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NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2011
Chemistry

9.30 am Saturday 19 November 2011
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.

A periodic table is provided on page 2.

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 2–26 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.

PERIODIC TABLE OF THE ELEMENTS

Atomic number: 1, **H**, 1.0 :Molar mass / g mol^{-1}

1	2	3	4	5	6	7	8	9	10	11	12	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											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** 63.5	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	71 **Lu** 175	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	103 **Lr** 262	104 **Rf** 261	105 **Db** 262	106 **Sg** 263	107 **Bh** 264	108 **Hs** 265	109 **Mt** 268	110 **Ds** 271	111 **Rg** 272							

Lanthanide Series	57 **La** 139	58 **Ce** 140	59 **Pr** 141	60 **Nd** 144	61 **Pm** 147	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
Actinide Series	89 **Ac** 227	90 **Th** 232	91 **Pa** 231	92 **U** 238	93 **Np** 237	94 **Pu** 239	95 **Am** 241	96 **Cm** 244	97 **Bk** 249	98 **Cf** 251	99 **Es** 252	100 **Fm** 257	101 **Md** 258	102 **No** 259

You have three hours to complete this examination.

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QUESTION ONE

(a) (i) Discuss how the charges on subatomic particles contribute to the size of atoms and their ions.

(ii) Explain the trends in the atom and ion sizes (in pm) in Figure 1 below.

Relate your answer to your discussion in part (i).

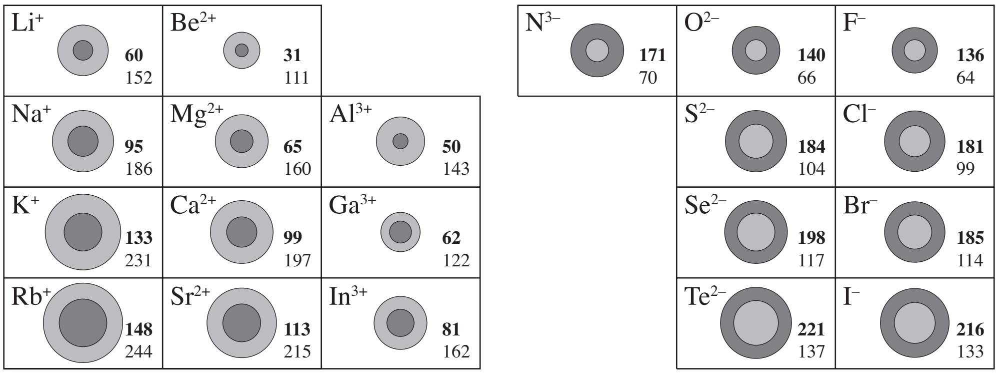

Figure 1: Atomic and ionic radii (pm)

Note:
- The dark circles represent the ions.
- The bolded numbers are the ionic radii.

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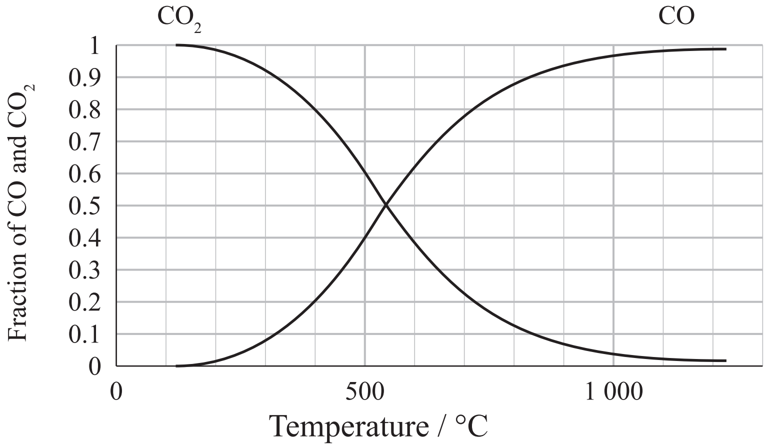
(b) The Boudouard reaction is the name given to the oxidation-reduction reaction involving a mixture of carbon (graphite), carbon dioxide and carbon monoxide at equilibrium, at a given temperature. The reaction is an important process inside a blast furnace in the production of metals from metal oxides.

The graph below shows how the reaction mixture composition of the gases present changes with changing temperature at atmospheric pressure (101 kPa).

Boudouard Equilibrium



(i) Identify, with justification, the product of the exothermic process in the Boudouard reaction.

Use your answer to discuss the reaction products when the hot gases from a blast furnace reach the cooler air at the top of the chimney.

(ii) A large, heat-proof syringe with a freely moveable airtight piston initially contained 50 mL of carbon dioxide at 101 kPa and 25°C, plus 1 g of granular carbon. The apparatus was heated and maintained at a certain constant temperature until equilibrium was reached. The pressure of the system remained constant at 101 kPa throughout. The apparatus was then cooled rapidly to 25°C. (At this temperature any further change in composition was negligible.) A total of 60 mL of gas was then present.

Determine the temperature at which the reaction was carried out.

Note:

- The same conditions apply to this experiment and to that represented by the graph on the previous page.
- The volume of a substance in its gas phase at a particular temperature and pressure is directly proportional to the amount in moles of the substance present.

QUESTION TWO

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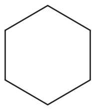
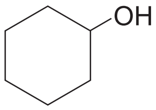
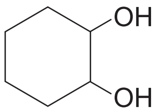
(a) Account for the differences in the properties of the compounds in the table below.

Name	**Structural formula**	**Melting Point / °C**	**Solubility in water at 25°C**
Cyclohexane C_6H_{12}		7	Insoluble
Cyclohexanol $C_6H_{11}OH$		25	Sparingly soluble
cis-cyclohexane-1,2-diol $C_6H_{10}(OH)_2$		98	Very soluble

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(b) A year 11 student carried out an experiment to compare the energy released when octane and ethanol were burned as fuels. Octane was found to release considerably more energy than ethanol. The student concluded that this was because octane was a larger molecule, and so there were more chemical bonds to break, and hence more energy released in the reaction.

Discuss the misconceptions in the student's explanation and use appropriate data from the table below to provide your own answer for the observation.

M(octane) = 114.0 g mol^{-1} M(ethanol) = 46.1 g mol^{-1}

Bond enthalpy data / kJ mol^{-1}

C–H	414	O–H	463
C–O	358	C≡O	1076
C=O	804	H–H	436
C–C	346	O=O	498

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QUESTION THREE

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(a) A mixture contains oxalic acid, $H_2C_2O_4$, sodium oxalate, $Na_2C_2O_4$, and a water soluble impurity that does not react with solutions of sodium hydroxide or potassium permanganate.

To determine the composition of the mixture, 2.496 g of the mixture was dissolved in water to give 100.00 mL of solution.

In one test, 5.00 mL of the solution was titrated with 0.01803 mol L^{-1} acidified potassium permanganate solution and needed 23.35 mL to reach the equivalence point.

In another test, 10.00 mL of the solution was titrated with 0.1040 mol L^{-1} sodium hydroxide solution and needed 17.30 mL to reach the equivalence point.

Determine the mass fractions of oxalic acid, oxalate ion and the impurity.

$M(H_2C_2O_4) = 90.04$ g mol^{-1} $\quad$ $M(Na_2C_2O_4) = 134.0$ g mol^{-1}

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(b) Manganese is an element that exhibits a number of different oxidation states. Half-cell reactions and potentials for the different oxidation states vary depending on the conditions. The table gives the standard reduction potentials for manganese species in aqueous solution ranging from Mn(II) to Mn(VII) at pH = 0 and at pH = 14.

Conditions	**Reduction half-equation**	$E°$ / V
pH = 0	$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	–1.19
	$MnO_4^-(aq) + H^+(aq) + e^- \rightarrow HMnO_4^-(aq)$	+0.90
	$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(\ell)$	+1.23
	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(\ell)$	+1.51
	$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$	+1.54
	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O(\ell)$	+1.69
	$HMnO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow MnO_2(s) + 2H_2O(\ell)$	+2.10
	$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+}(aq) + 2H_2O(\ell)$	+0.95
pH = 14	$2MnO_2(s) + H_2O(\ell) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$	+0.15
	$Mn_2O_3(s) + 3H_2O(\ell) + 2e^- \rightarrow 2Mn(OH)_2(s) + 2OH^-(aq)$	–0.23
	$Mn(OH)_2(s) + 2e^- \rightarrow Mn(s) + 2OH^-(aq)$	–1.19

(i) Explain why Mn(II) is not oxidised by O_2 in solutions at pH = 0, but is oxidised by O_2 solutions in which $[OH^-]$ is 1 mol L^{-1}.

$O_2(g) + 2H_2O(\ell) + 4e^- \rightarrow 4OH^-(aq)$ $E° = +0.40$ V (pH = 14)

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$ $E° = +1.23$ V (pH = 0)

(ii) $KMnO_4$ is a common oxidant, and in acidic conditions may be reduced to MnO_2 or Mn^{2+}.

Discuss why the intermediate species $HMnO_4^-$ does not accumulate during the reduction of MnO_4^- to MnO_2.

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(iii) Discuss the pH dependence of the stability of Mn(III) in aqueous solution.

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QUESTION FOUR

(a) (i) The normal pH in blood plasma is 7.40. The pH of body fluids is regulated by the presence of CO_3^{2-}, HCO_3^- and CO_2 dissolved in these fluids.

At 25°C, $K_a(H_2CO_3) = 4.2 \times 10^{-7}$ and $K_a(HCO_3^-) = 4.7 \times 10^{-11}$.

Identify the components from the list above that would form the best buffer at this pH and calculate their ratio.

Determine whether this buffer is more effective against added acid or base.

(ii) Lactic acid (HLac) is often said to be produced by the body during rapid exercise.

Show by calculation that lactic acid is mainly present as the lactate ion (Lac^-) at pH = 7.40.

pK_a(lactic acid) = 3.86

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(b) Predisposition for the condition known as gout occurs when the concentration of uric acid (HUr) and urate ions (Ur^-) in the blood becomes too high. Uric acid is a weak acid. $pK_a = 5.4$ at 37°C.

At 37°C, the solubility of sodium urate is 8.00×10^{-3} mol L^{-1} and the solubility of uric acid is 5.00×10^{-4} mol L^{-1}.

In blood serum, $[Na^+] = 0.130$ mol L^{-1} (ie at pH = 7.4 and temperature of 37°C).

(i) Calculate the maximum urate concentration at which sodium urate will not precipitate, and show by calculation that uric acid will not precipitate at this concentration either.

(ii) One form of kidney stone is made of crystals of uric acid. These can form when the concentration of uric acid and urate is high, and the pH of urine drops to around 5 to 6.

Calculate the pH at which these stones can form.

Assume that the total concentration of uric acid and urate is 2.00×10^{-3} mol L^{-1}.

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QUESTION FIVE

(a) Compound **A** has the molecular formula $C_4H_4O_4$. Compound **B** is a stereoisomer of Compound **A**. The melting points of Compound **A** and Compound **B** are 135°C and 287°C respectively, due to the ability of Compound **A** to form an intramolecular hydrogen bond. Compound **A** reacts, on heating, with dilute H_2SO_4 to form Compound **C**, $C_4H_6O_5$. Compound **C** is able to exist as enantiomers. Compound **A** will react with potassium permanganate to form Compound **D**, $C_4H_6O_6$. When Compound **D** is oxidised by periodate ions (IO_4^-), Compound **E** is produced. Compound **E** has the molecular formula $C_2H_2O_3$ and gives a positive test with Tollens' reagent (ammoniacal silver nitrate). Each molecule of Compound **D** produces 2 molecules of Compound **E**.

(i) Identify the structures of Compounds **A**–**E**. Justify your choice of the stereoisomers **A** and **B** and write a balanced equation for the reaction of Compound **E** with Tollens' reagent.

(ii) Draw two other isomers of Compound **A**: one that has different functional groups from Compound **A**, and another that has the same functional groups as Compound **A**.

Explain why neither of these isomers meet the requirements to be Compound **A** as described in part (a).

Question Five continues on the following page.

(b) Discuss the potential for Compound **C** to form polymers.

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Question	Mark
ONE	(8)
TWO	(8)
THREE	(8)
FOUR	(8)
FIVE	(8)
TOTAL	(40)