Name:		Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination 2015
Year 6

H2 CHEMISTRY

9647/03

Paper 3 Free Response

25 September 2015
2 hours

Additional Materials: Data Booklet
Writing Paper
Cover Sheet

INSTRUCTIONS TO CANDIDATES

Write your **name**, **register number** and **class** on this question paper and on the Cover Sheet provided.

Write in dark blue or black pen on both sides of the paper.

You may use a soft pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Start each question on a fresh sheet of paper.

You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination:

- Fasten all work securely together with the Cover Sheet on top.
- Hand in the question paper separately.

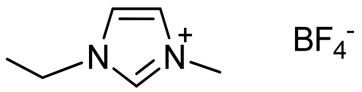
The total marks for this paper is 80 marks.

This question paper consists of **11** printed pages and **1** blank page.

Answer *any* **four** questions on writing paper.

1 **(a)** Non–aqueous ionic liquids, or simply ionic liquids, generally have high boiling point and low melting point. They are becoming popular solvents in organic synthesis.

Ionic liquids mainly consist of ions, and at least one of them is a bulky organic ion. 1–ethyl–3–methylimidazolium tetrafluoroborate, [emim]BF_4, is an example of ionic liquid.



[emim]$^+$

(i) Some ionic liquids, including [emim]BF_4, are liquid at room temperature. They are called 'room temperature ionic liquids'. Account for the low melting point of [emim]BF_4.

(ii) Explain why [emim]BF_4 has high boiling point.

(iii) Suggest an advantage of using ionic liquids over using organic solvents such as acetaldehyde (CH_3COCH_3) in organic synthesis. Explain your answer.

[4]

The two most abundant atmospheric gases react to a small extent to achieve dynamic equilibrium as shown:

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g) \qquad K_p = 0.40$$

(b) Atmospheric oxygen and nitrogen, each at a partial pressure of 0.80 atm, are put into a 1 dm^3 evacuated flask and equilibrium is established after 30 minutes. Calculate the equilibrium partial pressure for each of the three components at 298 K.

[3]

(c) On the grid provided at the back of the ***Cover Sheet***, sketch pressure versus time curves for N_2 and NO under the conditions described in **(b)** at 298K from 0 to 40 minutes. Label the axes, curves and indicate significant values on the axes.

[2]

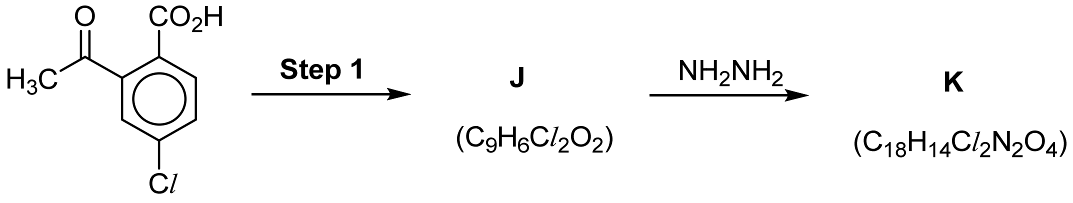
(d) State how the pressure verses time curves for N_2 and NO from 0 to 40 minutes will be different from that in **(c)**, when a catalyst is used in the reaction.

[1]

(e) The temperature of the system was raised to 350 K at 40 min.
Given the average bond energy of N=O bond is 607 kJ mol^{-1} and that the equilibrium is re–established at 60 min, sketch on the same axes, the pressure versus time curves for N_2 and NO from 40 min to 70 min.

[3]

(f) Halofenozide, **K**, is an insecticide commonly used for white grub control. It can be synthesised as shown below.



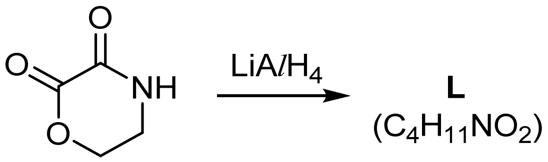
H

One mole of **H**, **J** and **K** each reacts with alkaline aqueous iodine and forms a yellow precipitate in a ratio of 1: 1: 2. Compound **J** and **K** does not give any effervescence with anhydrous Na_2CO_3.

Suggest the structures for **J** and **K** and give the reagents and conditions for step **1**.

[3]

(g) $LiAlH_4$ is a powerful reducing agent that reacts with most polar functional groups.



0.02 mol of **L** reacts with sodium metal to give 0.48 dm^3 of gas at room temperature and pressure. **L** turns moist red litmus paper blue.

formula	pK_b
L	?
$(CH_3CH_2)_2NH$	3.1
$C_6H_5NH_2$	9.4

Using the information given above, predict the structure for product **L** and its pK_b value. Explain the chemistry of the reaction and property of **L**.

[4]

[Total: 20]

2 One of the ingredients present in bread is calcium iodate(V), $Ca(IO_3)_2$. It is a dough conditioner added to bread dough to strengthen its texture.

(a) Draw a dot–and–cross diagram for calcium iodate(V).

[2]

(b) At high temperatures, calcium iodate(V) undergo decomposition to form a white solid, a colourless gas and violet iodine vapour.

(i) Construct an equation, with state symbols, to represent the above decomposition process.

(ii) Use the *Data Booklet*, explain the difference in thermal stability of calcium iodate(V) and barium iodate(V).

[4]

(c) When the violet iodine vapour formed from the above decomposition process is bubbled into a closed vessel, containing a gaseous alkene, the violet vapour was decolourised and a liquid compound, with relative molecular mass of 310 was obtained. However, a colourless liquid cyclohexane turns violet when iodine vapour is bubbled into it.

Given that this alkene exhibit geometric isomerism, deduce its identity and explain all the observations made.

[4]

(d) Consider the equilibrium dissolution of calcium iodate:

$$Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^{-}\,(aq)$$

(i) The standard enthalpy change, $\Delta H^\ominus$ and the standard entropy change, $\Delta S^\ominus$ for the process were +80 kJ mol^{-1} and + 152 J mol^{-1} K^{-1} respectively. $\Delta G^\ominus$, in Joules per mole, and K_{sp} are related by the following equation

$$\Delta G^\ominus = -2.303\ RT\ \lg K_{sp}$$

Calculate the value of the solubility product of calcium iodate(V) at 25 °C, stating its units.

(ii) The standard redox potential of iodate(V) ions is given below.

$$2IO_3^{-} + 12H^{+} + 10e^{-} \rightleftharpoons I_2 + 6H_2O \qquad E^\ominus = +1.20\ V$$

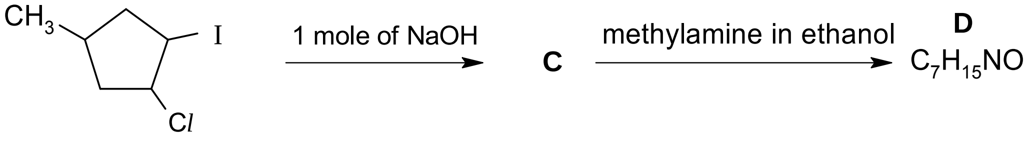
Use the *Data Booklet*, predict what you would expect to observe when acidified potassium iodate(V) is mixed with hydrogen peroxide. Calculate the $E^\ominus_{cell}$ for the reaction and write a balanced equation.

[6]

(e) Successive reactions of dihalgeno compounds are shown below. The following transformations show the different reactivities of organic halogeno compounds and of amines and alcohols.

Suggest the structures of compounds **C**, **D**, **E** and **F**.

(i)



(ii)

$$CH_3CHICOCl \xrightarrow{\text{ethane-1,2-diol}} \mathbf{E} \xrightarrow{\text{Na, warm}} \underset{C_5H_8O_3}{\mathbf{F}}$$

[4]

[Total: 20]

3(a) By selecting appropriate $E^\ominus$ values from the *Data Booklet*, explain why iron(II) iodide can be crystallised from an aqueous mixture of iron(II) sulfate and potassium iodide, but iron(III) iodide cannot be produced by mixing any aqueous solutions of iron(III) and iodide ions.

[3]

(b) The solubility products, K_{sp}, of two silver salts at 25 °C are given below.

salt	K_{sp} / $mol^2\ dm^{-6}$
AgSCN	1.03×10^{-12}
AgI	8.52×10^{-17}

The solubility product for silver ethanoate, CH_3CO_2Ag, was found by the following method.

A saturated solution was first prepared by shaking 40 cm^3 of 0.20 mol dm^{-3} silver nitrate with 40 cm^3 of 0.20 mol dm^{-3} sodium ethanoate and maintained for some hours at a temperature of 25 °C.

A 20.0 cm^3 portion of this saturated solution was pipetted through a glass–wool filter and acidified with nitric acid to prevent the interference of other ions like carbonates with silver ions. A few drops of iron(III) solution was added as an indicator and the mixture was then titrated against 0.10 mol dm^{-3} potassium thiocyanate, KSCN. A red colouration signalled the end–point.

(i) Write an equation, with state symbols, for the reaction that occurred during the titration.

(ii) What causes the red colouration at end–point?

(iii) Suggest why the red colouration only appears at end–point.

(iv) Explain why the silver nitrate – sodium ethanoate mixture was initially kept at 25 °C and suggest, with reason, whether the titration mixture should also be kept at 25 °C.

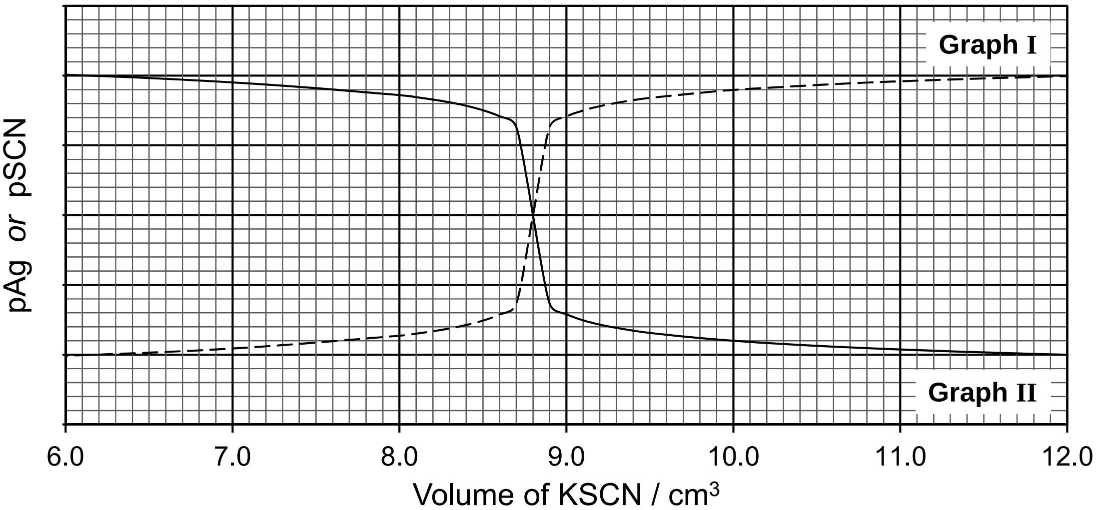
(v) Suggest another reason why the titration must be carried out in a strongly acidic solution if iron(III) chloride is used as an indicator.

[6]

(c) The concentrations of Ag^+ and SCN^- in the mixture during the titration in **(b)** were followed as a function of titrant volume by plotting two graphs, as shown below, of

- pAg against volume of KSCN
- pSCN against volume of KSCN

where pAg = $-\log_{10} [Ag^+]$ and pSCN = $-\log_{10} [SCN^-]$.



(i) Deduce which graph, **I** or **II**, corresponds to the titration curve of pAg against volume of KSCN.

(ii) At equivalence point, there is an equilibrium between solid AgSCN and its ions, Ag^+ and SCN^-.

Determine the values of pAg and pSCN at equivalence point.

(iii) From the graph, state the volume of KSCN needed for the reaction to reach equivalence point.

(iv) Calculate the solubility product of CH_3CO_2Ag at 25 °C and state its units.

[6]

(d) The mixture obtained at the end–point of the above titration was filtered and the solid residue, washed with distilled water. On shaking the residue with an excess of aqueous potassium iodide, a yellow solid **P** is observed in the resulting mixture.

Both the solid residue and **P** readily dissolve in excess aqueous potassium cyanide to produce colourless solutions which contain the same anion. When aqueous silver nitrate was added to a solution of this anion, a white solid **Q**, was formed with the following composition by mass:

Ag, 80.6 %; C, 8.96 %; N, 10.5 %

Q is ionic with a formula mass of 268. One formula unit of **Q** contains one cation and one anion.

Explain why both solid residue and **P** dissolve in excess aqueous potassium cyanide and suggest the formula units of **P** and **Q**.

[5]

[Total: 20]

4 Copper is a commonly traded commodity with wide applications. Its' ability to form various compounds makes copper a widely studied element in chemistry.

(a) **(i)** Write balanced equations with state symbols between the reaction of copper(II) ions and a few drops of aqueous ammonia till added in excess.

(ii) Although the copper atom has more electrons than the calcium atom, the atomic radius of copper atom is smaller than that of calcium atom. Suggest an explanation for this.

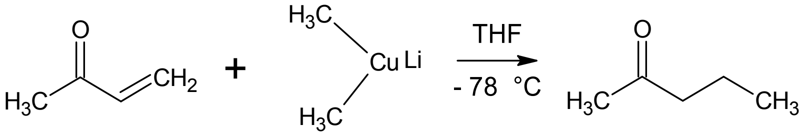
[4]

(b) **(i)** Explain why copper(I) chloride solution is a colourless solution.

(ii) Copper(I) chloride is a sparingly soluble salt in water at 20 °C. Predict and explain if copper(II) chloride salt would be more soluble than copper(I) chloride salt in water at 20 °C.

[4]

(c) In 1958, Henry Gilman reported the synthesis of organocopper compounds. These compounds, Gilman Reagents, are now used to perform organic reactions such as **Reaction I** given below.



Reaction I

THF = tetrahydrofuran

Gilman reagent, $(CH_3)_2CuLi$, the organocopper compound in **Reaction I** is synthesised in two steps. In Step **I**, methyllithium was reacted with copper(II) chloride to produce ethane, copper(I) chloride and lithium chloride. The copper(I) chloride produced in Step **I** was reacted with more methyllithium to produce the organocopper compound in Step **II**.

(i) Write balanced equations for Step **I** and Step **II**.

(ii) It has been suggested that **Reaction I** proceeds via the following two steps.

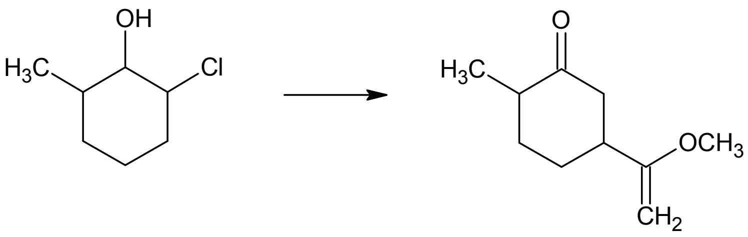
Step A: The carbon–copper bond undergoes a heterolytic fission with the bonding pair of electrons transferred to the carbon of the terminal alkene with the formation of a carbanion intermediate.

Step B: Protonation of the carbanion intermediate by water to yield the product.

Write the mechanism for **Reaction I**.

(iii) State the type of reaction in **Reaction I**.

(iv) Using a suitable Gilman Reagent, propose a three step synthesis to convert



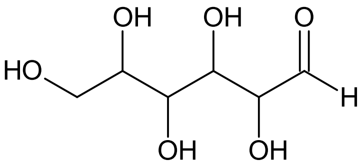
Your synthesis should include all reagents and conditions required for each step.

[10]

(d) Fehling's solution can be prepared by mixing copper(II) sulfate and aqueous potassium sodium tartrate with aqueous sodium hydroxide.

The open straight chain form of D–glucose is as follows.

D–glucose =



State what would be observed when a few drops of Fehling's solution is introduced to D–glucose solution. Write the balanced equation between Fehling's solution and D–glucose.

[2]

[Total: 20]

5 **(a)** Chromium is used as a heterogeneous catalyst in the polymerisation of ethene. Suggest how chromium can act as a heterogeneous catalyst.

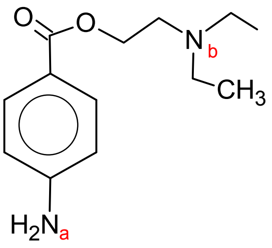
[2]

(b) Reaction of **A**, C_4H_8O, with acidified potassium dichromate(VI) first yields **B**, and then **C**. **B** and **C** give the same organic product CH_3CO_2H when treated with hot concentrated acidified potassium manganate(VI). However **B** and **C** give different products, **D** and **E** respectively, when reacted with hydrogen in the presence of platinum.

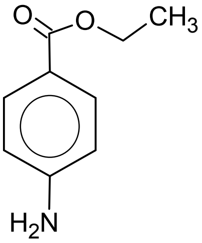
Deduce the structures of compounds **A** to **E**, explaining the chemistry of the reactions described.

[5]

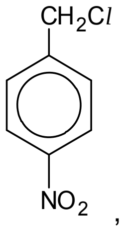
(c) **(i)** Procaine, a local anaesthetic is used primarily to reduce the pain of intramuscular injection of penicillin. It has the structure:



Procaine



Analogue of Procaine



The **analogue of Procaine** can be synthesised from the compound, , in no more than three steps. Suggest the reagents and conditions required for this synthesis and the structural formulae of the intermediate(s) formed.

(ii) A molecule of procaine contains two nitrogen atoms, N_a and N_b, both of which can act as a base. State which nitrogen atom, N_a and N_b, is the stronger base. Explain your reasoning.

(iii) Procaine can react with acidified $K_2Cr_2O_7$, under suitable conditions to give 4–aminobenzoic acid. Explain, with the aid of appropriate equations, how a solution of 4–aminobenzoic acid at pH 10 can resist pH changes when a small amount of aqueous hydrochloric acid or sodium hydroxide is added to its solution.

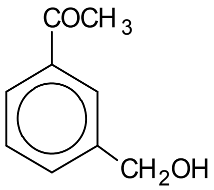
(iv) $HOCH_2CH_2N(C_2H_5)_2$, a weak monoacidic base, is another product formed from the hydrolysis of procaine. The base dissociation constant, K_b, is 4.00×10^{-4} mol dm^{-3} at 25 °C. A chemist starts with a solution containing 0.04 mol dm^{-3} $HOCH_2CH_2N(C_2H_5)_2$ and he wishes to make a buffer solution of pH 10 using $HOCH_2CH_2N(C_2H_5)_2$ and its salt.

I Calculate the pH of 0.04 mol dm^{-3} $HOCH_2CH_2N(C_2H_5)_2$ solution.

II Solid $HOCH_2CH_2N(C_2H_5)_2$ salt is added to $HOCH_2CH_2N(C_2H_5)_2$ to produce a buffer solution of pH 10. Calculate the concentration of the salt of $HOCH_2CH_2N(C_2H_5)_2$ in the buffer solution.

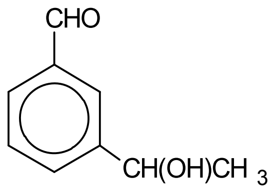
[10]

(d) Describe a simple chemical test that you could use to distinguish the following pair of compounds. You are to include reagents and conditions, observations and balanced equation(s) in your answers.



(I)

and



(II)

[3]

[Total: 20]

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