NZQA

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2012
Chemistry

9.30 am Saturday 17 November 2012
Time allowed: Three hours
Total marks: 40

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

You should answer ALL the questions in this booklet.

Pull out Resource Sheet S–CHEMR from the centre of 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 35 minutes on each question.

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

You have three hours to complete this examination.

QUESTION ONE

(a) (i) Account for the signs and relative magnitudes of the enthalpy changes in the reactions **A–F** shown below.

A	$Mg(s) \rightarrow Mg(g)$	$\Delta H =$	$+147$ kJ mol^{-1}
B	$\frac{1}{2}F_2(g) \rightarrow F(g)$	$\Delta H =$	$+79$ kJ mol^{-1}
C	$Mg(g) \rightarrow Mg^+(g) + e^-$	$\Delta H =$	$+744$ kJ mol^{-1}
D	$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	$\Delta H =$	$+1\,457$ kJ mol^{-1}
E	$F(g) + e^- \rightarrow F^-(g)$	$\Delta H =$	-334 kJ mol^{-1}
F	$Mg^{2+}(g) + 2F^-(g) \rightarrow MgF_2(s)$	$\Delta H =$	$-2\,957$ kJ mol^{-1}

(ii) Explain why the thermodynamic equations given in (i) can be used to determine the enthalpy of formation of magnesium fluoride, and then show how this is done.

(b) For many years the Group 18 elements were known as the inert gases, as a reflection of the belief that they would not form compounds. The synthesis of compounds like XeF_2, XeF_4, and XeO_3 showed this belief to be incorrect. The elements are now known as the noble gases, indicating a low, rather than absent, reactivity.

(i) Using your knowledge of periodic trends, explain why fluorine and oxygen are the elements most likely to combine with xenon, and why xenon is the noble gas most likely to form compounds (apart from radon, which is difficult to work with because of its radioactivity).

_____

_____

_____

_____

_____

_____

_____

_____

_____

(ii) Predict the shapes and approximate bond angles in XeO_3 and $[XeOF_3]^+$, giving reasons for your answer.

_____

_____

_____

_____

_____

_____

_____

_____

_____

(iii) Discuss the possibility of forming compounds between an element from Group 1 and a noble gas.

Consider whether such a compound is likely to be ionic or covalent and, if such a compound were to exist, state which elements from Group 1 would be the most likely candidates.

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____
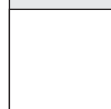
QUESTION TWO

(a)   Etidocaine is used as a local anaesthetic. Its hydrochloride is marketed as Duranest®.

The structural formula for etidocaine is:
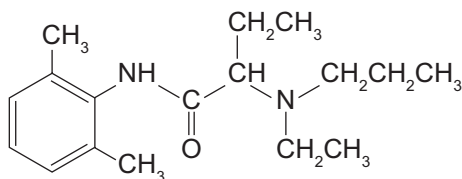
Propose a synthesis for etidocaine, starting with 2,6-dimethylaniline, 2-chlorobutan-1-ol, propan-1-ol and ethanol, and using any appropriate reagents.

Include structural formulae for each step of the synthetic pathway.

**NOTE:** Only the amine group of 2,6-dimethylaniline will be active under the conditions you will need for the reaction.
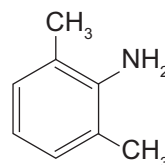
2,6-dimethylaniline

(b) Acid anhydrides are derivatives of carboxylic acids. Their reactivity makes them useful starting materials for organic synthesis reactions. Acid anhydrides are formed from the condensation reaction between two functional groups.
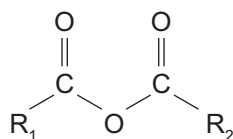

An acid anhydride where R_1 and R_2 can be the same or different alkyl groups.

Draw the structural formulae for the compounds **A** to **H** described below.

- Compound **A** has the molecular formula $C_6H_{10}O_3$. Compound **A** does not have enantiomers (optical isomers).

- Reaction of compound **A** with acidified potassium dichromate solution results in compound **B**, $C_6H_{10}O_5$.

- Reaction of compound **B** with anhydrous zinc chloride in concentrated hydrochloric acid produces compound **C**, $C_6H_9O_4Cl$.

- Compound **C**, reacts with alcoholic potassium hydroxide, followed by acidification, to produce compounds **D**, **E** and **F**, $C_6H_8O_4$. Compound **D** does not have stereoisomers, but compounds **E** and **F** are geometric isomers of each other.

- When compounds **D** and **F** are heated, two different compounds, **G** and **H**, with the molecular formula $C_6H_6O_3$, are produced. Compound **E** does not react on heating.

QUESTION THREE

(a) Vanadium is a transition metal that exhibits a range of oxidation states. These are summarised in the Latimer diagram below, which includes the standard electrode potentials (in volts) for reduction of successive vanadium species. Values are given for pH = 0.

$$VO_2^+ \xrightarrow{+0.99} VO^{2+} \xrightarrow{+0.34} V^{3+} \xrightarrow{-0.26} V^{2+}$$
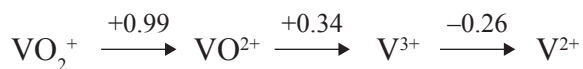
(i) Compare the relative oxidising and reducing strengths of the four ions listed above.

(ii) Ammonium vanadate, NH_4VO_3, in acidic solution contains the VO_2^+ ion. A 25.00 mL sample of acidified 0.09243 mol L^{-1} ammonium vanadate solution was reacted with SO_2. After boiling off any excess reductant, a blue solution remained. This blue solution required 21.38 mL of 0.0216 mol L^{-1} acidified $KMnO_4$ to give a pink colour to the solution.

Another 25.00 mL portion of the ammonium vanadate solution was shaken with a zinc amalgam to give a violet coloured solution. This solution was titrated under an inert atmosphere with the $KMnO_4$ solution. 64.14 mL was required to reach the end point.

Account for these observations.

Include your titration calculations and a discussion on the relative reduction potentials of the reacting species.

$$E^o(MnO_4^-/Mn^{2+}) = +1.51 \text{ V}$$

(iii) An alternative to using an inert atmosphere for the second titration described in (ii) is to quickly decant the violet solution into an excess of the ammonium vanadate solution. The titration with $KMnO_4$ then proceeds as described, using the same volume of permanganate to reach the end point.

Explain why this alternative procedure is useful and why the same volume of $KMnO_4$ solution is needed.

(b) Proteins are polymers of amino acids that contain different side chains, indicated as **R** in the diagram below. The properties of proteins are largely determined by the sequence of the amino acids from which they are made.

$$R - CH - \overset{\overset{O}{\|}}{C} - OH$$
$$\underset{NH_2}{|}$$
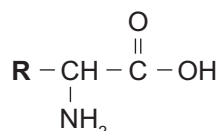
The table below shows some of the **R** groups of the amino acids that make up proteins.

| Amino acid	Side chain (R)	pK_a of side chain (where appropriate)
alanine	$-CH_3$	
aspartic acid	$-CH_2CO_2H$	4
glutamic acid	$-CH_2CH_2CO_2H$	4
leucine	$-CH_2CH(CH_3)_2$	
lysine	$-CH_2CH_2CH_2CH_2NH_3^+$	11
serine	$-CH_2OH$	

Classify, with reasons, whether the amino acid side chains in the table are charged, polar, or non-polar at physiological pH (7.4).

Discuss how the nature of each side chain could affect the observed tendency of proteins to fold up in aqueous solution.

ASSESSOR'S
USE ONLY

QUESTION FOUR

(a) DNA is an alternating polymer of deoxyribose sugars and phosphate groups, with DNA bases (often labelled A, T, C, and G) attached to the sugar units.

DNA usually exists as two strands that are linked to each other by hydrogen bonds between the bases in the different strands: A with T, and G with C, as shown below.
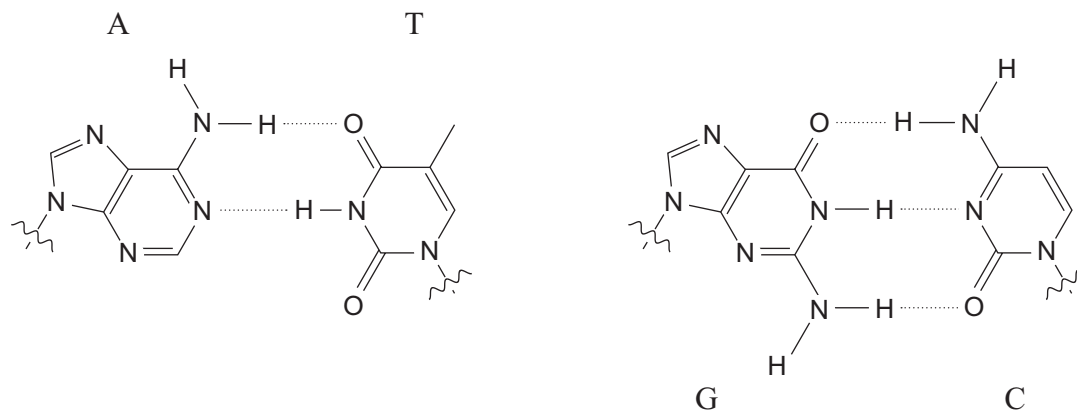
Separation of the two strands can be achieved by heating aqueous solutions of the DNA.

If urea is present, DNA strands can be separated at lower temperatures.

Urea has the structural formula:
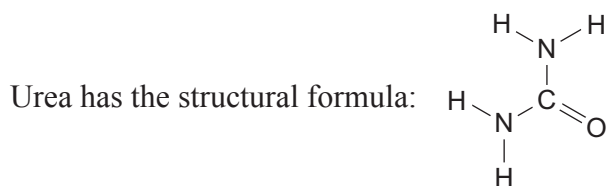
The separation temperature for a range of DNA fragments in aqueous solutions is given in the table below (the first and last two base pairs are the same in all cases).

	DNA Fragment	Separation Temperature (°C)
1	G–G–C–C–G–G–C–C C–C–G–G–C–C–G–G	32
2	G–G–C–C–A–T–G–G–C–C C–C–G–G–T–A–C–C–G–G	36
3	G–G–C–C–G–C–G–G–C–C C–C–G–G–C–G–C–C–G–G	40
4	G–G–C–C–A–A–T–T–G–G–C–C C–C–G–G–T–T–A–A–C–C–G–G	40
5	G–G–C–C–C–A–A–G–G–G–C–C C–C–G–G–G–T–T–C–C–C–G–G	44
6	G–G–C–C–C–A–T–G–G–G–C–C C–C–G–G–G–T–A–C–C–C–G–G	44

Account for variations in the separation temperatures of the DNA fragments, AND discuss the reasons for the decrease in the separation temperature when urea is present.

(b) The amount of carbon dioxide in the atmosphere is increasing due to the combustion of fossil fuels. The concentration of a dissolved gas in a solution is directly proportional to the partial pressure of that gas above the solution. This means that increasing the carbon dioxide in the Earth's atmosphere will increase the amount of dissolved carbon dioxide in the oceans. The concentration of carbonate ions, utilised by shell-forming organisms to form $CaCO_3$, varies with the amount of dissolved CO_2. This, in turn, affects the availability of dissolved calcium ions.

Information

- $CO_2(g) \rightleftharpoons CO_2(aq)$

- Solubility of CO_2 in water obeys Henry's Law: $\dfrac{\left[CO_2(aq)\right]}{P_{CO_2}} = K_h$,

   where P_{CO_2} is the partial pressure of CO_2 in the atmosphere.

- Henry's Law constant for CO_2 at 25°C, is 3.317×10^{-4} mol L^{-1} kPa^{-1}.

- The current partial pressure of CO_2 in the atmosphere is 0.0397 kPa.

- Dissolved carbon dioxide reacts with the water to form carbonic acid:

   $CO_2(aq) + H_2O(\ell) \rightleftharpoons H_2CO_3(aq)$ $K_1 = 1.70 \times 10^{-3}$

- H_2CO_3 is a weak acid: $H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$ $K_2 = 2.51 \times 10^{-4}$

- HCO_3^- also reacts with water: $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ $K_3 = 5.62 \times 10^{-11}$

- $CaCO_3$ is a sparingly soluble salt $K_s = 4.8 \times 10^{-9}$

- The pH of the oceans is currently about 8.10.

Calculate the concentration of Ca^{2+} ions at the current pH of the ocean, using the data given above.

QUESTION FIVE

(a)   Discuss briefly why adding 70.0 mL of 0.400 mol L^{-1} ethanoic acid (pK_a = 4.76) to 100.0 mL of 0.0200 mol L^{-1} hydrochloric acid would not greatly change the pH of the original solution.

Justify your answer by including a calculation of the concentration, in mol L^{-1}, of ethanoate ions.

(b)   (i)   Carry out the appropriate calculations to enable you to sketch the titration curves for the following titrations on the grid provided.
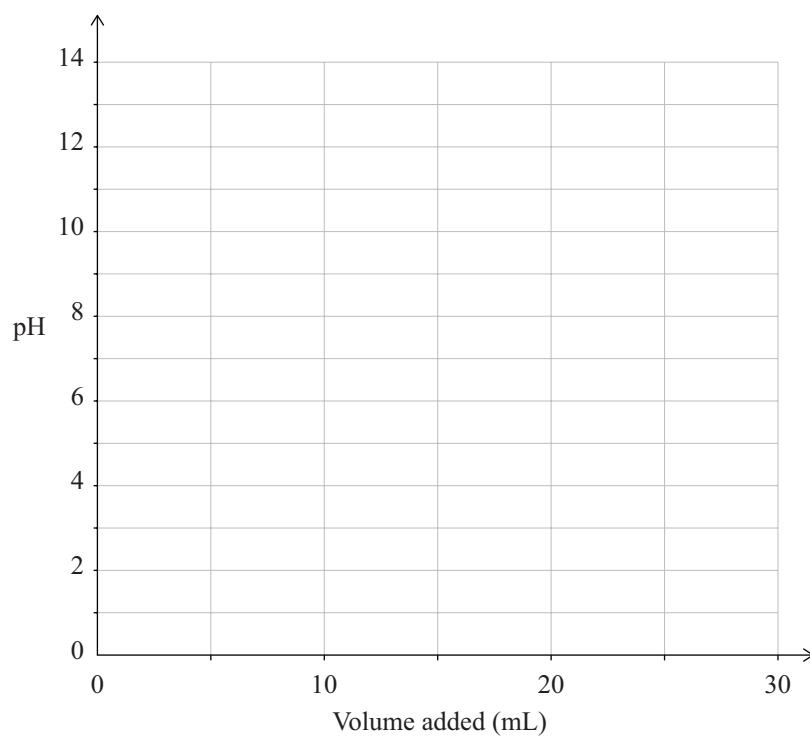
Show your working for your calculations.

Titration 1: 40.00 mL of 0.0500 mol L^{-1} NH$_4$Cl with 0.200 mol L^{-1} NaOH
(up to 20 mL)

Titration 2: 40.00 mL of 0.0500 mol L^{-1} NH$_3$(*aq*) with 0.200 mol L^{-1} HCl
(up to 20 mL)

pK_a (NH$_4^+$) = 9.24

Calculation space:

Volume added (mL)

(ii) Discuss the similarities and differences between the two curves in terms of the species present in the titration solutions.

(c) An indicator is usually a weak acid or base that has different colours in its neutral or ionic forms. The pK_a of an indicator can be used to determine its usefulness in a titration. For the indicator HIn:

$$HIn(aq) + H_2O(\ell) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$
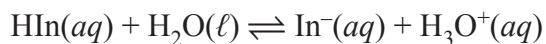
When methyl red is used as an indicator for the titration of NH_3 with HCl (as described in (b)(i)), the initial colour of the indicator is yellow, and after 15.00 mL of HCl has been added, it is red. The end point of the titration is indicated by an orange colour. It is easier to observe this colour change when the colour is intensified by using more than a few drops of indicator.

pK_a (methyl red) = 5.1

Discuss the colour changes that are observed during this titration, relating these to the different forms of the indicator that are present AND explain any consequences for the accuracy of a titration of using more than a few drops of indicator.

QUESTION NUMBER	

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

QUESTION
NUMBER

93102

QUESTION
NUMBER

ASSESSOR'S
USE ONLY