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93102

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2006
Chemistry

2.00 pm Saturday 25 November 2006
Time allowed: Three hours
Total Marks: 48

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

A Periodic Table is printed on page 2 of this booklet.

Answer ALL questions.

Write all your answers in this booklet.

If you need more space for any answer, use the page(s) provided at the back of this booklet and clearly number the question.

Check that this booklet has pages 2–26 in the correct order.

You are advised to spend approximately 30 minutes on each question.

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

PERIODIC TABLE OF THE ELEMENTS

Atomic Number | **Symbol** | Molar Mass / g mol^{-1}

1	*2*											*13*	*14*	*15*	*16*	*17*	*18*
																	2 **He** 4.0
3 **Li** 6.9	4 **Be** 9.0											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
11 **Na** 23.0	12 **Mg** 24.3	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 40.0
19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.6	30 **Zn** 65.4	31 **Ga** 69.7	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** 98.9	44 **Ru** 101	45 **Rh** 103	46 **Pd** 106	47 **Ag** 108	48 **Cd** 112	49 **In** 115	50 **Sn** 119	51 **Sb** 122	52 **Te** 128	53 **I** 127	54 **Xe** 131
55 **Cs** 133	56 **Ba** 137	57–71 Lanthanide Series	72 **Hf** 179	73 **Ta** 181	74 **W** 184	75 **Re** 186	76 **Os** 190	77 **Ir** 192	78 **Pt** 195	79 **Au** 197	80 **Hg** 201	81 **Tl** 204	82 **Pb** 207	83 **Bi** 209	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226	89–103 Actinide Series	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 264	108 **Hs** 265	109 **Mt** 266									

Lanthanide Series	57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 145	62 **Sm** 150	63 **Eu** 152	64 **Gd** 157	65 **Tb** 159	66 **Dy** 163	67 **Ho** 165	68 **Er** 167	69 **Tm** 169	70 **Yb** 173	71 **Lu** 175
Actinide Series	89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 244	95 **Am** 243	96 **Cm** 247	97 **Bk** 247	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259	103 **Lr** 262

QUESTION ONE (8 marks)

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(a) Discuss reasons for the variation in the observed $\Delta_{fus}H^{o}$ and $\Delta_{vap}H^{o}$ of the substances in the table below.

	$\Delta_{fus}H^{o}$ / kJ mol^{-1}	$\Delta_{vap}H^{o}$ / kJ mol^{-1}
Chlorine (Cl_2)	3.2	10.2
Sodium chloride (NaCl)	28	205

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(b) The lattice enthalpy of an ionic solid is the enthalpy change on converting the solid into its ions in the gas phase. For sodium chloride this is represented by the equation:

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$$

Lattice enthalpies may be estimated by combining known enthalpy changes including the ionisation energy of a metal and the electron affinity of a non-metal. Electron affinity is the enthalpy change for removing an electron from a negative ion in the gas phase. For chlorine this is represented by the equation:

$$Cl^-(g) \rightarrow Cl(g) + e^-$$

Some useful enthalpy changes are given in the table below.

	Enthalpy change / kJ mol^{-1}
$\Delta_f H^o$(NaCl, *s*)	−411
$\Delta_{vap} H^o$(Na)	104
$\Delta_{fus} H^o$(Na)	2.6
First ionisation energy (Na)	502
Bond enthalpy (Cl_2)	242
First electron affinity (Cl)	355

(i) A student claims that the major driving force for the formation of sodium chloride from elemental sodium and chlorine is the spontaneous transfer of electrons from sodium to chlorine atoms.

ie for the reaction $Na(g) + Cl(g) \rightarrow Na^+(g) + Cl^-(g)$

Calculate the enthalpy change for this reaction and discuss the validity of the student's claim.

(ii) Calculate the lattice enthalpy in kJ mol^{-1} for sodium chloride.

Assessor's use only

QUESTION TWO (8 marks)

Assessor's use only

(a) The first ionisation enthalpy is the enthalpy change in the process

$$E(g) \rightarrow E^{+}(g) + e^{-}(g)$$

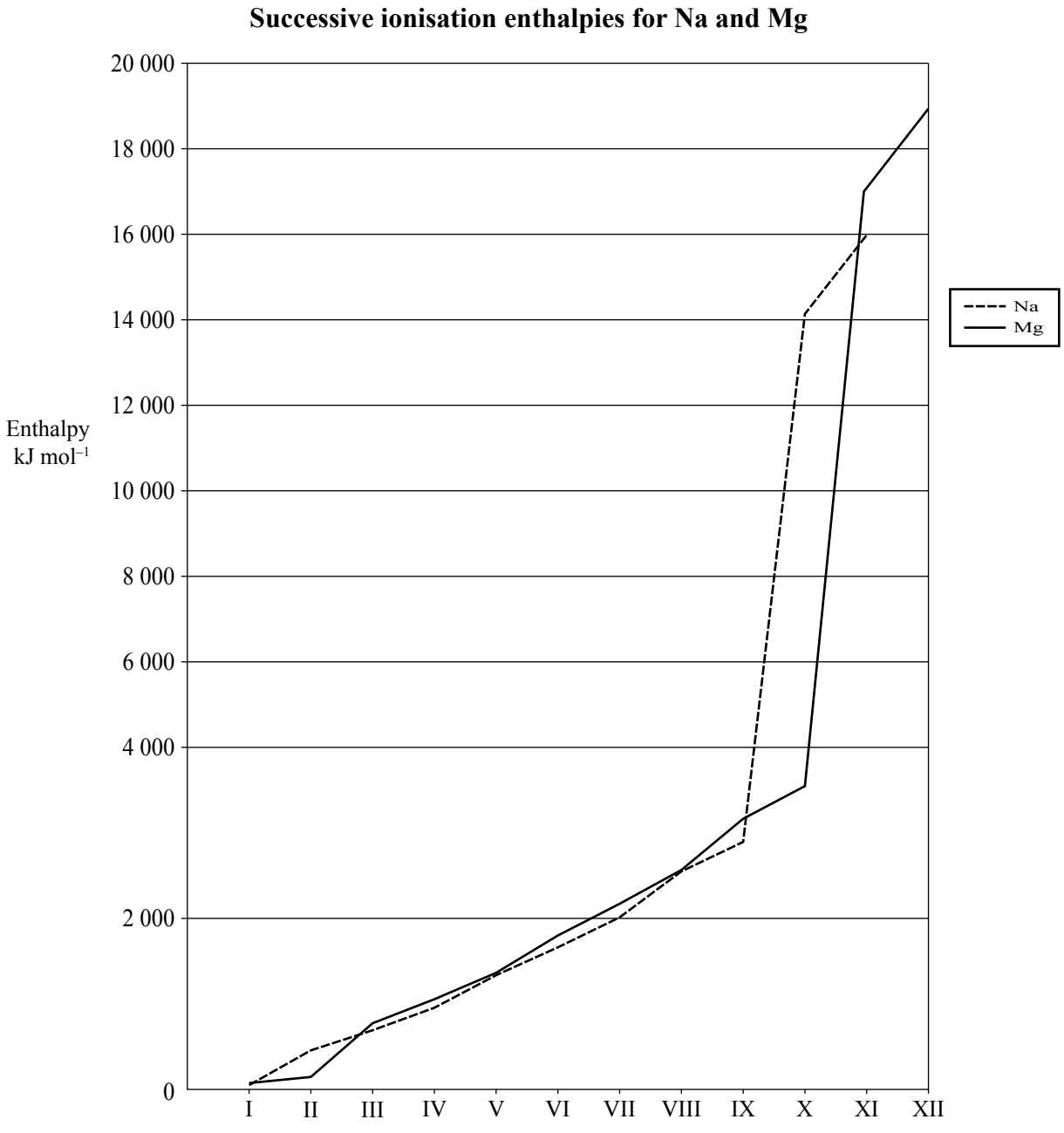
The second ionisation enthalpy is the enthalpy change in the process

$$E^{+}(g) \rightarrow E^{2+}(g) + e^{-}(g)$$

Each successive ionisation enthalpy is defined in a similar way.

Successive ionisation enthalpies (in kJ mol^{-1}) for sodium and magnesium are given in the table and the graph below.

Mass No	Element	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
11	Na	502	4 569	6 919	9 550	13 356	16 616	20 121	25 497	28 941	141 373	159 806	
12	Mg	744	1 457	7 739	10 547	13 636	18001	21 710	25 663	31 650	35 469	170 003	189 379



Account for the trends in the successive ionisation enthalpies of **magnesium**. Comment on the similarities and differences in the trends for the successive ionisation energies of the two elements, sodium and magnesium.

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(b) Compound **A**, $C_6H_{12}O_2$, is optically active. After refluxing with aqueous sodium hydroxide, the mixture is acidified and shaken with a non-polar solvent, diethyl ether.
Compound **B**, which is also optically active, is found in the ether layer.

Deduce as many possibilities as you can for the identity of the structures of Compounds **A** and **B**, and explain how these structures are consistent with the observations above.

Assessor's use only

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QUESTION THREE (8 marks)

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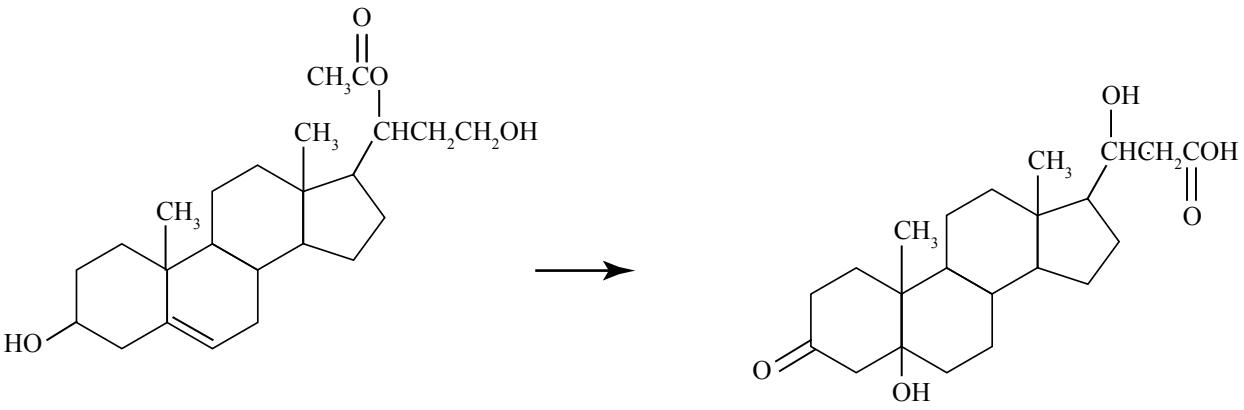
The steroid derivative **Z** is to be derived from the starting material **X**.



Starting material **X**

Steroid derivative **Z**

Devise a multi-step reaction scheme for this synthesis.

Include in your answer:

- the functional group transformation occurring at each step
- the reagents that would be used for each transformation
- an explanation for the order in which the reactions need to take place
- comments on any by-products that may be formed at any stage in the reaction scheme proposed.

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QUESTION FOUR (8 marks)

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The following three aqueous solutions are available.

Solution **A**: 0.100 mol L^{-1} CH_3NH_2

Solution **B**: 0.100 mol L^{-1} CH_3NH_3Cl

Solution **C**: 0.100 mol L^{-1} in both CH_3NH_3Cl and CH_3NH_2

$pK_a(CH_3NH_3^+) = 10.6$

(a) Discuss how the pH of each solution compares with the pH of pure water. Include relevant chemical equations in your answer. No calculations are necessary.

(b) 15.0 mL of 0.100 mol L^{-1} hydrochloric acid is added to 25.0 mL of Solution **A** (0.100 mol L^{-1} CH_3NH_2).

Calculate the pH of the solution after mixing.

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(c) Explain why the sparingly soluble base $Cu(OH)_2$ dissolves in both Solution **A** (0.100 mol L^{-1} CH_3NH_2) and Solution **B** (0.100 mol L^{-1} CH_3NH_3Cl).

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(d) Calculate the minimum mass of CH_3NH_3Cl that must be added to 1.00 L of a solution that contains 0.100 mol $Mg(NO_3)_2$ and 0.100 mol CH_3NH_2 in order to prevent precipitation of $Mg(OH)_2$.

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$K_s(Mg(OH)_2) = 1.50 \times 10^{-11}$

$pK_a(CH_3NH_3^+) = 10.6$

$M(CH_3NH_3Cl) = 67.5 \text{ g mol}^{-1}$

QUESTION FIVE (8 marks)

Assessor's use only

(a) Electrolysis cells have two electrodes immersed in the same solution. The electrodes are connected to a battery. Flow of current through the solution causes a redox reaction to occur. Commonly the strongest oxidant in the solution reacts at one electrode, and the strongest reductant in the solution reacts at the other electrode.

Electrolysis of an aqueous sodium iodide solution containing a drop of phenolphthalein is carried out.

Predict the observations at the two electrodes. Explain your answer.

$E^o(O_2/H_2O) = +0.82$ V (at pH 7)

$E^o(I_2/I^-) = +0.62$ V

$E^o(H_2O/H_2) = -0.42$ V (at pH 7)

$E^o(Na^+/Na) = -2.71$ V

(b) Autooxidation-reduction reactions or disproportionation reactions are oxidation-reduction reactions in which an atom in a particular oxidation state acts as both the oxidant and the reductant.

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Identify the species from the standard electrode potentials given below that are most likely to undergo autooxidation-reduction in basic conditions. Justify your answer and write a balanced equation for any reactions that occur.

The standard electrode potentials given are for basic conditions.

$E^{o}(H_3IO_6^{2-}/IO_3^{-}) = +0.70$ V

$E^{o}(IO_3^{-}/IO^{-}) = +0.14$ V

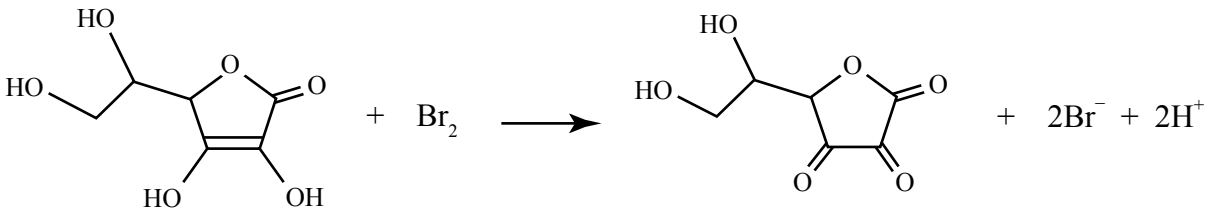
$E^{o}(IO^{-}/I_2) = +0.45$ V

$E^{o}(I_2/I^{-}) = +0.54$ V

QUESTION SIX (8 marks)

Assessor's use only

Vitamin C can be oxidised by bromine or iodine. The equation for oxidation by bromine is shown below. The reaction for iodine is similar, with the product being I^-.



This reaction is used in a variety of different methods for the quantitative determination of vitamin C in fruit juices. The bromine or iodine used in the titration is generated by adding an excess amount of KBr or KI to an acidified solution of bromate or iodate according to the following reactions:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Two methods are discussed in the following parts (a) and (b).

(a) **Method 1**

An excess of standard potassium iodate solution is added to the juice sample along with excess potassium iodide and sulfuric acid. The resulting mixture is titrated against standard thiosulfate solution using a starch indicator.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Iodine is only slightly soluble in water and is volatile at room temperature. Iodide is oxidised by atmospheric oxygen.

Explain how the accuracy of the experimental value for the vitamin C concentration would be affected by:

- vigorous swirling of the solution during the titration
- allowing the solutions to stand before being titrated
- excess iodide ion in the solution which reacts with iodine to produce I_3^-.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Note that Question Six continues on the next page.

(b) **Method 2**

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A standard potassium bromate solution was prepared by dissolving 1.33 g of potassium bromate in sufficient water to make 500.0 mL of solution. This solution was diluted by taking 100.0 mL and diluting it to 500.0 mL.
50.00 mL of fruit juice was mixed with 5 g of KBr and 20 mL of 0.5 mol L^{-1} sulfuric acid. The resulting mixture was titrated against the diluted standard potassium bromate solution until a faint yellow colour indicated the presence of bromine. At this point, 14.04 mL of potassium bromate had been added.

3 g of potassium iodide and starch indicator were then added, and the iodine produced required 2.36 mL of 0.00238 mol L^{-1} $Na_2S_2O_3$ solution to reach the end point.

Calculate the percentage of Vitamin C in mg in the fruit juice and comment on the validity of the results.

$M(KBrO_3)$ = 167 g mol^{-1} M(Vitamin C) = 176 g mol^{-1}

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Extra paper for continuation of answers if required.
Clearly number the question.

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Question number	

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For Assessor's Use Only	
Question Number	Marks
Q1	(8)
Q2	(8)
Q3	(8)
Q4	(8)
Q5	(8)
Q6	(8)
TOTAL	(48)

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