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NEW ZEALAND QUALIFICATIONS AUTHORITY
MANA TOHU MĀTAURANGA O AOTEAROA

Scholarship 2008
Chemistry

9.30 am Saturday 15 November 2008
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.

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 2–22 in the correct order and that none of these pages is blank.

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** 63.6	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.

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QUESTION ONE (8 marks)

(a) Labels have fallen off six bottles known to contain the following aqueous solutions.

$NaCl$ KI Na_2CO_3 $Fe(NO_3)_3$ $NaOH$ $Zn(NO_3)_2$

Outline a procedure that uses only the contents of the unlabelled bottles to identify each solution. Include balanced equations for any reactions that occur.

Use the following information where it is relevant.

$E°(Cl_2 / Cl^-) = +1.36$ V $E°(I_2 / I^-) = +0.54$ V

$E°(Fe^{3+} / Fe^{2+}) = +0.77$ V $E°(Fe^{2+} / Fe) = –0.44$ V $E°(Zn^{2+} / Zn) = –0.76$ V

(b) A sample of water is to be analysed to determine the chloride ion content. Before carrying out the analysis, a pH meter is used to ensure the pH of the water is in the range 7–8. If the solution is too basic, 1 mol L^{-1} ethanoic acid is added dropwise until the pH is reduced to just below 8. If the solution is too acidic, 1 mol L^{-1} sodium carbonate solution is added until the pH is increased to just below 8.

A 20.00 mL sample of water containing chloride ions was placed in a conical flask and 3.00 mL of 0.100 mol L^{-1} K_2CrO_4 solution was added as an indicator. The resulting solution was then titrated with 0.0500 mol L^{-1} silver nitrate solution, causing the formation of a precipitate of AgCl. 18.35 mL was required to reach the end-point of the titration, the point when there is a slight red-brown tinge due to the formation of a red-brown precipitate of silver chromate.

(i) In terms of the species present in the flask during the titration, explain why there would be a problem in the analysis if the solution were very acidic, and also why there would be a problem if the solution were very basic.

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(ii) Calculate the concentration of chloride ions remaining in the solution at the point when the silver chromate starts to form. Show that the amount, in moles, of chloride ions remaining in the solution at the end-point is less than 0.1% of the original amount present.

K_s (AgCl) = 1.77×10^{-10} K_s (Ag_2CrO_4) = 2.60×10^{-12}

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QUESTION TWO (8 marks)

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(a) In order to identify the organic compound **A** with molecular formula $C_{10}H_{18}O_3$, the following series of reactions was carried out.

$$\mathbf{A} \xrightarrow{\text{dil. } H_2SO_4} \mathbf{B}: C_4H_8O_3 + \mathbf{C}: C_6H_{12}O$$

$$\mathbf{B} \xrightarrow{\text{conc. } H_2SO_4} \mathbf{D}: C_4H_6O_2$$

$$\mathbf{D} \xrightarrow{MnO_4^- / H^+} \mathbf{E}$$

$$\mathbf{E} \xrightarrow{Cr_2O_7^{2-} / H^+} \mathbf{F}: C_4H_6O_5$$

$$\mathbf{F} \xrightarrow{\text{conc. } H_2SO_4} \mathbf{G}: C_4H_4O_4$$

Deduce the structures of Compounds **A** to **G**.

Additional information:
Compound **A** exists as enantiomers (optical isomers).
Compound **C** has a six-membered ring.

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(b) The compound **X** can be synthesised from the given starting materials: benzoic acid, methanamine and 4–chloro–3,5–dimethylcyclopent–1–ene.

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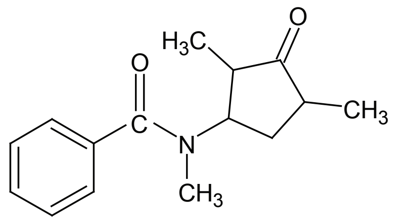
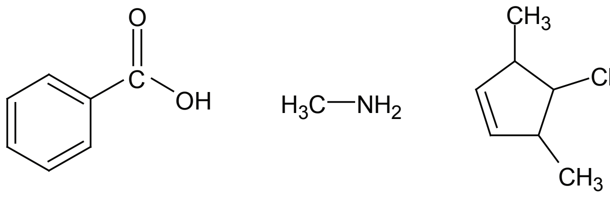


Compound X



Starting Materials

Note: For clarity, the hydrogens have been left off the cyclopentane and benzene rings.

Draw a reaction scheme to show how compound **X** can be synthesised from the starting materials. Give an explanation for the order in which the reactions are carried out.

The following reagents are available:

$SOCl_2$
NaOH(*aq*)
NaOH(*in ethanol*)
Conc HCl
MnO_4^-/H^+
$Cr_2O_7^{2-}/H^+$

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QUESTION THREE (8 marks)

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(a) Nitrogen trihalide compounds have varying stability. At room temperature, nitrogen triiodide, NI_3, is a black-red solid. When it is touched, it decomposes violently into its elements, nitrogen gas and solid iodine. At room temperature, nitrogen trichloride, NCl_3, is a pale yellow oil that is explosive. In contrast, nitrogen trifluoride, NF_3, is a colourless gas, which does not react with water, and only reacts with most metals on heating. Unlike NH_3, NF_3 does not act as a base.

DATA

Average bond enthalpies ($kJ\ mol^{-1}$)

F–F	+159
I–I	+151
N–F	+278
N–I	+159
N≡N	+945

Pauling electronegativities

H	2.20
N	3.04
F	3.98
Cl	3.16
I	2.66

$\Delta_{sub}H°(I_2) = 62\ kJ\ mol^{-1}$

Account for:

(i) the different states of the nitrogen trihalide compounds at room temperature

(ii) the different stability of NF_3 and NI_3 towards decomposition

(iii) the differing basicities of NF_3 and NH_3.

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(b) (i) A lithium atom has 3 electrons. The accepted model for the ground state electronic structure of Li is that 2 electrons occupy the lowest energy level, with the remaining electron occupying a higher energy level.

	1st IE / kJ mol^{-1}
Li	526
He	2379

Discuss how the relative ionisation energies of Li and He are consistent with this model rather than the alternative that has all 3 electrons of a lithium atom in the lowest energy level.

(ii) Match the following atoms and ions to the radii given. Justify your answer.

Atom or Ion	Ga	Ga^{3+}	Se^{2-}	Se	S
Radius / pm	122	198	62	103	135

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QUESTION FOUR (8 marks)

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(a) (i) A 'Latimer Diagram' can be used to summarise the reduction potential data for elements that exist in several oxidation states in aqueous solutions. The oxidation numbers decrease from left to right and $E°$ for each couple is written above the line joining the two species involved in the couple.
The Latimer Diagram below shows the standard electrode potentials for chlorine in basic conditions.

$$ClO_4^- \xrightarrow{+0.37\text{ V}} ClO_3^- \xrightarrow{+0.30\text{ V}} ClO_2^- \xrightarrow{+0.68\text{ V}} ClO^- \xrightarrow{+0.42\text{ V}} Cl_2 \xrightarrow{+1.36\text{ V}} Cl^-$$

In disproportionation reactions, an atom in a particular oxidation state acts as both the oxidant and the reductant.

Account for the disproportionation of Cl_2 in basic aqueous solution, and identify any other chlorine species that will disproportionate in these conditions. Explain how the extent of disproportionation of Cl_2 is pH dependent.

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(ii) At a pH of 6.5, an aqueous solution of hypochlorous acid, HClO, at 20°C is 7.6% dissociated.

Calculate the pK_a of HClO and hence find the pH of a 40 mg L^{-1} solution of $Ca(ClO)_2$.

$M(Ca(ClO)_2) = 143.0 \text{ g mol}^{-1}$

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(b) Solutions of quinine, like those of sodium hypochlorite, NaClO, are basic. Solutions of quinine can be standardised by titration with hydrochloric acid.

(i) Explain why hydrochloric acid is not used to standardise NaClO.

(ii) The solubility of quinine is 0.577 g L^{-1}.

pK_a (quinineH^+) = 8.9 M(quinine) = 324.4 g mol^{-1}

Calculate the pH at the equivalence point when 100.0 mL of a saturated solution of quinine is titrated against 0.0100 mol L^{-1} HCl.

QUESTION FIVE (8 marks)

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(a) A calorimeter that is perfectly heat insulated is filled with water that is initially at a temperature of 22.55°C.
7.80 g of solid $ZnSO_4$ is added, and the mixture is stirred until the solid completely dissolves. The temperature of the water increases to 23.52°C.

In a second experiment the same calorimeter is filled with water that is initially at a temperature of 22.15°C. When 12.30 g of the salt $ZnSO_4.7H_2O$ is added to the water the temperature drops to 21.84°C as a result of the dissolution process.

The heat capacity of the calorimeter and its contents is 0.900 kJ °C^{-1}.

Calculate $\Delta_r H$ for the following process:

$$ZnSO_4(s) \quad + \quad 7H_2O(\ell) \quad \rightarrow \quad ZnSO_4.7H_2O(s)$$

$M(ZnSO_4) = 161.5 \text{ g mol}^{-1}$

(b) The box below contains data relating to the dissolving process for $MgCl_2$ and AgCl.

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The **lattice enthalpy**, $\Delta_{LE}H°$, of an ionic solid is the enthalpy change when 1 mole of the ionic solid is separated into its ions in the gas phase. For example the lattice enthalpy for $MgCl_2$ is the energy change for the reaction:

$$MgCl_2(s) \rightarrow Mg^{2+}(g) + 2Cl^-(g)$$

The **enthalpy of solution** is the enthalpy change that occurs when 1 mole of solid dissolves to form a solution.

The **enthalpy of hydration**, $\Delta_{hyd}H°$, is the enthalpy change when 1 mole of gaseous ions is hydrated. For example:

$$Mg^{2+}(g) \rightarrow Mg^{2+}(aq)$$

	Melting points /°C
$MgCl_2$	714
AgCl	455

	Lattice enthalpy $\Delta_{LE}H°$/ kJ mol^{-1}
$MgCl_2(s)$	2523
$AgCl(s)$	915

	$\Delta_{hyd}H°$ / kJ mol^{-1}
Ag^+	–474
Mg^{2+}	–1931
Cl^-	–361

Explain why it is possible to dissolve some ionic solids in water in spite of the strong ion–ion forces of attraction in the crystal lattice of the solid. Use the data given to support your explanation and to outline factors that contribute to $MgCl_2$ being a more soluble salt than AgCl.

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

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Question Number	Marks
ONE	(8)
TWO	(8)
THREE	(8)
FOUR	(8)
FIVE	(8)
TOTAL	(40)