S

93102

931020

For Supervisor's use only

NZQA

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2007
Chemistry

2.00 pm Saturday 24 November 2007
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.

Answer ALL questions.

A periodic table is provided on page 2 of this booklet.

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 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

H 1.0

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	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									

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.

Assessor's use only

QUESTION ONE (8 marks)

(a) Discuss the misconceptions found in each of the following two statements. Your discussion should include a correct explanation with reference to the examples given.

(i) "*Chemical reactions occur to enable atoms to obtain full outer electron shells or octets".*
Eg hydrogen and chlorine gases react spontaneously to form hydrogen chloride.

(ii) "*Successive ionisation energies for any atom increase because when an electron is removed from an atom or ion, the remaining electrons receive an extra share of the attraction from the nucleus*."

Eg the first three ionisation energies for sodium are:

$Na(g) \rightarrow Na^{+}(g) + e^{-} \qquad \Delta H = 502 \text{ kJ mol}^{-1}$

$Na^{+}(g) \rightarrow Na^{2+}(g) + e^{-} \qquad \Delta H = 4569 \text{ kJ mol}^{-1}$

$Na^{2+}(g) \rightarrow Na^{3+}(g) + e^{-} \qquad \Delta H = 6919 \text{ kJ mol}^{-1}$

Assessor's use only

Assessor's use only

(b) Silane (SiH_4) ignites spontaneously in air to produce H_2O and SiO_2 (a giant covalent lattice with single bonds).

Use the table below to compare the heat of combustion of silane with that of methane, and discuss whether these values account for the differing reactions of these two compounds in air.

Assessor's use only

Bond	Bond enthalpy / kJ mol^{-1}
C–H	413
C–O	358
C=O	804
Si–H	323
Si–O	466
O–H	463
O=O	498

Assessor's use only

QUESTION TWO (8 marks)

Assessor's use only

(a) A sample of steel contains 10% nickel and 70% iron by mass.

0.200 g of this steel is dissolved completely in acid and the solution is diluted to 200 mL. The iron is then treated and separated by precipitation as iron(III) hydroxide.

Calculate the separate concentrations of iron and nickel ions in the 200 mL of solution. Then using the solubility product values below, determine the pH range over which iron can be precipitated so that no more than 0.100% of the iron remains in solution, while none of the nickel(II) hydroxide precipitates.

$K_s\,(Fe(OH)_3) = 2.79 \times 10^{-39}$ $K_s\,(Ni(OH)_2) = 5.48 \times 10^{-16}$

Assessor's use only

Assessor's use only

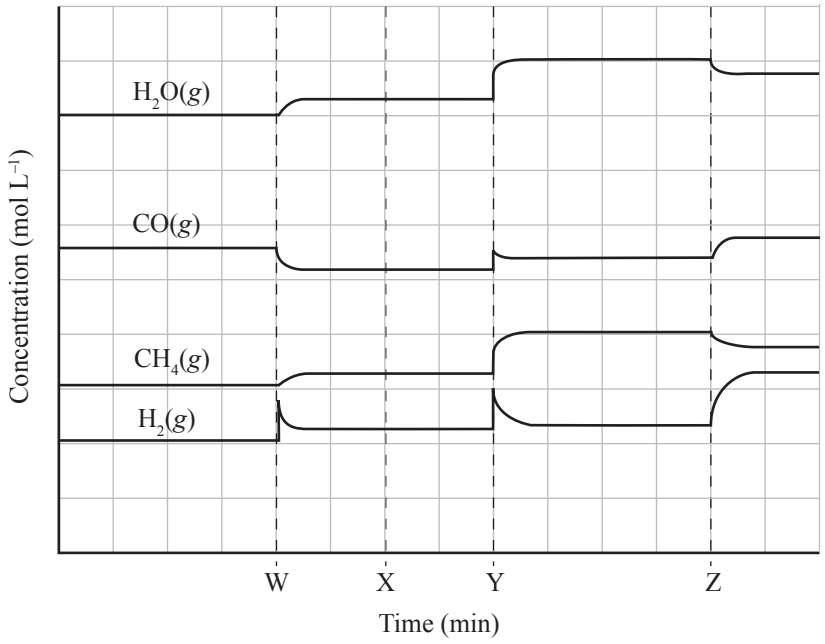
(b) The concentrations of the species present in a system at equilibrium can be altered by applying a variety of stresses to the system.

Typically these involve either

- increasing or decreasing pressure (by changing the total volume of the system or by adding an inert gas)
- addition or removal of heat
- addition or removal of one (or more) of the reactants or products.

The graph below shows changes in the concentration of the species present in a system involving the following reaction at equilibrium. The reaction is endothermic in the forward direction.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$



Discuss the nature of the stresses applied to the system at positions **W, X, Y** and **Z**, and how these stresses result in the changes in the concentrations of the species present in the system.

Assessor's use only

QUESTION THREE (8 marks)

Assessor's use only

(a) Primary chloroalkane molecules undergo substitution of the Cl^- by CN^- when warmed with potassium cyanide in ethanol. The organic molecule formed can then be warmed with dilute sulfuric acid to convert it into a carboxylic acid.

$$RCl \xrightarrow{KCN\,/\,ethanol} RCN \xrightarrow{H_2SO_4(aq)} RCOOH$$

Compound **A**, $C_5H_{11}OCl$, is an organic molecule with no branching in the carbon chain.

Reaction of Compound **A** with a solution of acidified potassium dichromate produces compound **B**, C_5H_9OCl. Compound **B** does not have any stereoisomers and has no reaction with Tollens' reagent.

When compound **A** is reacted with concentrated sulfuric acid it produces Compounds **C**, **D** and **E** (C_5H_9Cl). Compound **C** does not have stereoisomers, but Compound **D** and Compound **E** are geometric isomers of one another.

Compound **A** is reacted with potassium cyanide in ethanol to produce an organic compound that is warmed with dilute sulfuric acid to give compound **F** ($C_6H_{12}O_3$). On further heating with concentrated sulfuric acid a sweet smelling liquid, compound **G** ($C_6H_{10}O_2$) is produced.

Draw the structural formulae for compounds **A** – **G**, and justify your answers.

Assessor's use only

Assessor's use only

(b) You have 5 bottles labelled A to E. Each bottle contains one of the following liquids:
propanone,
water,
propan-2-ol,
methanol
hexane.

The following data were collected about the liquids.

Time for 1 drop of each sample to completely evaporate at room temperature:

Sample	Time (s)
A	135
B	more than 1200
C	65
D	30
E	20

Solubility of glucose, $C_6H_{12}O_6$, in each liquid (at room temperature):

B dissolved glucose in the greatest amount.
A and C dissolved a small amount of glucose.
E dissolved even less glucose than A and C.
D dissolved almost no glucose.

Miscibility (ability of two liquids to mix):

B and D were not miscible, forming two distinct layers.
A, B , C and E were miscible with one another.

Use the data above to identify the contents of each bottle, and justify your answer by relating the data to the structure and bonding of the compounds.

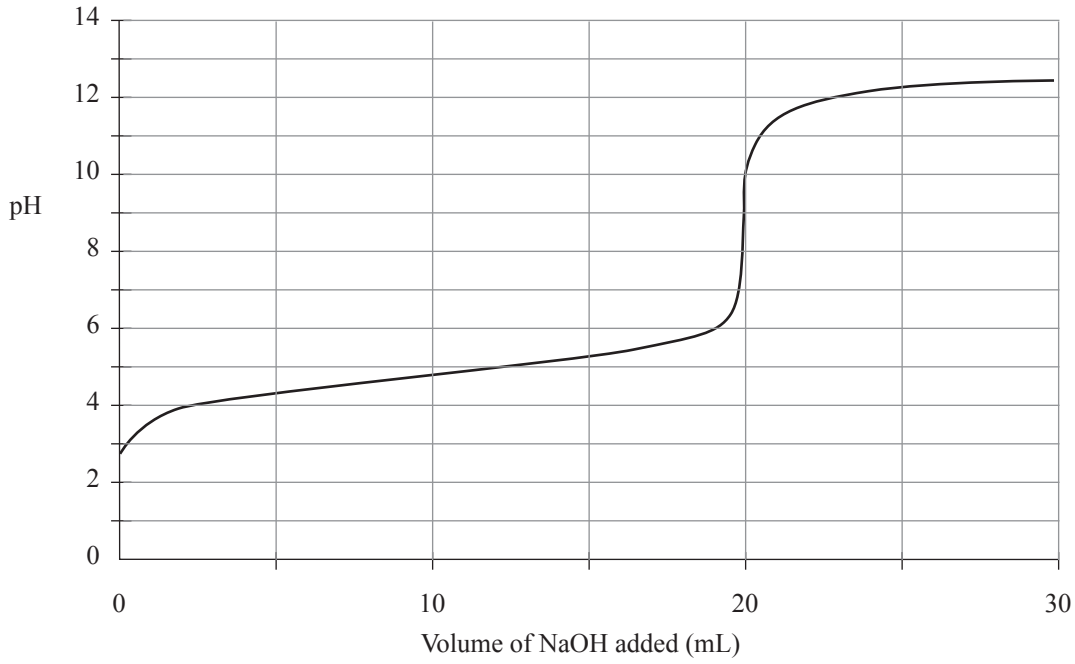
Assessor's use only

QUESTION FOUR (8 marks)

Assessor's use only

The titration curve below shows the change in pH as 0.100 mol L^{-1} NaOH(*aq*) is added to 10.0 mL of ethanoic acid, $CH_3COOH(aq)$.

Titration Curve



A second titration is carried out in which 0.100 mol L^{-1} NaOH(*aq*) is added to 10.0 mL of 0.200 mol L^{-1} hypobromous acid, HOBr, a weak acid with pK_a (HOBr) = 8.69.

(a) Calculate the initial pH of the HOBr solution and the pH at the equivalence point.

Assessor's use only

(b) (i) Sketch the second titration curve on the graph opposite (from 0.0 mL NaOH to addition of 25.0 mL of NaOH).

(ii) Discuss similarities and differences between the two curves.

Assessor's use only

(iii) Explain, in terms of the species present in solution, why the pH of the HOBr titration curve halfway to equivalence point is basic, while the pH of CH_3COOH curve at the same point is acidic.

Assessor's use only

(iv) 5.0 mL of 0.100 mol L^{-1} NaOH(*aq*) is added to a mixture of 10.0 mL of 0.200 mol L^{-1} HOBr(*aq*) and 10.0 mL of 0.200 mol L^{-1} CH_3COOH(*aq*).

Consider the relative strengths of the acids and calculate the pH of the resulting mixture.

QUESTION FIVE (8 marks)

Assessor's use only

(a) Glycerine, a mixture of glycerol and water, weighing 100.0 mg was treated with 50.0 mL of 0.0837 mol L^{-1} Ce^{4+} solution in 4 mol L^{-1} HCl at 60°C for 15 minutes. The excess Ce^{4+} solution needed 12.11 mL of 0.0448 mol L^{-1} iron(II) ammonium sulfate to reach the end point.

The unbalanced equations are:

$$\underset{\text{(glycerol)}}{HOCH_2CH(OH)CH_2OH} \rightarrow \underset{\text{(methanoic acid)}}{HCOOH}$$

$$Ce^{4+} \rightarrow Ce^{2+}$$

$$Fe^{2+} \rightarrow Fe^{3+}$$

(i) Calculate the percentage glycerol in the glycerine sample.
M(glycerol) = 92.0 g mol^{-1}

Assessor's use only

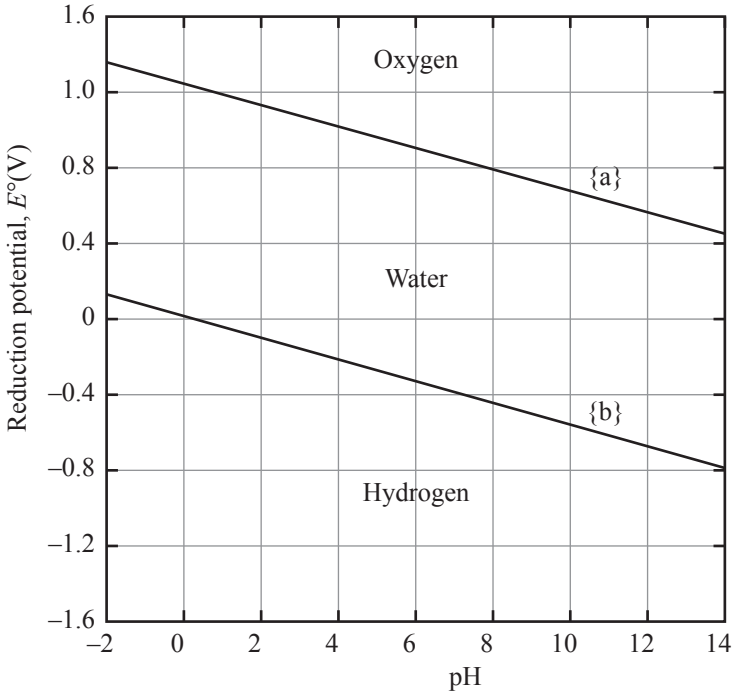
(ii) Discuss why a back titration is used and compare the errors introduced in a back titration with a direct titration.

Assessor's use only

(b) The lines on the diagram below show the variation in reduction potential of water with acidity for the following reactions.

Line {a}: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$

Line {b}: $2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$



Use the information from this diagram to answer the question below.

Discuss how the vanadium species present in aqueous solution (saturated with oxygen) changes as the pH is raised from 0 to 14.

$VO_2^+ + 2H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O$ $\quad E° = +1.00$ V

$VO^{2+}(aq) + 2H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O$ $\quad E° = +0.34$ V

Assessor's use only

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

Assessor's use only

Question number	

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

Assessor's use only

Question number	

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

Assessor's use only

Question number	

93102

For Assessor's Use Only	
Question Number	Marks
Q1	(8)
Q2	(8)
Q3	(8)
Q4	(8)
Q5	(8)
TOTAL	(40)

For Assessor's Use Only.

Keep Flap Folded In.