HWA CHONG INSTITUTION
JC2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**10S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9647/02

Paper 2 Structured

21 September 2011

2 hours

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1) Write your **name**, **CT group, centre number** and **index number** clearly in the spaces at the top of this page.

2) Answer **all** questions in the spaces provided in this Question Booklet.

INFORMATION FOR CANDIDATES

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

A Data Booklet is provided.

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

You may use a calculator.

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

For Examiner's Use	
1	**/ 12**
2	**/ 23**
3	**/ 16**
4	**/ 9**
5	**/ 12**
Total	**/ 72**

1 Planning (P)

Ammonium salts are commonly used in instant cold packs. The cold pack contains water, and in the water is another pouch containing the ammonium salt. When the pack is squeezed, this inner pouch is broken, releasing the salt, which quickly dissolves and lowers the pack's temperature.

To determine whether ammonium chloride or ammonium nitrate is more effective as the ingredient in the cold pack, a student decided to conduct an experiment to find out the enthalpy change of solution of the two salts, starting with ammonium chloride.

He added ammonium chloride to water and found the temperature change by plotting a suitable graph to correct for surrounding heat transfer.

Solubility of ammonium chloride at 25 °C = 6.95 mol dm^{-3}
4.3 J are required to raise the temperature of 1.0 cm^3 of any solution by 1 °C.

In a preliminary investigation, the enthalpy change of solution of ammonium chloride was found to be approximately +15 kJ mol^{-1}.

(a) Draw a labelled diagram to show the apparatus you could use in a school laboratory to carry out the experiment.

[1]

(b) (i) By considering the apparatus chosen in your diagram, state a volume of water you could use in the experiment.

Volume of water = …….. cm^3

(ii) Calculate the maximum mass of ammonium chloride that can be added to the volume of water stated in **(b)(i)**.

[2]

(c) Suggest a minimum mass of ammonium chloride that could be used. Justify your choice with relevant calculations, stating any assumptions you made.

[2]

(d) Describe the procedure to find the enthalpy change of solution of ammonium chloride.

In your plan, you should:

- allow for the plotting of a suitable graph
- include appropriate apparatus, masses and volumes of reagents, using your answers in parts **(a)**, **(b)** and **(c)**, and
- draw table(s) with headings to show the measurements you would make.

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Table(s) with headings

[4]

(e) Draw a sketch of the graph that you expect to obtain in the experiment. Indicate clearly on the graph the initial and final temperatures that you would read.

[1]

(f) In the student's experiment, he dissolved ***m*** g of ammonium chloride in ***v*** cm^3 of water, and obtained a temperature change of ***T*** °C.

Outline how you would use his results to calculate a value for the enthalpy change of solution of ammonium chloride.

[1]

(g) The student repeats the same procedure for ammonium nitrate. How might he conclude which of the two salts is more effective as the ingredient in the cold pack?

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[1]

[Total: 12]

2 (a) Elements and compounds react with each other in numerous ways. Nearly every inorganic chemical reaction falls into one or more of four broad categories.

Category of reaction	Description
Synthesis (or direct combination)	Two or more reactants combine to form one product: $A + B \rightarrow AB$
Decomposition	A compound breaks down into two or more substances: $XY \rightarrow X + Y$
Single displacement	One element being displaced from a compound by another element: $A + BX \rightarrow AX + B$
Double displacement	Elements from two compounds displace each other to form new compounds: $AX + BY \rightarrow AY + BX$

(i) Write a balanced chemical equation, including state symbols, of a reaction to illustrate each of the four categories of reactions above. ***Each equation must include at least one element or compound from Group II or Group VII.***

The first has been done for you.

Category of reaction	Equation from Group II or Group VII
Synthesis (or direct combination)	$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$
Decomposition	
Single displacement	
Double displacement	

(ii) The reaction of aqueous potassium iodide with aqueous copper(II) sulfate does not fall neatly into any of the four categories above. State the type of reaction and write a balanced equation, including state symbols, for this reaction

Type of reaction: ……

Equation: ……

(iii) Write equations for the **two** reactions that occur when solid sodium bromide is warmed with concentrated sulfuric acid.

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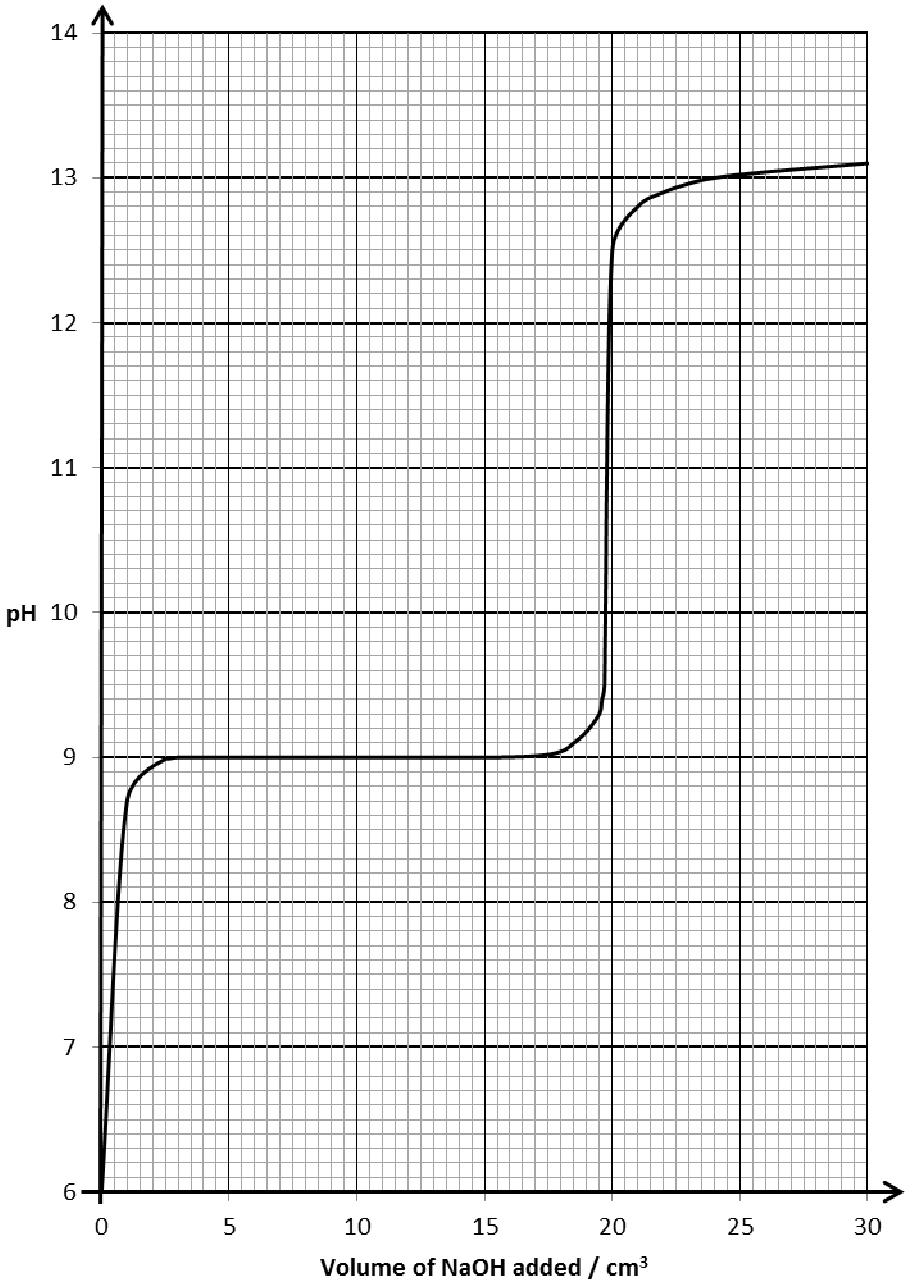
[7]

(b) In an experiment, 50.0 cm^3 of aqueous magnesium chloride were titrated with 1.00 mol dm^{-3} sodium hydroxide. The pH of the solution changed as given in the diagram.



(i) In the experiment, the hydrated magnesium ion, $Mg(H_2O)_6^{2+}$, acts as an acid. Write the mathematical expression for the K_a of this ion.

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(ii) Explain the pH observed at the following points of the titration:

I. when the volume of alkali added is between 5 cm^3 and 10 cm^3

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II. when the volume of alkali added is 20 cm^3

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(iii) Calculate the initial concentration of magnesium ions, and hence calculate the K_a for the hydrated magnesium ion.

(iv) When 10 cm^3 of alkali have been added, calculate
I. the hydroxide ion concentration,
II. the hydrated magnesium ion concentration.
Hence calculate the solubility product for magnesium hydroxide.

[8]

(c) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex. For example,

$$[Co(H_2O)_6]^{2+}(aq) + 4SCN^-(aq) \rightleftharpoons [Co(SCN)_4]^{2-}(aq) + 6H_2O(l)$$

$$K_c = K_{stab} = \frac{[Co(SCN)_4^{2-}]}{[Co(H_2O)_6^{2+}][SCN^-]^4}$$

The table below lists the colours and stability constants (in logarithm form) of some cobalt(II) and cobalt(III) complexes.

Complex	**Colour**	**lg K_{stab}**
$[Co(SCN)_4]^{2-}$ (aq)	Bright blue	3.00
$[Co(NH_3)_6]^{2+}$ (aq)	Light brown	5.11
$[Co(NH_3)_6]^{3+}$ (aq)	Dark reddish brown	35.2
$[Co(edta)]^{2-}$ (aq)	Pink	16.3
$[Co(edta)]^{-}$ (aq)	Magenta	36.0

[edta = $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$]

(i) Explain the meaning of the term *complex*, and state the *coordination number* for the complex, $[Co(edta)]^-$ (aq).

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(ii) Use the data in the table to predict and explain what you will observe when a solution of pink Co^{2+}(aq) is treated with excess KSCN(aq), followed by the addition of excess edta.

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(iii) Use the data in the table to predict and explain the effect, if any, of excess NH_3(aq) on the $E^{\ominus}$ value of the $Co^{3+} + e^- \rightleftharpoons Co^{2+}$ system.

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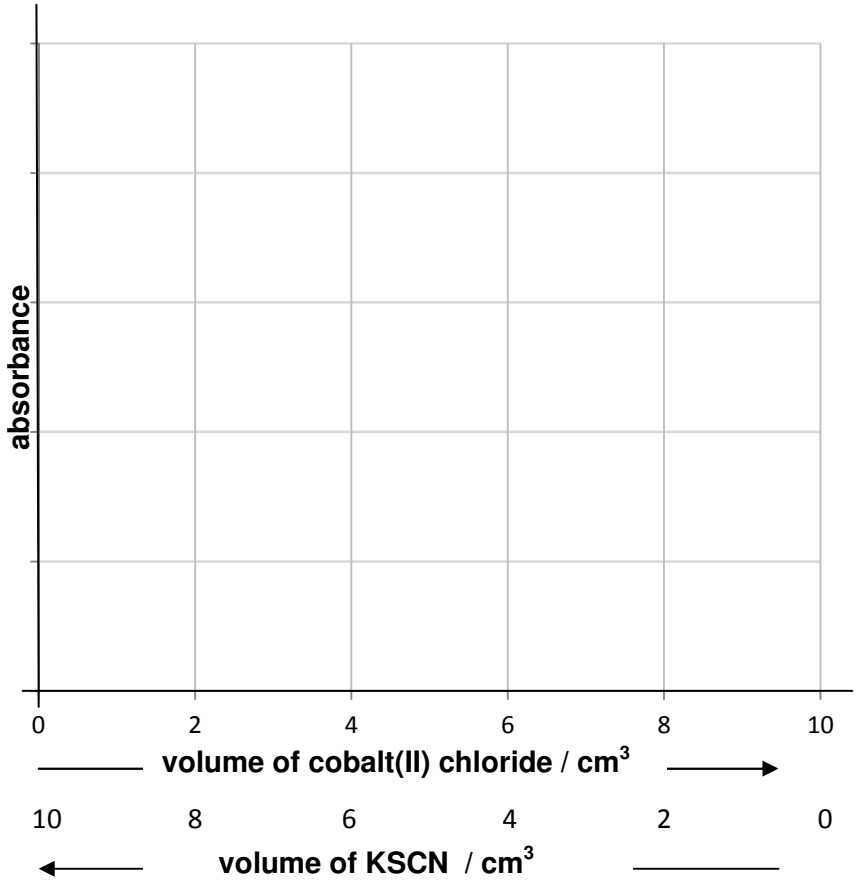
(iv) An experiment is conducted to study the stoichiometry of the complex $[Co(SCN)_4]^{2-}(aq)$.

In the experiment, a solution of 1 x 10^{-3} mol dm^{-3} cobalt(II) chloride is mixed with different proportions of a solution of 1 x 10^{-3} mol dm^{-3} KSCN(aq) such that the total volume of each mixture is kept constant at 10 cm^3. The absorbance due to the complex in each mixture is measured with a colorimeter, using an appropriate filter. The absorbance is directly proportional to the concentration of the complex.

In the grid below, sketch the graph you would expect to obtain.



(v) The two different coloured Co(II) complex ions, $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$, co-exist by ligand exchange as shown in the following equilibrium:

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$$
pink blue

Heating a solution of cobalt(II) chloride turns it blue, and cooling the blue solution in an ice-water bath restores the pink colour.

What conclusion can be drawn from this observation?

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[8]

[Total: 23]

3 (a) Iron(III) oxide, a reddish brown solid, is an inorganic compound with the formula of Fe_2O_3.

Construct a Born-Haber Cycle for the formation of Fe_2O_3 from its elements.

Use the cycle to calculate the lattice energy of Fe_2O_3, using the following data as well as relevant data given in the *Data Booklet*.

Data:

Enthalpy change of atomization of iron = +414 kJ mol^{-1}

First electron affinity of oxygen = -141 kJ mol^{-1}

Second electron affinity of oxygen = +844 kJ mol^{-1}

$8Fe(s) + 6O_2(g) \rightarrow 4Fe_2O_3(s)$ ΔH = -3288 kJ mol^{-1}

[4]

(b) Potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ and potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$ are examples of compounds comprising of the iron ion in the +2 and +3 oxidation states. $K_4[Fe(CN)_6]$ forms lemon-yellow crystals at room temperature while $K_3[Fe(CN)_6]$ appears as deep red crystals at room temperature.

Explain why these iron compounds are coloured.

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[3]

(c) Potassium ferrate(VI), K_2FeO_4, is a rare example of an Fe(VI) compound. Reflecting its high oxidation state, FeO_4^{2-} is a powerful oxidant.

The standard electrode potential for the following half reaction is +2.00 V.

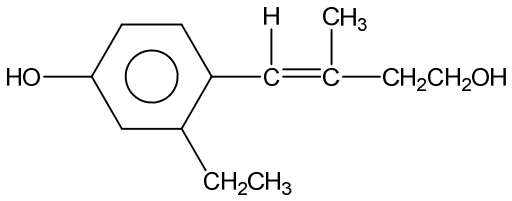
$$FeO_4^{2-}(aq) + 8H^+(aq) + 3e \rightleftharpoons Fe^{3+}(aq) + 4H_2O(l)$$

Using relevant data from the *Data Booklet*, predict whether a reaction will occur when K_2FeO_4 crystals are warmed with an aqueous solution of chromium(III) sulfate.

Describe the expected appearance of the resultant solution and write an equation for any reaction that occurs.

[3]

(d) Give the structural formulae of the organic products formed when compound **A** reacts with the following reagents.



A

(i) hot alkaline $KMnO_4$

(ii) dilute HNO_3

[3]

(e) Describe the mechanism of the reaction between methylbenzene and concentrated nitric acid in the presence of concentrated sulfuric acid. Your answer should include curly arrows showing the movement of electrons, and all charges.

[3]
[Total: 16]

4 (a) Describe what you would see when phosphorus is burned in oxygen, and write an equation, including state symbols, for the reaction that occurs.

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[2]

(b) Phosphorus acid, H_3PO_3, is most commonly used in the production of phosphites. It is produced when phosphorus trichloride is reacted with steam according to the equation below:

$$PCl_3(g) + 3\ H_2O(g) \rightarrow H_3PO_3(l) + 3HCl\ (g)$$

Phosphorus acid can also be formed when phosphorus(III) oxide, P_4O_6, reacts with steam or HC*l* at 100°C.

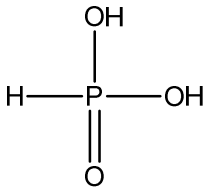
Reaction with steam: $P_4O_6(l) + 6H_2O(g) \rightarrow 4\ H_3PO_3(l)$ $\Delta H_{rxn} = +729\ kJ\ mol^{-1}$

Reaction with HC*l*(g): $P_4O_6(l) + 6HCl(g) \rightarrow 2H_3PO_3(l) + 2PCl_3(g)$ $\Delta H_{rxn} = +177\ kJ\ mol^{-1}$

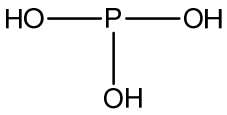
Using the data provided, draw an energy cycle and use it to calculate the enthalpy change of reaction when 1 mol of PCl_3 reacts with steam to form phosphorus acid.

[2]

(c) Two possible structures can be drawn for phosphorus acid.



Structure **B**



Structure **C**

Using the following data, and relevant data from the Data Booklet, explain why structure **B** is more likely to be formed.

Bond	**Bond energy/ kJ mol^{-1}**
P – H	322
P – O	335
P = O	544

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[3]

(d) Apart from PCl_3, phosphorus also forms another chloride, PCl_5. When PCl_5 hydrolyses in water, it forms H_3PO_4.

(i) Draw the structure of H_3PO_4.

(ii) With reference to the structures of the two acids, suggest why H_3PO_4 is a weaker acid than H_3PO_3.

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[2]

[Total: 9]

5 (a) Pseudohalogen is a class of compounds that show a chemical reactivity similar to halogens. An example is thiocyanogen, $(SCN)_2$.

NC−S−S−CN

Thiocyanogen

(i) Draw the shape of the hybrid orbitals around **one** of the carbon atoms in thiocyanogen.

(ii) Draw a diagram to illustrate the shape of thiocyanogen about the two sulfur atoms.

(iii) Thiocyanogen can be synthesized by reacting sodium thiocyanate, NaSCN, with chlorine gas. Write an equation for the formation of thiocyanogen.

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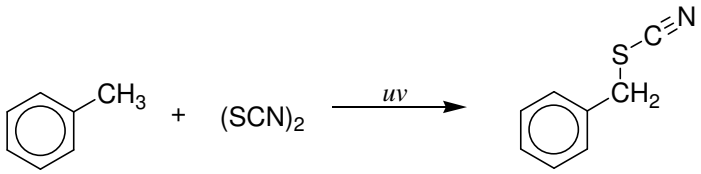
[3]

(b) Thiocyanogen can react with hydrocarbons such as methylbenzene via free radical substitution.



(i) Write equations that describe the following steps.

Initiation

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Propagation

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Termination

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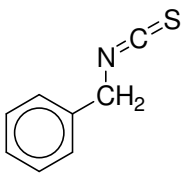
(ii) An isomer of the product, shown below, was also isolated. Suggest a reason for the formation of this isomer.



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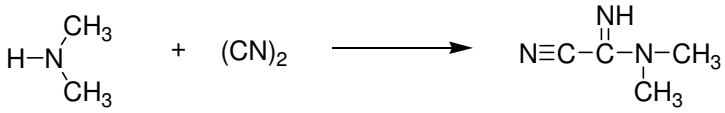
[5]

(c) Cyanogen, $(CN)_2$, is another example of a pseudohalogen. It reacts readily with dimethylamine via nucleophilic addition.



(i) The product exhibits geometric isomerism. Suggest the structures of the isomers.

(ii) Describe the mechanism that accounts for formation of the product. Your answer should include curly arrows showing the movement of electrons, and all charges.

(iii) Cyanogen can be readily reduced to CN^-, which is highly toxic to the human body. Explain the toxicity of CN^-.

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[4]

[Total: 12]

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