NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY

9647/03

Paper 3 Free Response

19 Sep 2013

2 hours

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
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.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

2

Answer any **four** questions.

1 The elements of Group VII of the Periodic Table are called halogens, which mean "salt formers". They lack only one electron to form a complete shell, and are extremely active chemically.

This question examines the chemistry of two reactions of halogens.

(a) In the first reaction, a 1:2 mixture of H_2 and I_2 gases was mixed at a constant temperature of 430 ^oC and a constant pressure of 2 atm. The following equilibrium was set up.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g) \qquad \Delta H = -11\ kJ\ mol^{-1}$$

(i) Given that degree of dissociation of H_2 is 86 %, calculate the equilibrium constant, K_p for the above reaction under these conditions.

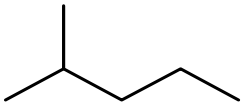
(ii) Suggest, with reasoning, a way to increase degree of dissociation of H_2 for the above reaction.

(iii) Deduce how K_p for the following system would be compared to your answer in **(i)**.

$$H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g)$$

[7]

In another reaction, halogens can react with unreactive alkanes to form mono-substituted product. An example is the reaction of chlorine with 2-methylpentane shown below.



2-methylpentane

(b) **(i)** Explain why alkanes are generally unreactive.

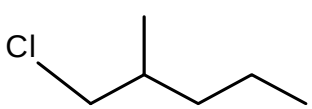
(ii) This reaction is seldom used for synthesis as there are many associated problems. Firstly, several isomeric products are formed. The relative ratio of the isomeric products may be more accurately determined if relative rates of abstraction of H atoms are taken into account.

The relative rates of abstraction of H atoms are

Type of H atoms	Relative rate of abstraction
Primary	1
Secondary	4
Tertiary	6

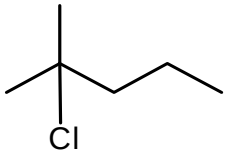
By examining the difference in stability of the intermediates formed when different types of H atom are abstracted, explain the trend in relative rate of abstraction.

(iii) Predict the ratio of the following two products **A** and **B**, taking into account the relative rates of abstraction given in **(ii)**. Explain your reasoning.



A

and



B

(iv) Describe suitable chemical test(s) to distinguish compounds **A** and **B** in **(iii)**.

[7]

(c) Another problem of the reaction is multi-substitution.

(i) Suggest the conditions that will give rise to formation of multi-substituted products.

(ii) A di-substituted product **C** with molecular formula $C_6H_{12}Cl_2$ was obtained in the reaction of chlorine with 2-methylpentane.

C does not exhibit optical activity. On warming with alcoholic KOH, a major product **D** is formed. When **D** is treated with hot acidified potassium manganate(VII) solution, effervescence was observed and the only organic product remaining gives a yellow precipitate with alkaline aqueous iodine.

Use this information to deduce the structure of **C** and **D**, explaining your reasoning.

[6]

[Total: 20]

4

2 Precipitation plays an important function in growth of bones and teeth in our bodies. Teeth and bones are largely composed of calcium phosphate salt $Ca_3(PO_4)_2$. In order for this precipitation to occur, the concentrations of the ions in blood must exceed the solubility product in the immediate region of deposition.

(a) Write an ionic equation with state symbols to show the formation of teeth and bones at the deposition region and hence an expression for the solubility product of the $Ca_3(PO_4)_2$ deposits. [2]

(b) **(i)** At a temperature of 37 ^oC, the solubility product for calcium phosphate $Ca_3(PO_4)_2$ has a numerical value of 4×10^{-27}. In a sample of blood at a pH of 7.4, the concentrations of calcium and phosphate ions are found to be 1.2×10^{-3} mol dm^{-3} and 1.6×10^{-8} mol dm^{-3} respectively. State and explain if the above composition in blood will result in the growth or degeneration of teeth and bones.

(ii) Hence, state and explain if the pH environment of 7.4 in **(i)** is that for a growing child, a fully grown man or an old person.

[3]

(c) The pH at the area of growth may change due to metabolic processes in the body. The hydrogen ions that are present combine phosphate ions as hydrogen phosphate ions. This prevents growth of strong teeth and bones.

$$PO_4^{3-}(aq) + H^+(aq) \rightleftharpoons HPO_4^{2-}(aq)$$

Assuming that the $[HPO_4^{2-}]$ is maintained at 1.7×10^{-4} mol dm^{-3} by cell functions,

(i) calculate the pH that will result in neither growth nor degeneration at the teeth and bones deposition region when the concentration of calcium ions in blood is maintained at 1.2×10^{-3} mol dm^{-3}.
[K_a of $HPO_4^{2-} = 4.4 \times 10^{-13}$ mol dm^{-3}]

(ii) Suggest another acid–conjugate base equation that accounts for the constant supply of HPO_4^{2-} ions from cell functions.

[3]

(d) **(i)** Construct an energy level diagram for the formation of $Ca_3(PO_4)_2$ from its elements using relevant data from the table below and other appropriate values in the *Data Booklet*. Hence calculate the lattice energy of $Ca_3(PO_4)_2$.

Enthalpy	ΔH / kJ mol^{-1}
Standard enthalpy change of formation of $Ca_3(PO_4)_2$	−4132
Standard enthalpy change of atomisation of Ca	+178
Standard enthalpy change of atomisation of P	+315
$P(g) + 4O(g) + 3e \rightarrow PO_4^{3-}(g)$	−2810

(ii) Using your answers to **(i)** and other enthalpy change value if any, explain why $Ca_3(PO_4)_2$ is insoluble.

[6]

(e) *Use of the Data Booklet is relevant to this question.*

Group VII elements exist as ions and play a vital role in bodily functions. The following observations are made about Group VII elements and their reactions. Explain the observations made.

(i) F_2 cannot be prepared by electrolytic oxidation of aqueous F^- solutions.

(ii) HI can be prepared by treating NaI with phosphoric acid, H_3PO_4 but not with concentrated sulfuric acid.

(iii) Interhalogen compounds such as IF_3, IF_5 and IF_7, BrF_3, BrF_5, ClF_3, ICl_3 exists. On the other hand, ClF_5 is not easily formed and $BrCl_3$ does not exists.

[6]

[Total: 20]

6

3 **(a)** Period 3 elements react with oxygen to form the corresponding oxides of varying acid-base nature. Using magnesium, aluminium and phosphorus as examples, describe the acid-base nature of the oxides across Period 3 with suitable equations. [4]

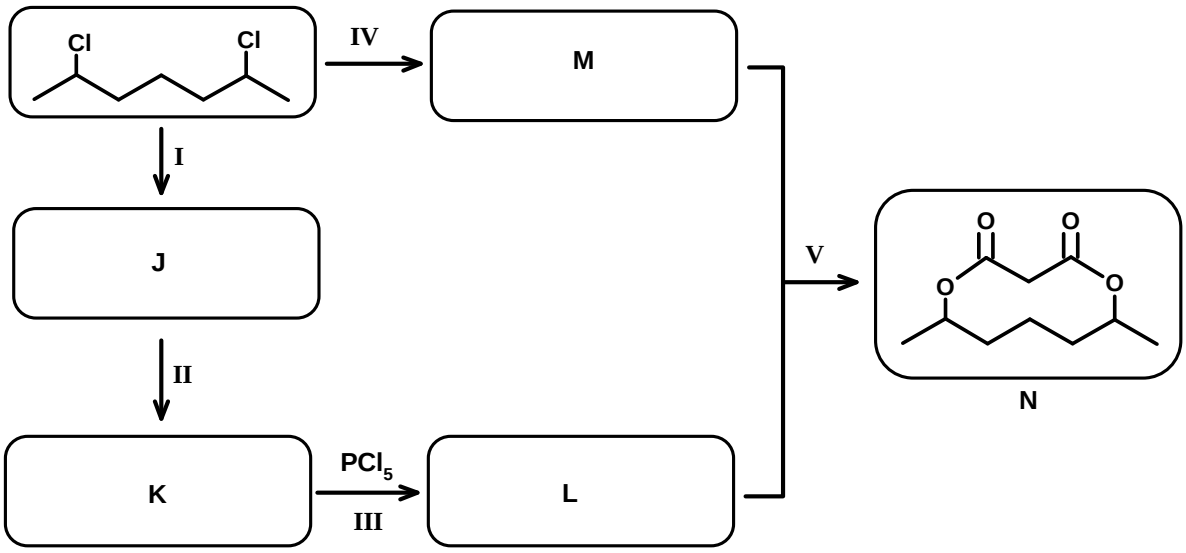
(b) Aluminium is a reactive metal but its reactivity is limited due to a layer of inert aluminium oxide being formed. Both aluminium and its oxide react readily with aqueous sodium hydroxide to give similar products. Aluminium, however, produces another product which is a combustible gas.

(i) Write a balanced equation for the reaction when aluminium is heated in aqueous sodium hydroxide.

(ii) Explain why a homogenous solution is obtained in **(i)**.

[3]

(c) Using 2,6−dichloroheptane as the starting compound, suggest the reagents and conditions for steps I, II and IV and the products **J** to **M** in the synthetic scheme below. [7]



7

(d) (i) Propyne, C_3H_4, like ethyne, C_2H_2, is commonly used for blow torches to cut metals in heavy metal industries.

By drawing an appropriate energy cycle, determine the enthalpy of combustion of propyne, given the following enthalpy values:

$\Delta H_f(C_3H_4) = +184 \text{ kJ mol}^{-1}$
$\Delta H_c(C) = -394 \text{ kJ mol}^{-1}$
$\Delta H_c(H_2) = -286 \text{ kJ mol}^{-1}$

(ii) Determine the enthalpy of combustion of propyne using bond energy values. Explain why the use of bond energy values to calculate the enthalpy of combustion is significantly less exothermic that those obtained in **(i)**.

[6]

[Total: 20]

8

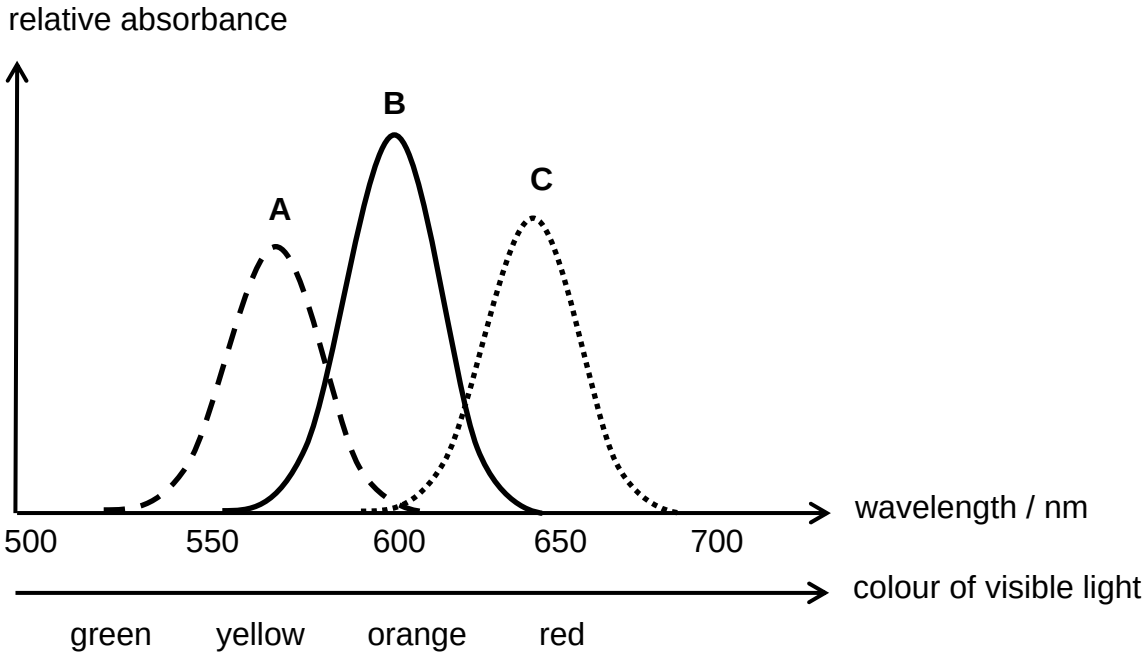
4 Nickel is a typical transition element which is commonly used as a catalyst and metal for electroplating. Nickel also forms complex ions with ligands such as H_2O, NH_3 and $NH_2CH_2CH_2NH_2$ to give various coloured complexes.

(a) What do you understand by the terms *transition element*, *ligand* and *complex ion*? [3]

(b) **(i)** Explain why transition metal complexes are coloured.

(ii) Complex ions of nickel such as $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ are green, blue and violet colour respectively.

The visible absorption spectra of the three complex ions of nickel are shown below:



Suggest an explanation for the difference in colour of the three complexes and using the colours of the complexes given, assign the peaks **A**, **B** and **C** to the three complex ions of nickel.

[5]

9

(c) When Ni^{2+} (aq) is mixed with an excess of NH_3 (aq), each H_2O is replaced by a NH_3 at a time. The stepwise formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$ can be summarised by the following equations with their associated equilibrium constants:

Step 1: $[Ni(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Ni(H_2O)_5(NH_3)]^{2+} + H_2O$ $K_1 = 630\ mol^{-1}dm^3$

Step 2: $[Ni(H_2O)_5(NH_3)]^{2+} + NH_3 \rightleftharpoons [Ni(H_2O)_4(NH_3)_2]^{2+} + H_2O$ $K_2 = 160\ mol^{-1}dm^3$

and so on for steps 3, 4 and 5.

Step 6: $[Ni(H_2O)(NH_3)_5]^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + H_2O$ $K_6 = 1.1\ mol^{-1}dm^3$

(i) The stepwise formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$ undergoes a dissociative mechanism which resembles a S_N1 mechanism in organic chemistry. Suggest a possible mechanism for Step 1 and show clearly how the shape of the complex ion changes.

(ii) Sketch an energy profile diagram for the suggested mechanism in **(i)** given the reaction is exothermic.

(iii) Suggest a possible reason for the decrease in value of the equilibrium constant for each successive replacement of water by ammonia ligands.

[6]

(d) $[Ni(H_2O)_6]^{2+}$ can also undergo ligand exchange reaction with $NH_2CH_2CH_2NH_2$ to form $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$. Using the signs of ΔG, ΔH and ΔS, explain how the formation of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ would compare to that of $[Ni(NH_3)_6]^{2+}$.

[3]

(e) With the aid of a clearly labelled diagram, show the calculations you would carry out to determine a value for the Avogadro constant by the electroplating of nickel from nickel(II) ions.

You may assume that you are provided with the following data.

- mass of nickel deposited, m
- current used, I
- time taken, t

[3]

[Total: 20]

5 **(a)** Amino acids play central roles both as building blocks of proteins and as intermediates in metabolism. The 20 amino acids that are found within proteins convey a vast array of chemical versatility and they have relatively high melting points and are soluble in water.

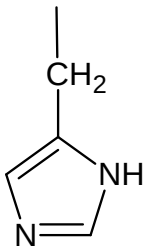
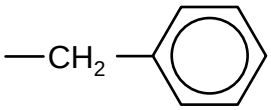
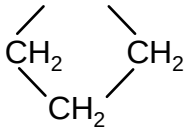
(i) Define the secondary structure of proteins.

(ii) What is meant by the term denaturation of proteins?

(iii) Suggest a brief outline of one method by which proteins may be denatured.

[4]

(b) An octapeptide **A** was analyzed and contained the following amino acids:

Amino acid	abbreviation	R-group	Number of residues
Aspartic acid	Asp	$-CH_2CO_2H$	1
Glycine	Gly	– H	2
Histidine	His		1
Phenylalanine	Phe		1
Proline	Pro	 (cyclic)	2
Valine	Val	$-CH(CH_3)_2$	1

(i) Analysis showed that the C-terminus contained an amino acid which is optically inactive and partial hydrolysis gives the following fragments:

Val-Pro-His, Gly-Asp-Pro-Phe, Pro-Phe-Val

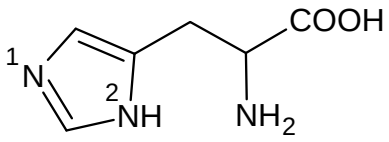
Use the above results to deduce the amino acid sequence of the octapeptide **A** and explain your reasoning.

(ii) Draw the displayed formula of Gly-Asp-Pro which is part of the octapeptide chain in **A**.

[4]

11

(c) Histidine is utilized by your body to develop and maintain healthy tissues. It is especially important in the myelin sheath that coat nervous cells to ensure the transmission of messages from your brain to organs throughout your body. Histidine also stimulates the secretion of the digestive enzymes gastrin and is also required to manufacture both red and white blood cells.



Structure of histidine

Histidine contains a total of 3 nitrogen atoms and each N atom exhibit different properties in aqueous solution.

(i) Considering the orbital arrangement of the atoms, explain why ^{2}N atom in histidine is less basic than ^{1}N atom.

(ii) There are three pK_a values associated with the histidine: 1.8, 6.0, 9.2. Assuming that the ^{2}N atom does not exhibit any basic properties, make use of the three pK_a values to suggest the major species present in solutions of histidine with the following pH values.

- pH 1
- pH 5
- pH 7
- pH 11

(iii) Consider the buffer solution at pH = 5, calculate what fraction of the histidine side chains will carry a positive charge at pH 5.

[8]

(d) 25.0 cm^3 of 0.150 mol dm^{-3} of diethylamine solution, $(CH_3CH_2)_2NH$, was placed in a conical flask and titrated against a solution of 0.200 mol dm^{-3} hydrochloric acid from a burette.

Given that the K_b of $(CH_3CH_2)_2NH$ is 8.60 x 10^{-4} mol dm^{-3},

(i) explain what is meant by the term base dissociation constant, K_b of diethylamine.

(ii) Calculate the pH at equivalence point.

[4]

[Total: 20]