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NZQA

NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2010
Chemistry

9.30 am Saturday 20 November 2010
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 of 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 2–30 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									

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.

QUESTION ONE (8 marks)

(a) Most metal sulfides are very slightly soluble in water. The solubility constant for thallium(I) sulfide is 6×10^{-22} at 25°C. The hydrosulfide ion, HS^-, has a pK_a of 11.96. The atomic number of thallium is 81.

Calculate the solubility of thallium(I) sulfide at 25°C. Discuss how changing the pH of the solution, by the addition of acid or base, affects the solubility of thallium(I) sulfide.

(b)   The data in the table below show physical properties for some organic compounds for which the size of the electron cloud is similar.

The dipole moment is a measure of the polarity of a molecule.

	Name	Compound	Dipole moment/D	Boiling point/°C
1	pentane	$CH_3CH_2CH_2CH_2CH_3$	0	36
2	ethoxyethane	$CH_3CH_2–O–CH_2CH_3$	1.15	35
3	butan-1-amine	$CH_3CH_2CH_2CH_2NH_2$	1.42	78
4	butan-1-ol	$CH_3CH_2CH_2CH_2OH$	1.52	118
5	butanone	$CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$	2.76	80

Account for the differences in the properties of the molecules.

Include in your discussion, a comparison of the relative contribution of the types of intermolecular forces to the overall attractive force between the molecules in relation to the dipole moment and boiling point.

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QUESTION TWO (8 marks)

(a) The second ionisation energy is the energy required for the complete removal of one mole of electrons from one mole of gaseous ions.

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

The graph shows the second ionisation energy for the elements of Period 4.
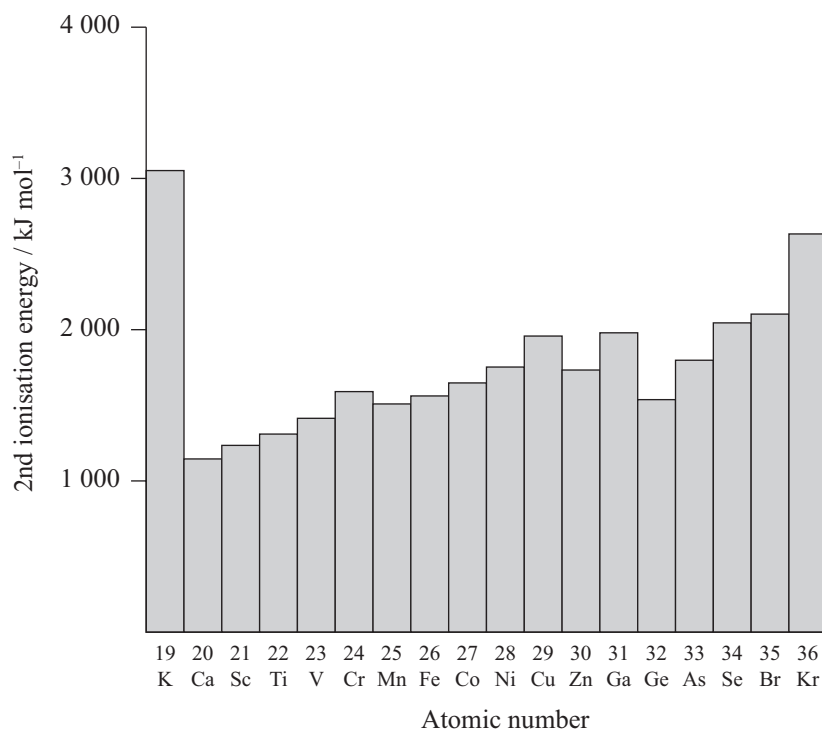
Discuss the trend in second ionisation energy for the elements of Period 4. Account for deviations from the trend in terms of electron configuration.

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(b) 0.746 g of a mixture of sodium chloride and potassium chloride was dissolved in water and made up to 250 mL of solution in a volumetric flask. A 50.00 mL portion of this solution required 25.6 mL of 0.0970 mol L^{-1} silver nitrate solution for titration to the end point.

Calculate the percentage of sodium chloride in the mixture.

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QUESTION THREE (8 marks)

(a)   Nicotinic acid is a compound that can act both as an acid and as a base. When dissolved in water it exists as a zwitterion, as shown in the diagram below.
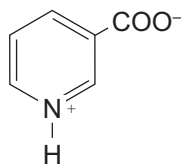
$$pK_{a_1} = 3.0 \qquad pK_{a_2} = 4.9$$

(i)   Predict the pH range of a solution of nicotinic acid in water.

- Justify your answer, using the K_a expression.
- Include in your answer the structures of the conjugate acid and conjugate base of nicotinic acid and assign the pK_a values given above to their functional group.
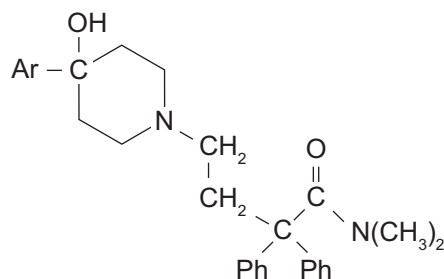
No calculations are required.

(ii) An aqueous solution of nicotinic acid is titrated with sodium hydroxide.

Predict the pH at the centre of the buffer region, and justify your answer.
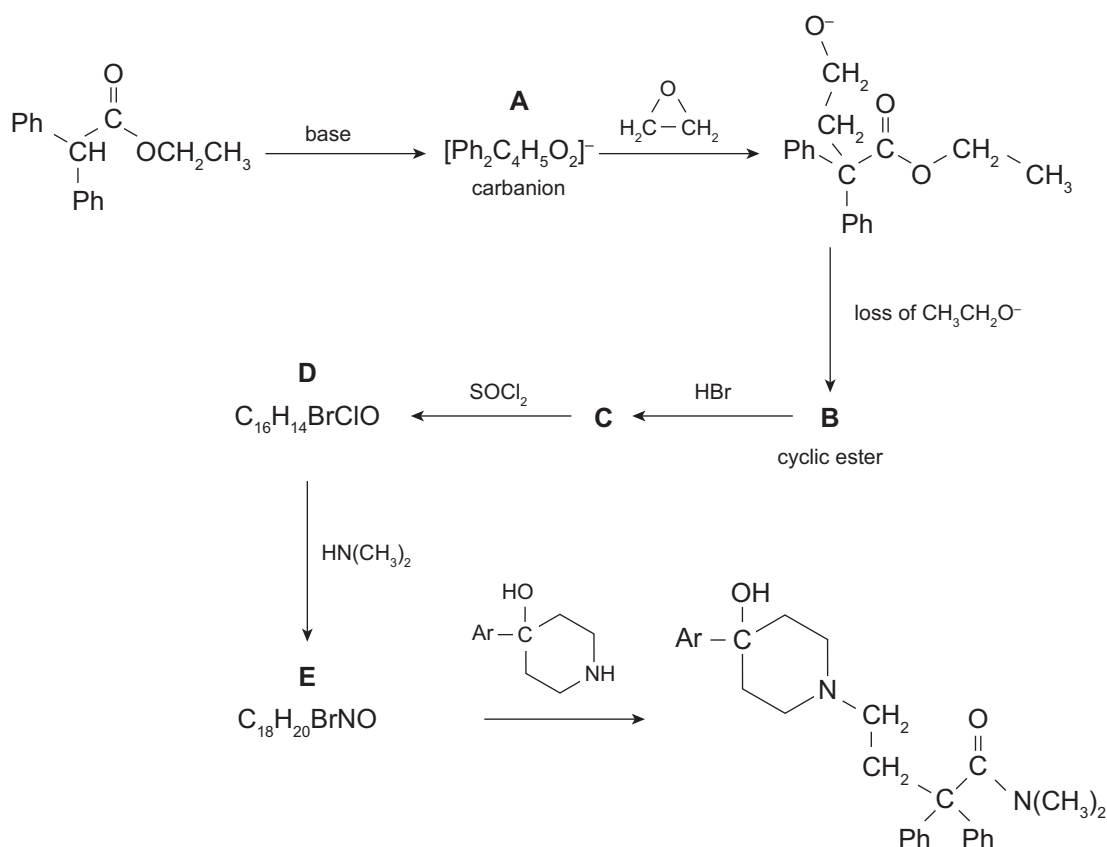*No calculations are required.*

(b)   The compound shown below is loperamide, an anti-diarrhoea medicine.

Note that Ph represents a phenyl group (C₆H₅) and Ar represents *p*-chlorophenyl (C₆H₄Cl).
Each corner of the ring is a −CH₂− group.

A possible synthesis of this compound involves several steps and intermediate compounds, some of
which are isolated and purified.

Additional information: The cyclic ester **B** has both the carbonyl carbon and the oxygen
as part of a ring.

(i)   Draw the structures of intermediates **A** to **E**.

You may prefer to start from the final product and work backward.

(ii) Drugs are often administered as salts that are prepared by reaction of the organic compound with either strong acid or base.

Suggest a reason why loperamide would be better administered as a salt.

Explain how a suitable salt of loperamide could be prepared.

Justify your answer and include a structural formula of the salt.

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QUESTION FOUR (8 marks)

(a) Compounds **M**, **N**, **O**, **P** and **Q** may all be formed by the reaction of the hydrocarbon C_7H_{14} (**R**) with chlorine gas in the presence of light. The structures of the compounds **M** to **R** may be deduced from the information below.

- Compound **R** is a six or seven carbon ring.
- Compounds **M**, **N**, **O**, **P** and **Q** all have the formula $C_7H_{13}Cl$.
  - Only **O** and **P** have chiral carbons and can exist as enantiomers.
- **M**, **N**, **O**, **P** and **Q** react with KOH in ethanol to give various isomers of C_7H_{12}.
  - **M** and **Q** each react to give one C_7H_{12} isomer.
  - **N**, **O** and **P** each react to give two C_7H_{12} isomers.
  - Both C_7H_{12} isomers arising from **P** and the C_7H_{12} isomer arising from **Q** can exist as pairs of enantiomers.

Identify compound **R**.

Draw structures for **M** to **Q** and the alkene products arising from their reaction with KOH in ethanol.

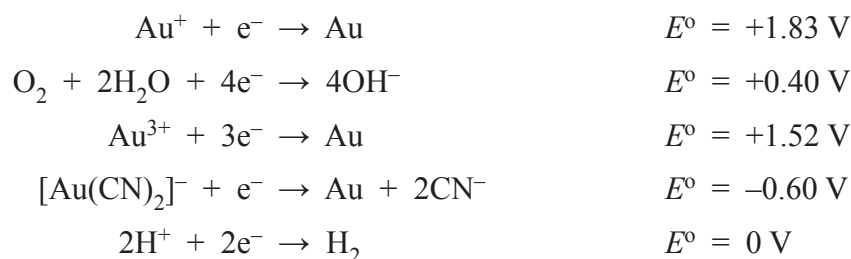Justify your choices on the basis of the information given above.

(b) Gold and silver are extracted from finely ground ore by complexing with cyanide ions (CN⁻) to give soluble complex ions [M(CN)₂]⁻. Gold occurs in its elemental form, and silver is found in the same deposits as silver sulfide.

Sodium cyanide solution is sprayed over the ore in the presence of oxygen. Soluble sodium dicyanoaurate(I), Na[Au(CN)₂], and sodium dicyanoargentate(I), Na[Ag(CN)₂], are collected. The process is carried out at pH 10.5.

$$Au^+ + e^- \rightarrow Au \qquad\qquad E^o = +1.83 \text{ V}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad\qquad E^o = +0.40 \text{ V}$$

$$Au^{3+} + 3e^- \rightarrow Au \qquad\qquad E^o = +1.52 \text{ V}$$

$$[Au(CN)_2]^- + e^- \rightarrow Au + 2CN^- \qquad\qquad E^o = -0.60 \text{ V}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad E^o = 0 \text{ V}$$

$$K_a(HCN) = 6.17 \times 10^{-10}$$

Show, using the electrode potentials given above, that the recovery of gold by the cyanidation process is preferred to the possible alternative of dissolving the ore in hydrochloric acid.

Include balanced equations in your answer.

Discuss any difference in the chemistry of the recovery of gold and silver by the cyanidation process.

Discuss why the process is carried out at pH 10.5

QUESTION FIVE (8 marks)

(a) Five elements designated as **V**, **W**, **X**, **Y**, **Z** have the following properties. Note that these letters bear no relationship to the symbols of the elements.

- Elements **V** and **Z** have the same number of valence electrons.
- The molar mass of the elemental form of element **V** is 2.00 g mol^{-1}.
- Element **W** is the most reactive member of its group, which contains only non-metals.
- The valence electrons of elements **X**, **Y** and **Z** are in the same shell.
- Element **Y** has a lower first ionisation energy than element **X**.
- Elements **Z** and **Y** react to form the compound Z_2Y, which dissolves in water to give a basic solution that conducts electricity.
- Element **V** reacts with element **X** to form XV_3, a poisonous gas.
- The ions of elements **W** and **Z** have the same total number of electrons.
- Element **V** reacts with element **W** to form **VW**, a gas at 25°C.
- Element **V** reacts with element **Z** to form **ZV**, an ionic solid.

Identify each of the five elements **V**, **W**, **X**, **Y**, **Z**.

Justify your answers.

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(b) A solution containing sodium carbonate and sodium hydrogencarbonate was analysed by titration with 0.143 mol L^{-1} hydrochloric acid. A 25.00 mL portion of this solution needed 21.45 mL of hydrochloric acid for titration to reach the end point. Methyl orange was used as the indicator.

A second 25.00 mL portion was taken and treated with 10.00 mL 0.128 mol L^{-1} sodium hydroxide. Barium chloride was added to precipitate the carbonate ions as barium carbonate, which was then quantitatively removed by filtration. The excess sodium hydroxide was titrated with the same hydrochloric acid, using phenolphthalein as indicator. 6.23 mL of hydrochloric acid was needed to reach the end point.

pK_a(methyl orange) $= 3.7$ $\qquad$ $pK_a(H_2CO_3) = 3.6$

pK_a(phenolphthalein) $= 9.3$ $\qquad$ $pK_a(HCO_3^-) = 10.3$

(i) Calculate the concentrations of sodium carbonate and sodium hydrogencarbonate in the solution.

(ii) An alternative method for analysing solutions of carbonate and hydrogencarbonate ions involves directly titrating the mixture with hydrochloric acid using two indicators with different pK_a values. The first titration is carried out using phenolphthalein. Another sample, of the same volume, is then titrated with the same acid, using methyl orange indicator.

Comment on the sources of error in the two methods described, and explain which is the more reliable method.

(iii) Suggest a compound that could be used as a primary standard for the standardisation of the hydrochloric acid.

Discuss the criteria that should be considered when selecting a primary standard and comment on how well the compound you have suggested meets those criteria.

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