S

93102

931020

For Supervisor's use only

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2009
Chemistry

9.30 am Saturday 28 November 2009
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.

You should answer ALL the questions in this booklet.

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 2–25 in the correct order and that none of these pages is blank.

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: 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									

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) (i) Draw a 3-dimensional structure for each of the possible isomers of the pentahalide PCl_3F_2, indicating the size of the F-P-F bond angle in each isomer.

(ii) In VSEPR theory it is assumed that the bond from the central atom to an atom of lower electronegativity occupies more space than the bond from the central atom to an atom of higher electronegativity.

Comment on the polarity of each of the isomers of PCl_3F_2 and identify the isomer that is most likely to occur.

(iii) Upon standing for several days at low temperature, phosphorus pentahalide compounds convert to isomeric ionic solids.

In crystalline PBr_4Cl, only one of the two ions formed contains phosphorus.

Predict the formulae of the ions in solid PBr_4Cl, and justify your answer.

Assessor's use only

(b) Two possible isomers may be formed when H^+ reacts with isocyanate, NCO^-, as the H^+ may bond to either nitrogen or oxygen. A structural study of one of the isomers that is produced shows that it has a bond angle of 105° at the atom to which the H is attached.

- Draw Lewis diagrams for the two possible structures of the product.
- Identify and explain which Lewis diagram better represents the structure of the product with the bond angle of 105° mentioned above.

Assessor's use only

QUESTION TWO (8 marks)

Assessor's use only

(a) Titanium is a Group 4 transition metal. There are three different chlorides of titanium: $TiCl_2$, $TiCl_3$ and $TiCl_4$. One of these chlorides, **A,** is a solid that dissolves in water to produce a mildly acidic purple solution. On standing in the presence of air, the colour of this solution fades, and a white solid, TiO_2, is formed. The chlorides **B** and **C** are very reactive toward water. **B** is a liquid and reacts to produce a strongly acidic solution and TiO_2. **C** reacts with acidified water to produce a purple solution and hydrogen gas.

(i) Identify which of the chlorides of titanium is **A**, which is **B** and which is **C**.

Justify your answers using the properties of transition metals, including the colours and reactions outlined above, and/or by analogy with the chemistry of other transition metals. Include balanced equations for the reactions described.

Assessor's use only

(ii) Determine the upper limit for the reduction potential for each of the Ti(IV) / Ti(III) couple and the Ti(III) / Ti(II) couple.

$E^o(H_2O/H_2) = -0.42$ V $\qquad E^o(O_2/H_2O) = 0.82$ V

(b) Titanium occurs naturally both as ilmenite ($FeTiO_3$) and TiO_2. The isolation of titanium metal from ilmenite involves heating ilmenite, chlorine and carbon to form $TiCl_4$. This is then converted into titanium metal by treatment with magnesium.

$$2FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO$$

Discuss the possible oxidation number changes and electron transfers that occur in the conversion of ilmenite to $TiCl_4$, taking into consideration the variety of oxidation numbers that are possible for the metals.

Assessor's use only

QUESTION THREE (8 marks)

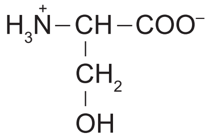
Assessor's use only

(a) (i) The structural formula of the amino acid glycine can sometimes be written as $H_3\overset{+}{N}CH_2COO^-$ (a zwitterion) and sometimes as H_2NCH_2COOH.

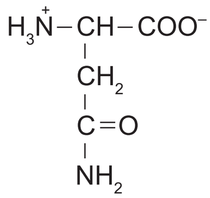
Explain which structure is more appropriate, taking into account functional group chemistry and the fact that glycine is a crystalline solid that has a melting point of 233°C.

Assessor's use only

(ii) The amino acids serine and asparagine have the zwitterion structures shown below.



serine



asparagine

These amino acids can be linked to form two different dipeptides.

Discuss how the structures of these dipeptides change as the pH of the aqueous solutions change from highly acidic, through neutral, to highly basic.

Include structural formulae in your answer.

(b) Esters are hydrolysed by reaction with dilute acid. This reaction and the purification of the organic products involve the use of both reflux and distillation.

Discuss how each of these two processes is involved in preparing and isolating pure samples of the organic products.

Assessor's use only

Assessor's use only

(c) Compound **A** has the formula $C_9H_{18}O_3$.

When compound **A** is refluxed with dilute sulfuric acid, it forms compound **B**, $C_6H_{12}O_3$ and compound **C**, C_3H_8O. Both compounds **B** and **C** react with acidified potassium dichromate to produce compounds **D**, $C_6H_{10}O_3$ and **E**, C_3H_6O respectively. Neither compound **D** nor **E** reacts with Tollens' reagent.

When compound **B** is reacted with concentrated sulfuric acid, it produces THREE structural isomers **F**, **G** and **H**, of molecular formula $C_6H_{10}O_2$, all of which are optically active. **F** exists as geometrical isomers, but **G** does not. Both **F** and **G** decolourise a solution of bromine, **H** does not.

Give the structural formulae for compounds **A** to **H** that are consistent with the information above.

Space for working.

Assessor's use only

QUESTION FOUR (8 marks)

Assessor's use only

(a) Models are representations used to explain observed phenomena.

A model useful for describing the physical properties of Group 18 elements views the particles of these elements as individual atoms.

In contrast, various properties of metals, both in solid and liquid form, can be explained by a model that views the structure of the metal as cations submerged in a "sea of electrons". In this model, the "electron sea" consists of valence electrons moving freely throughout the metal structure.

The table below shows the melting points (mp) and boiling points (bp) for selected elements in Groups 1 and 18 of the periodic table.

1	*2*		*13*	*14*	*15*	*16*	*17*	*18*
Li mp: 180°C bp: 1342°C	**Be**							**Ne** mp: –249°C bp: –246°C
Na mp: 98°C bp: 883°C	**Mg**							**Ar** mp: –189°C bp: –186°C
K mp: 63°C bp: 760°C	**Ca**							**Kr** mp: –157°C bp: –152°C
Rb mp: 39°C bp: 686°C	**Sr**							**Xe** mp: –112°C bp: –108°C

(i) Explain the trend in boiling points of the Group 18 elements.

(ii) Discuss how each of the statements below is evidence for the different models described above.

- *The boiling point of a Group 18 element is significantly lower than the boiling point of the Group 1 element with the next higher atomic number.*
- *The* ***difference*** *between the boiling point and the melting point of a Group 1 metal, such as sodium, is much larger than the* ***difference*** *between the boiling point and melting point of a Group 18 element, such as argon.*

(iii) Predict, using the "electron sea" model described above, how the boiling points for the Group 1 metals would compare with those for the Group 2 metals.

Assessor's use only

(b) The standard enthalpy of atomisation, $\Delta_{at}H^{\circ}$, is defined as the enthalpy change when 1 mole of atoms, in the gas phase, is formed from the element in its standard state at 25°C.

Assessor's use only

Element	**Standard Enthalpy of Atomisation, $\Delta_{at}H^{\circ}$ / kJ mol^{-1}**
C	717
F	79
Cl	122

	Bond Enthalpy / kJ mol^{-1}
C–F	485
C–Cl	328

Calculate the standard enthalpy of formation, $\Delta_{f}H^{\circ}$, of trichlorofluoromethane, $CCl_3F(g)$.

QUESTION FIVE (8 marks)

Assessor's use only

(a) When silver ions are dissolved in an aqueous ammonia solution, complex ions of $Ag(NH_3)_2^+(aq)$ form. The formation of $Ag(NH_3)_2^+(aq)$ occurs in two steps that are represented by the equations below, together with the corresponding equilibrium constant for each reaction.

$$Ag^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)^+(aq) \qquad K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_2 = 8.2 \times 10^3$$

0.15 mol of $AgNO_3(s)$ is dissolved in 1.00 L of a 1.00 mol L^{-1} solution of aqueous ammonia.

Use the values of the equilibrium constants to identify the major species in this solution at equilibrium, and hence calculate the concentrations in mol L^{-1} of the Ag^+, $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ ions.

Assessor's use only

(b) 15.35 g of a mixture of sodium nitrate, $NaNO_3$, and magnesium nitrate, $Mg(NO_3)_2$, was heated until no more gases were evolved. The $NaNO_3$ decomposes giving sodium nitrite, $NaNO_2$, and oxygen gas, while the $Mg(NO_3)_2$ decomposes to give the metal oxide, nitrogen dioxide and oxygen. The water-soluble part of the residue produced on heating was used to prepare 1.00 L of solution. 10.00 mL of this solution was reacted with 20.00 mL of 0.0200 mol L^{-1} acidified potassium permanganate (which oxidises nitrite to nitrate). The excess potassium permanganate required 10.25 mL of 0.0500 mol L^{-1} oxalic acid, $H_2C_2O_4$, for complete reaction in which oxalic acid is oxidised to form CO_2.

Write balanced equations for all of the reactions occurring above, and hence calculate the mass, in grams, of each metal nitrate present in the original mixture.

Assessor's use only

QUESTION SIX (8 marks)

Assessor's use only

Three flasks contain aqueous solutions of the **same pH**. One of the solutions is 0.0010 mol L^{-1} nitric acid, one is 0.0060 mol L^{-1} methanoic acid (HCOOH) and one is 0.040 mol L^{-1} anilinium hydrochloride ($C_6H_5NH_3Cl$).

(a) Use the information above to calculate the pK_a for HCOOH and for $C_6H_5NH_3^+$.

Explain why the different concentrations of the three acids produce the same pH.

(b) The three acid solutions in part (a) are diluted by a factor of 10.

Discuss the change in both the pH of each of the solutions and the concentrations of the species present.

NO CALCULATIONS ARE REQUIRED.

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

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
ONE	(8)
TWO	(8)
THREE	(8)
FOUR	(8)
FIVE	(8)
SIX	(8)
TOTAL	(48)

For Assessor's use only.
Keep flap folded in.