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QUALIFY FOR THE FUTURE WORLD
KIA NOHO TAKATŪ KI TŌ ĀMUA AO!

Scholarship 2015
Chemistry

9.30 a.m. Friday 27 November 2015
Time allowed: Three hours
Total marks: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

Pull out Resource Sheet S–CHEMR from the centre of this booklet.

You should answer ALL the questions in this booklet.

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 2–20 in the correct order and that none of these pages is blank.

You are advised to spend approximately 45 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

Question	Mark
ONE	
TWO	
THREE	
FOUR	
TOTAL	/32

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QUESTION ONE

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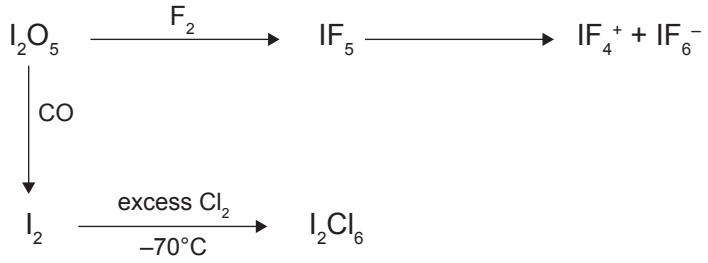
Almost all the elements of the periodic table form halides, which may be simple molecular compounds, ionic compounds or infinite atomic arrays. When interhalogen compounds form, there is often more than one possible product, depending on the temperature of the reaction or the relative proportions of the halogens.

(a) IF_5 can be formed by the action of F_2 on diiodine pentoxide, I_2O_5. IF_5 self-ionises to IF_4^+ and IF_6^-.

I_2 can be extracted from I_2O_5 with CO.

I_2Cl_6 is produced by reacting I_2 with excess Cl_2 at −70°C.



(i) Predict, with reasoning, the shape of the ions IF_4^+ and IF_6^-.

Include a diagram and suggested bond angles in your answer.

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(ii) I_2Cl_6 is a molecular compound. Molecules of I_2Cl_6 are symmetrical with no I–I bonds. Al_2Cl_6 is also a molecular compound, containing symmetrical molecules with no Al–Al bonds.

Compare and contrast the geometry around the I and Al atoms in these molecules, and predict, on the basis of the molecular structure, which of the compounds would have the higher melting point.

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(b) Diiodine pentoxide (I_2O_5) can be used to determine quantitatively the concentration of carbon monoxide in air. The iodine resulting from the reaction of CO and I_2O_5 is titrated with thiosulfate, and the end point is detected by the disappearance of the blue-black colour produced by starch and iodine.

Thiosulfate ions, $S_2O_3^{2-}$, are oxidised to tetrathionate ions, $S_4O_6^{2-}$, by iodine.

Thiosulfate solutions can be standardised using a primary standard, potassium iodate, KIO_3.

In order to standardise a thiosulfate solution, a standard solution of potassium iodate was prepared by dissolving 0.5466 g of $KIO_3(s)$ in sufficient water to make 250.00 mL of solution.

10.00 mL of this KIO_3 solution was pipetted into a conical flask, and 10 mL of 2 mol L^{-1} sulfuric acid was added, followed by the slow addition of 10 mL of 0.25 mol L^{-1} potassium iodide solution. A red-brown solution is formed. The equation for the reaction is:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

The iodine generated was then titrated against the unknown thiosulfate solution using a starch indicator. The average titre for three concordant results was 25.48 mL.

To determine the concentration of carbon monoxide in a sample of air, 23.20 L samples were passed through a series of cold traps to remove nitrogen oxides, water and other interfering compounds. The remaining gas was passed through a sample of acidified I_2O_5, which reacted quantitatively with the CO fraction of the gas to produce I_2 and CO_2. The resulting iodine was flushed with nitrogen into a reaction flask, and titrated with the standardised sodium thiosulfate solution described above. The average titre for the samples tested was 17.23 mL.

Determine the concentration of CO in the air sample, in g L^{-1}.

$M(KIO_3) = 214.0$ g mol^{-1} $\qquad$ $M(CO) = 28.00$ g mol^{-1}

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QUESTION TWO

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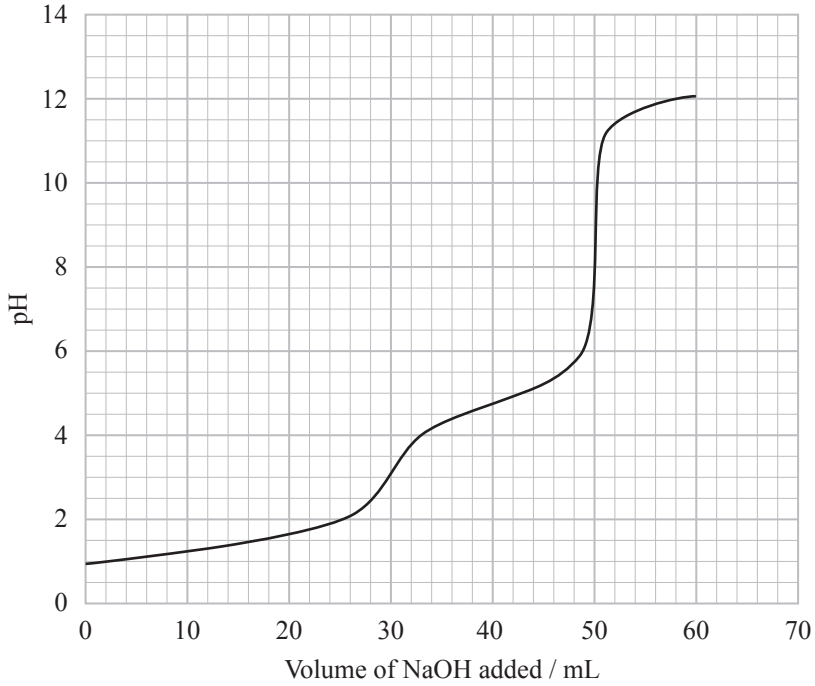
A mixture of 15.00 mL of 0.200 mol L^{-1} HCl and 10.00 mL of 0.200 mol L^{-1} CH_3COOH is titrated against 0.100 mol L^{-1} NaOH solution.

The titration curve shows two equivalence points, one at 30.0 mL and one at 50.0 mL of added NaOH.



(a) (i) Calculate the pH after the addition of 5 mL, 29 mL, and 50 mL of NaOH.

Comment on the validity of any assumptions made for the calculations.

Note: The pK_a of the acid should be approximated from the graph.

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(ii) Account for the variation in pH, in terms of the species present in the solution, between the addition of 30 mL and 60 mL of NaOH solution.

Include balanced equations in your discussion.

There is more space for your answer to this question on the following page.

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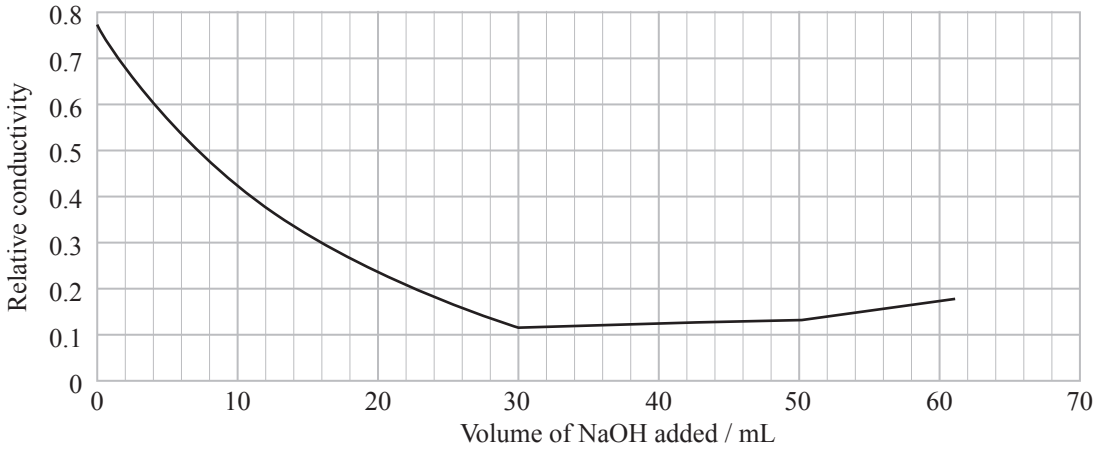
(b) Solutions of mixed strong and weak acids are often analysed using a conductometric titration. In a conductometric titration, the equivalence points are determined by monitoring changes in the conductivity of the solution. These changes depend on the concentration and the relative conductivities of the ions in solution.

The relative conductivities of some ionic species are shown in the table below.

Ionic species	Relative conductivity
Na^+, Cl^-, CH_3COO^-	1
OH^-	3
H_3O^+	5

The conductivity curve for the titration described in part (a) is given below.



Account for the shape of the conductivity curve as the volume of NaOH increases from 0 mL to 60 mL by commenting on why the conductivity decreases or increases in each phase of the plot. Link your answers to the relative concentrations of the species present in the solution in the reaction flask.

It can be assumed that the total conductivity in a solution is the sum of the conductivities of the ions present.

There is more space for your answer to this question on the following pages.

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QUESTION THREE

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(a) A solution is made by adding 42.69 g of a mixture of the aldehydes methanal, HCHO, and ethanal, CH_3CHO, to 76.59 g of water.

Addition of excess ammoniacal silver nitrate solution to 2.18 g of the mixed aldehyde solution results in the precipitation of 4.64 g of silver metal.

Determine, by carrying out the appropriate calculation, the mass, in g, of each of the aldehydes, methanal, and ethanal, in the mixture.

$M(Ag) = 107.9 \text{ g mol}^{-1}$ $M(HCHO) = 30.03 \text{ g mol}^{-1}$ $M(CH_3CHO) = 44.05 \text{ g mol}^{-1}$

(b)

INFORMATION
The reaction of an alkene with acidified potassium permanganate results in the breaking of the double bond. The reaction product depends on the number of hydrogen atoms present on the double-bonded carbon atoms. If there are no hydrogen atoms, a ketone is formed; if one hydrogen atom is present, a carboxylic acid is formed; if there are two hydrogen atoms present, carbon dioxide gas is produced. Oxalic acid (ethanedioic acid) also reacts with warmed, acidified, potassium permanganate to give two mole equivalents of CO_2 gas.

Four compounds, **A**, **B**, **C**, and **D,** have the molecular formula $C_5H_8O_2$. They all turn moist blue litmus paper red. Spectral data indicate that none of the compounds is cyclic. Each compound is reacted with warmed, acidified, potassium permanganate and, for some compounds or reaction products, further reactions are carried out as outlined below.

- Compound **A**, on reaction with warmed, acidified, potassium permanganate, produces Compound **E**, C_3H_6O, and a colourless gas is observed. Compound **E** does not react with sodium carbonate solution. Compound **A** also reacts with water in the presence of an acid catalyst to give Compound **F**, $C_5H_{10}O_3$, as the major product. Compound **F** is not optically active, and does not react with acidified potassium dichromate.
- Compound **B**, on reaction with warmed, acidified, potassium permanganate, produces a colourless solution containing Compound **G**, and a colourless gas is observed. Compound **B** reacts with water in the presence of an acid catalyst to give Compound **F** as the major product.
- Compound **C**, on reaction with warmed, acidified, potassium permanganate, produces a colourless solution containing Compound **H**. Bubbles of gas are also observed. Compound **H** does not exist as enantiomers. One mole of Compound **H** reacts with 2 mol equivalents of a standard solution of sodium hydroxide. Compound **C** reacts with water in the presence of an acid catalyst to give Compound **I**, $C_5H_{10}O_3$, as the major product. Compound **I** exists as enantiomers, and in the presence of concentrated sulfuric acid, produces Compound **J,** $C_5H_8O_2$. Compound **J** is neutral to litmus paper, and does not rapidly decolourise bromine water.
- Compound **D** reacts with warmed acidified potassium permanganate to give a colourless solution containing two compounds, **K** and **L**. Titration of this mixture requires 2 mol equivalents of a standard solution of sodium hydroxide. Compound **K** distils first from the mixture of compounds. Neither compound reacts further with Tollens' reagent.

Draw the structures of ALL the possible isomers of $C_5H_8O_2$ that turn moist blue litmus paper red, and select the best match for Compounds **A**, **B**, **C**, and **D**.

Draw structures for all the reaction products **E** to **L**. Ignore any geometric isomer possibilities.

Extra pages for planning/working are provided at the back of this booklet.

Isomers of $C_5H_8O_2$:

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Structures **E** to **L**:

QUESTION FOUR

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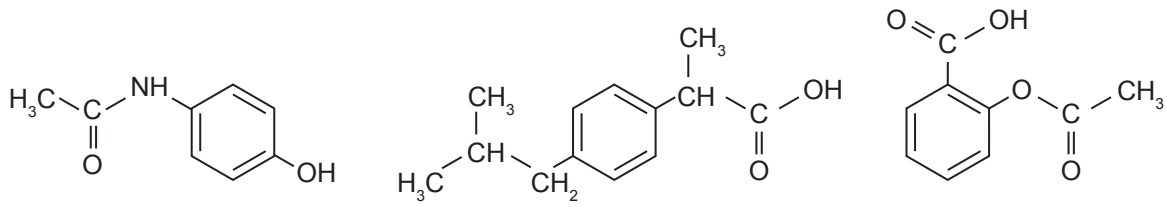
(a) The structural formulae for the molecules of three common pain relievers found on the market today are shown below.



Paracetamol **Ibuprofen** **Aspirin**

In order for the pain relievers to have their physiological effect, they need to be carried in the bloodstream. Blood is mostly water. Of the three pain relievers, paracetamol is the most soluble at 13 mg mL^{-1}, aspirin is slightly less at 3 mg mL^{-1}, while ibuprofen has limited solubility at 0.021 mg mL^{-1}. The solubility of aspirin and ibuprofen can be increased by supplying each as its calcium salt.

Account for the trend in the solubilities of the pain relievers described above.

M(paracetamol) = 151.2 g mol^{-1}, M(ibuprofen) = 206.3 g mol^{-1}, M(aspirin) = 180.2 g mol^{-1}

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(b) Nitrogenase is an enzyme present in rhizobia (soil bacteria) that live in the root nodules of legumes. Nitrogenase catalyses the reduction of dinitrogen, N_2, to two equivalents of ammonia, with additional production of one equivalent of dihydrogen, H_2.

A balanced half-equation for this reaction is:

$$N_2(g) + 8H^+(aq) + 8e^- \rightarrow 2NH_3(g) + H_2(g)$$

Discuss the enthalpy and entropy of this half-reaction, with reference to the data below.

Bond Dissociation Reaction	Bond Dissociation Enthalpy (kJ mol^{-1})
$N_2 \rightarrow 2N$	945
$H_2 \rightarrow 2H$	436
$NH_3 \rightarrow NH_2 + H$	444
$NH_2 \rightarrow NH + H$	385
$NH \rightarrow N + H$	351

Atom	First Ionisation Enthalpy (kJ mol^{-1})
H	1312

Ion	**Hydration Enthalpy (kJ mol^{-1})
$H^+(g)$	−1150

** Hydration enthalpy is the enthalpy change when 1 mole of gaseous ions dissolve in sufficient water to give an infinitely dilute solution. It is a measure of the energy released when attractions are set up between positive or negative ions and water molecules.

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Extra paper if required.
Write the question number(s) if applicable.

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