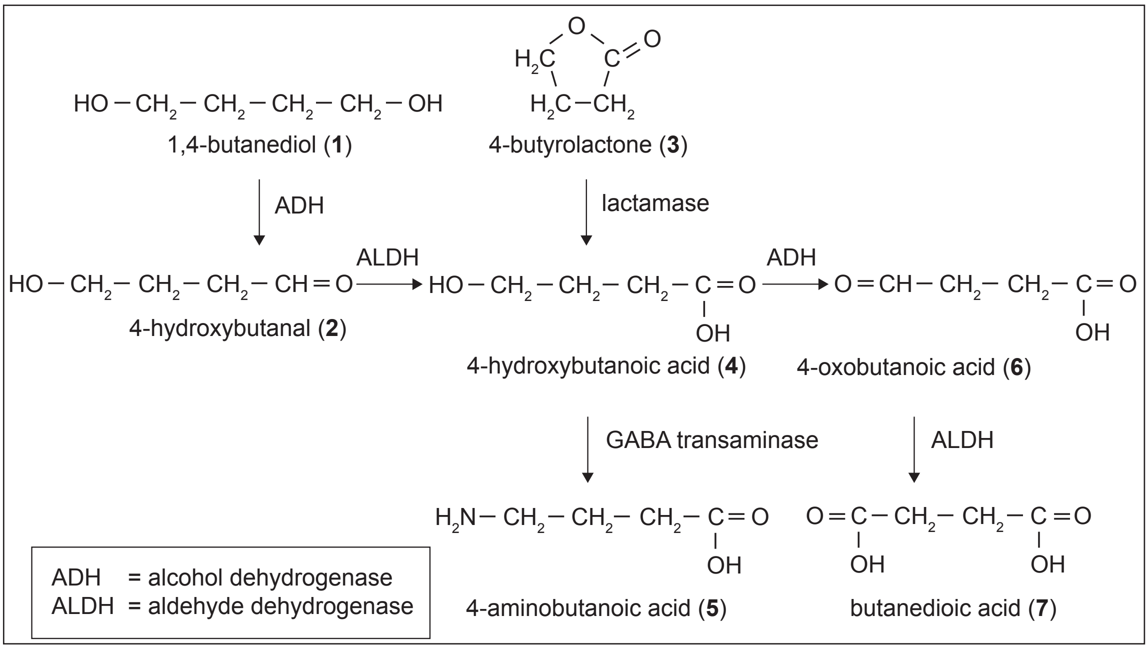
(b) The following metabolic pathway shows the reaction products when 1,4-butanediol and 4-butyrolactone are processed by enzymes (shown on the arrows) in the body.



^{13}C NMR and IR spectra are provided in the resource booklet for three compounds **Q**, **R**, and **S**, known to be from the pathway above.

Identify each of the Compounds **Q**, **R**, and **S** on the basis of the spectra given.

Justify your answer by comparing the structures of all the molecules and their expected ^{13}C NMR and IR spectra.

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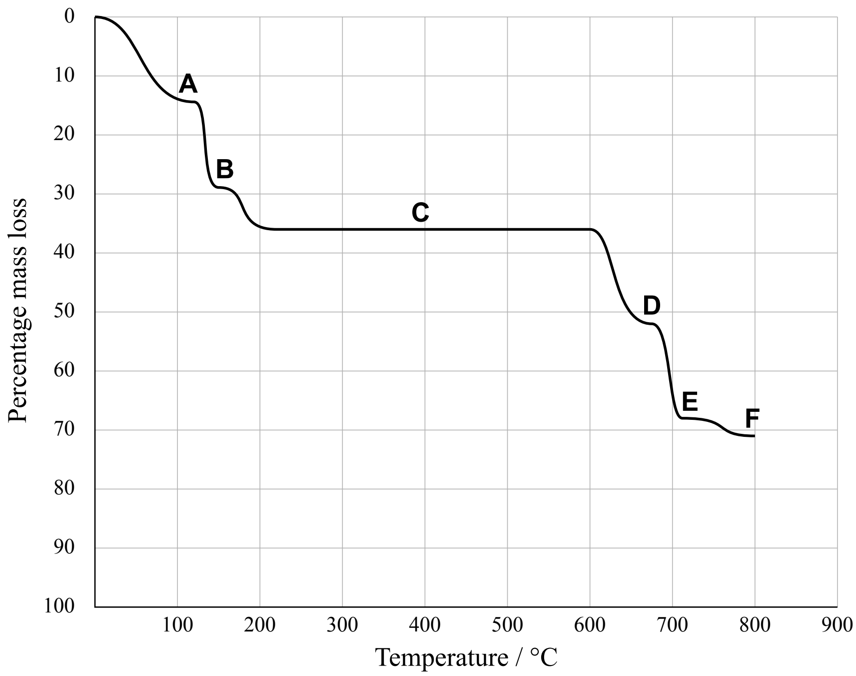
(c) The following graph shows the mass loss when a sample of solid copper sulfate pentahydrate, $CuSO_4{\cdot}5H_2O(s)$, is heated. The solid undergoes a series of reactions, and from the change in mass as the heating proceeds it is possible to identify the products formed at each stage of the process.

Copper sulfate pentahydrate heating curve



Compound **D** is formed when exactly half of Compound **C** has been converted to Compound **E**.

Compound **F** is a red solid.

Give the formula for each of Compounds **A** to **F** (for Compound **D** provide the empirical formula).
Justify your answers.

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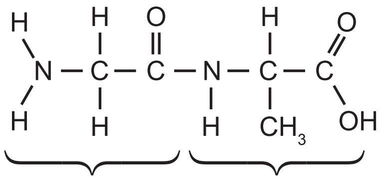
QUESTION TWO

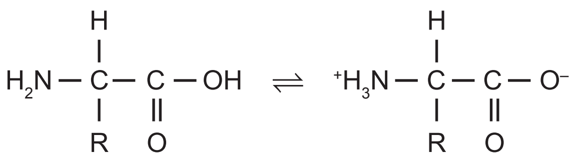
Amino acids are organic compounds that contain both a carboxylic acid and an amine functional group. Amino acids can react to form peptides, where an amide group, commonly known as a peptide bond, forms a link between the two amino acids.

The 20 different amino acids from which proteins can be made are shown in the resource booklet.

The diagram below shows the structure of a simple dipeptide formed when the amino acids glycine and alanine are combined.

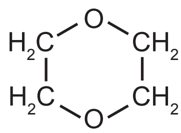


Although amino acids are often drawn with a –COOH and $–NH_2$ functional group, their actual structure is normally ionic and depends on pH. At low pH, all the amine and carboxylic acid functional groups will be protonated while at high pH it would be expected that all acidic protons would be lost. At pH 7, the acid group loses a proton to become a carboxylate ion, $–COO^–$, and the amine group accepts a proton to become an ammonium ion, $–NH_3^+$. The resulting ion is known as a zwitterion.



(a) In aqueous solution, the equilibrium constant, K_c, for the molecule–zwitterion equilibrium given above is between 10^4 and 10^6, measured across a range of amino acids. When 1,4-dioxane is used as the solvent the equilibrium constant decreases. Amino acids tend to be less soluble in dioxane than in water.

The structure of 1,4-dioxane is:



Discuss the change in the equilibrium constant with the change in the solvent and the difference in the solubility of amino acids in the two solvents.

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(b) A tetrapeptide is isolated in the laboratory. It has the molecular formula $C_{16}H_{28}O_8N_4$. To determine the amino acids in this compound, a sample is completely hydrolysed using hydrochloric acid solution. The resulting four organic products (amino acids), **A, B**, **C**, and **D** are separated out, and further analysis gives the following results:

Only Compound **A** is NOT optically active.

A sample of Compound **B** reacts with concentrated sulfuric acid, H_2SO_4, to produce constitutional isomers, Compounds **E** and **F**, both of which are able to decolourise bromine water. Compound **F** is produced in larger amounts than Compound **E**.

A sample of Compound **C**, in the fully protonated form, reacts completely with 3 mole equivalents of sodium hydroxide, NaOH. Compound **C** also reacted at high temperatures with 2 mole equivalents of methanol, CH_3OH, in the presence of a concentrated sulfuric acid catalyst, to produce an oily product, Compound **G**, with the ionic formula, $C_6H_{12}O_4N^+$.

The mass spectrum of Compound **D** has a molecular ion peak (M+) at 131 m/z. The ^{13}C NMR spectrum has six distinct peaks.

Determine, with justifications, the identities of the amino acids **A** to **D**, and the structures of Compounds **E** to **G**, using the information given above and the amino acid structures in the resource booklet.

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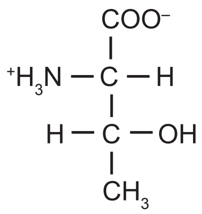
(c) Threonine, $C_4H_9NO_3$ is an amino acid with the structure shown below in the zwitterion form:



Devise a scheme to prepare threonine from 4-hydroxybutanoic acid, $HOCH_2CH_2CH_2COOH$.

Some useful information about an organic reaction is given in the box below.

USEFUL INFORMATION
Adding bromine, Br_2, to a carboxylic acid, in the presence of a base such as lithium diisopropylamide (LDA), will cause the substitution of a hydrogen on the carbon next to the acid functional group with a bromine atom.

Scheme for the conversion of **4-hydroxybutanoic acid** to the amino acid **threonine**:

QUESTION THREE

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(a) In water purification processes, contamination by metal ions is a common problem. Metal ions in solution can be removed by precipitation using a sodium hydroxide solution. Precipitating the ions separately allows the precipitates to be refined for further use.

A 1.00 L sample of waste water, with pH of 2.0, is known to contain 0.0099 mol Al^{3+}, 0.021 mol Ca^{2+}, and 0.010 mol Fe^{3+}.

Outline a strategy to individually precipitate the THREE cations, Al^{3+}, Ca^{2+}, and Fe^{3+}, using only concentrated sodium hydroxide solution, NaOH(*aq*), and a pH meter.

Your answer should be supported by appropriate equations and calculations.

$K_s(Al(OH)_3) = 1.90 \times 10^{-33}$, $K_s(Ca(OH)_2) = 5.50 \times 10^{-6}$, $K_s(Fe(OH)_3) = 6.00 \times 10^{-38}$

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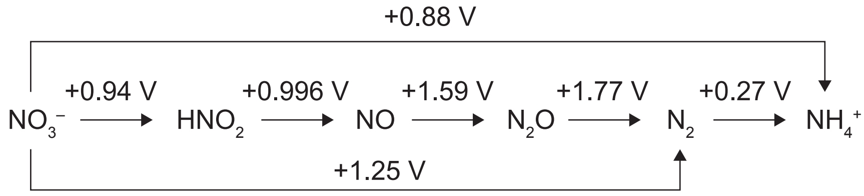
(b) Water purification plants are designed to treat water for both human consumption and for the return of used water back to the environment with an acceptable purity. To remove nitrogen present as $NH_4^+(aq)$, *nitrification* is carried out with oxygen, $O_2(g)$, from the air, producing $NO_3^-(aq)$. This is followed by *denitrification*, where $NO_3^-(aq)$ is reduced to $N_2(g)$.

The denitrification is performed by bacteria under anaerobic conditions (i.e. in an absence of oxygen) with oxidisable organic compounds. If there is not enough oxidisable substrate in the crude water then additional methanol, $CH_3OH(\ell)$, is added.

The Latimer diagram below shows the standard electrode potentials (in volts) for the reduction of different nitrogen species at 25°C.



$$E^\circ\,(O_2\,/\,H_2O) = +1.23\text{ V}$$
$$E^\circ\,(CO_2\,/\,CH_3OH) = +0.23\text{ V}$$

(i) Write an account of the oxidation-reduction processes occurring in the water purification plant, including the spontaneity of the reactions under standard conditions, the circumstances requiring the addition of methanol, and the direction of electron transfer.

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(ii) The acid produced in the overall nitrification process is removed by reaction with calcium hydroxide, $Ca(OH)_2(aq)$. In a purification plant, 1.50×10^4 m^3 of waste water with a concentration of 25.0 mg L^{-1} of NH_4^+ runs through the nitrification zone daily.

Calculate the mass of $Ca(OH)_2(s)$ that must be added each hour to ensure that the pH is kept constant.

1 m^3 = 1 000 L $\quad$ $M(Ca(OH)_2) = 74.1$ g mol^{-1} $\quad$ $M(NH_4^+) = 18.0$ g mol^{-1}

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QUESTION FOUR

(a) The box below is an extract from the NZ Winegrowers Labelling Guide.

> **Alcohol by volume**
> A wine label must include an alcohol declaration (Standard 2.7.1). The acceptable form for the declaration is "mL/ 100 g" or "mL/ 100 mL" or "x"% alcohol by volume, or words or expression of the same or similar meaning: e.g. "% vol" will suffice.
>
> Tolerances of the declared alcohol content from the actual alcohol content are:
>
> - wine and sparkling wine ± 1.5%

A bottle of wine to be analysed is labelled as "13.5% vol". The following analytical procedure was carried out to check the accuracy of this labelling.

A 1.000 mL sample of freshly opened wine was pipetted into a round bottom flask. To this was added 100.0 mL of potassium dichromate solution, $K_2Cr_2O_7(aq)$, and 25.00 mL of 2 mol L^{-1} sulfuric acid solution, $H_2SO_4(aq)$. This wine-dichromate mixture was refluxed for an hour, then left to cool to room temperature.

A standard solution of iron(II) was prepared by placing 10.30 g of iron(II) ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, into a 250.0 mL volumetric flask along with 50 mL of 2 mol L^{-1} H_2SO_4 and sufficient water to make 250.0 mL of solution.

To standardise the potassium dichromate solution, 25.00 mL samples of the standard iron(II) solution were acidified and titrated against the potassium dichromate solution using sodium diphenylamine-4-sulfonate indicator. An average volume of 17.43 mL was required to reach the end-point, as indicated by the appearance of a red colour.

To analyse the wine sample, the wine-dichromate mixture was also titrated against acidified samples of the standard iron(II) solution. Using 10.00 mL samples of the standard solution required, on average, 19.88 mL of the wine-dichromate reaction mixture to reach the end-point.

Determine whether the bottle of wine meets the required labelling guide rules as described in the box above.

$M(Fe(NH_4)_2(SO_4)_2.6H_2O) = 392.2$ g mol^{-1} $\quad$ $M(CH_3CH_2OH) = 46.07$ g mol^{-1}

$d(CH_3CH_2OH) = 0.7893$ g mL^{-1} $\quad$ $d = \frac{m}{v}$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

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

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(b) (i) Equal volumes of sulfuric acid, $H_2SO_4(aq)$, and 0.100 mol L^{-1} ethanoic acid, $CH_3COOH(aq)$, are mixed. The pH of the resulting solution is found to be 0.30 pH units less than that of the ethanoic acid solution.

Calculate the concentration of the sulfuric acid solution (assume the sulfuric acid completely dissociates to form two H_3O^+ ions).

$pK_a(CH_3COOH) = 4.76$

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(ii) While it is often assumed that sulfuric acid completely dissociates in water to form two H_3O^+ ions, there are two different pK_a values for sulfuric acid: p$K_{a,1}$ = –2, p$K_{a,2}$ = 1.99.

Explain how these two pK_a values affect the concentration of sulfuric acid calculated in part (i).

A further calculation is not needed.

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Extra paper if required.
Write the question number(s) if applicable.

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