SERANGOON JUNIOR COLLEGE
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9746/03

Preliminary Examination
Paper 3 Free Response

20 August 2009
2 hours

Candidates answer on separate paper.

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 work.
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

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

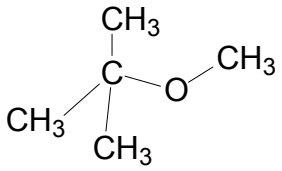
Answer any **four** questions.

1 **(a)** A student dissolved 8.4 g of sodium fluoride in 250 g of water. Given the following data, calculate the initial temperature of water if the final temperature of the solution is 20.0 °C. Assume that the specific heat capacity of sodium fluoride solution is 4.2 J g^{-1} K^{-1}.

Lattice energy of NaF	–918 kJ mol^{-1}
Enthalpy change of hydration of F^-	–457 kJ mol^{-1}
Enthalpy change of hydration of Na^+	–390 kJ mol^{-1}

[3]

(b) In the manufacture of fuel for industries, liquid MTBE is added as a solvent to petroleum to reduce pollution.



Methyl t-butyl ether (MTBE)

(i) What is meant by the term *standard enthalpy change of formation of MTBE*? Support your answer with the aid of an appropriate equation with state symbols.

(ii) Use the following data and by means of an appropriate energy cycle, prove that the bond energy for the C–H bond in MTBE is +418 kJ mol^{-1}.

Enthalpy change of atomisation of C(s)	+715 kJ mol^{-1}
Enthalpy change of formation of MTBE	–383 kJ mol^{-1}
Enthalpy change of vapourisation of MTBE	+30.4 kJ mol^{-1}
Bond Energy of H-H	+436 kJ mol^{-1}
Bond Energy of O=O	+496 kJ mol^{-1}
Bond Energy of C-O	+360 kJ mol^{-1}
Bond Energy of C-C	+350 kJ mol^{-1}

(iii) Suggest a reason for the difference in the C–H bond energy in **(b)(ii)** from the value given in the *Data Booklet*.

[7]

(c) Magnesium chloride, $MgCl_2$, is an important coagulant used in the preparation of soy products. The lattice energy of magnesium chloride is given to be –2490 kJ mol^{-1}.

(i) How would you expect the numerical magnitude of the lattice energy of barium chloride, $BaCl_2$ (s) to compare with that of $MgCl_2$ (s)? Hence predict a likely value for the lattice energy of barium chloride.

(ii) The enthalpy change of reaction, for the reaction below is given to be –391 kJ mol^{-1}.

$$2MgCl\ (s) \rightarrow\ MgCl_2\ (s) + Mg\ (s)$$

Comment on the stability of $MgCl$ (s) relative to that of $MgCl_2$ (s).

[4]

(d) Part of the research on Supramolecular Chemistry focuses on Host-Guest Chemistry, in which cationic transition metal complexes are involved in second-sphere coordination which is provided by ligands with an organised set of donors.
For example, a transition metal rhodium complex that contains hydrogen bond donor groups (ammonia or water ligands) in its primary coordination sphere can be considered as a guest capable of binding to a hydrogen bond acceptor host via second sphere coordination.

(i) State the bonding formed between rhodium and ammonia.

(ii) Describe the chemical structure and bonding in solid rhodium.

(iii) Show, with aid of a diagram, the intermolecular bonding in ammonia.

(iv) Predict and account for the boiling point of ammonia relative to water.

(v) Predict and account for the solubility of ammonia in water.

[6]
[Total: 20]

2 (a) The table below gives some data on some oxides of elements in Period 3 of the Periodic Table.

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_2
Boiling point / K	1548	3873	3253	2503	448	263

(i) Explain, in terms of chemical bonding and structure, why the boiling point of MgO is higher than P_4O_6.

(ii) Write an equation for the reaction of Al_2O_3 with dilute hydrochloric acid.

(iii) Write an equation for the reaction of SO_2 and Al_2O_3 separately with dilute sodium hydroxide.

(iv) Comment on the role of Al_2O_3 in reactions **(a)(ii)** and **(iii)** above.

[8]

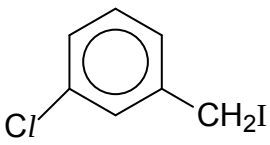
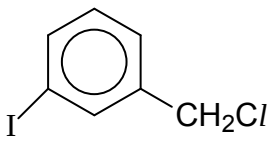
(b) (i) Write a balanced equation for the action of heat on magnesium nitrate.

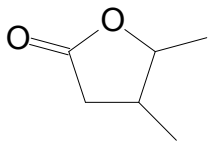
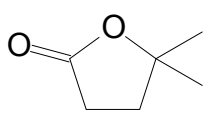
(ii) Magnesium nitrate decomposes at a lower temperature than strontium nitrate. Explain why the two nitrates decompose at different temperatures. Predict if barium nitrate would decompose at a higher or lower temperature compared to strontium nitrate.

[4]

(c) For each of the following pairs of structural isomers, describe **one** chemical test which would enable you to distinguish them. You should state the reagents and conditions for each test, and describe the observations.

(i) $CH_2(NH_2)COCl$ and $CH_2ClCONH_2$

(ii)  and 

(iii)  and 

[8]
[Total: 20]

3 (a) (i) In Singapore, chlorine is added to the drinking water. Explain briefly the importance of the addition of chlorine to drinking water.

(ii) Explain, with the aid of an equation, why the addition of a base at room temperature will result in the elimination of chlorine smell from drinking water. State the type of reaction that chlorine undergoes.

[3]

(b) The oxyacids of chlorine are:

Chemical formula	HOC*l*	HOC*l*O	HOC*l*O_2	HOC*l*O_3
Chemical Name	chloric (I) acid	chloric (III) acid	chloric (V) acid	chloric (VII) acid
K_a	$10^{-7.50}$	$10^{-1.96}$	10^{1}	10^{10}

(i) Describe and explain how an increase in oxygen content of the acids affects K_a.

(ii) Draw the dot-and-cross diagram of C*l*O_2^-. Suggest the shape and state the bond angle of the ion.

[4]

(c) (i) A sample of sodium hypochlorite, NaOC*l*, was dissolved in 100 cm^3 of 0.123 mol dm^{-3} HOC*l* solution forming a buffer of pH 6.20. Determine the ratio of the concentration of OCl^- to HOC*l* in the solution.

(ii) The buffer is then used to absorb HC*l* gas. By using the above ratio or otherwise, calculate the amount of gaseous HC*l* (in mol) that is required to be added to the buffer solution until it reaches pH 6.

[5]

(d) In the production of CH_3Cl using methane and chlorine under certain conditions, it has been noticed that a small quantity of chloroform, $CHCl_3$, has been produced.

Using CH_3Cl as the starting material, name and describe the mechanism of this reaction that would result the production of chloroform.

[3]

(e) **A**, $C_5H_9Cl_3$, is an optically active compound which reacts with hot aqueous sodium hydroxide to form **B**, $C_5H_{12}O_3$. **B** reacts with warm alkaline aqueous iodine to give a yellow precipitate **C** as well as **D**, $C_4H_7O_4Na$. When **D** undergoes vigorous oxidation in acidic medium, **E**, $C_4H_6O_5$, is produced. **E** gives a negative test with 2,4-dinitrophenylhydrazine.
Suggest the structural formulae of **A – E**, indicating clearly on **A** the chiral carbon.

[5]
[Total: 20]

4 The use of the *Data Booklet* is required for this question

(a) **(i)** Given the following half cells:

H_2O (*l*) / H_2 (g)
PbO_2 (s) / Pb^{2+}(aq)
MnO_4^- (aq) / MnO_2 (s)

Suggest the half cell which, when combined with a Cu^{2+} (aq) / Cu (s) half cell, will generate the highest E^{θ}_{cell}. State the anode and the cathode of the electrochemical cell, indicating the direction of electron flow in the external circuit.

(ii) The set up from **(a)(i)** was then used as the battery in the electrolysis of a solution of copper (II) sulphate with inert platinum electrodes. An ammeter showed a reading of 0.45 A in the external circuit of the cell. 0.30 g of copper metal was deposited at the cathode after 30 minutes. Determine the actual current used in the electrolysis process. Hence, determine the percentage error (if any) of the ammeter reading.

(iii) A student carried out a reaction involving potassium dichromate (VI) with an unknown half cell which consists of transition metal ions. The Gibbs Free Energy of the reaction was known to be –324 kJ mol^{-1} and the procedure involved transfer of 6 mol of electrons from the unknown solution to potassium dichromate (VI).

Using the expression of $\triangle G^{\theta} = -nFE^{\theta}_{cell}$, where n is the number of electrons transferred, F is the Faraday constant and E^{θ}_{cell} is the overall cell potential, determine the E^{θ}_{cell} value and hence deduce the identity of the unknown half cell.

[8]

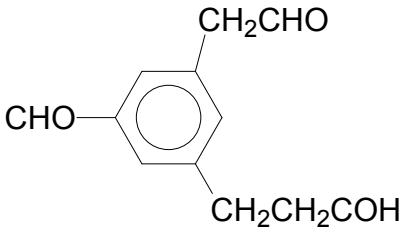
(b) **(i)** Copper is a transition element and can exist in variable oxidation states. Suggest why transition elements have the tendency to have variable oxidation states.

(ii) When dilute ammonia is gradually added to a solution containing copper (II) ions, a pale blue precipitate is formed, which re-dissolves on adding excess dilute ammonia. Explain the above observations, writing equations where appropriate.

(iii) Explain why aqueous copper (II) ions are coloured.

[7]

(c) **(i)** Fehling's solution, which is a solution of alkaline aqueous copper (II) complex, is commonly used to test for the presence of a functional group. Determine the organic product formed when compound **F** reacts with Fehling's solution.

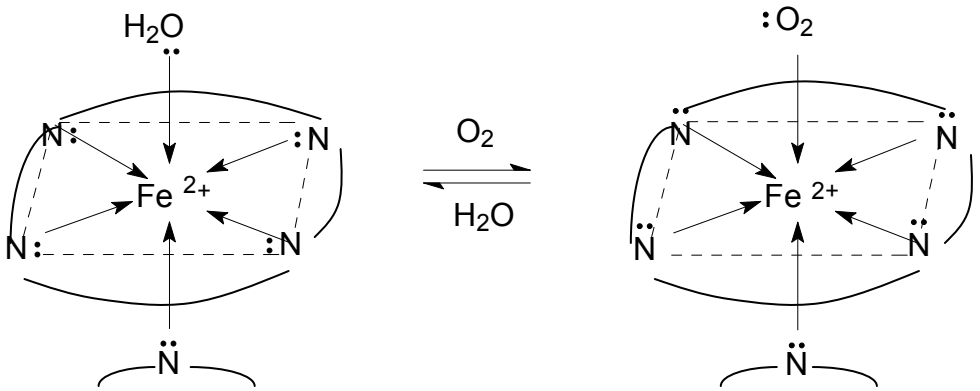


Compound **F**

(ii) Compound **F** was allowed to react with hydrogen in the presence of nickel catalyst. Explain why nickel is able to catalyse the reaction and draw the product formed in this reaction.

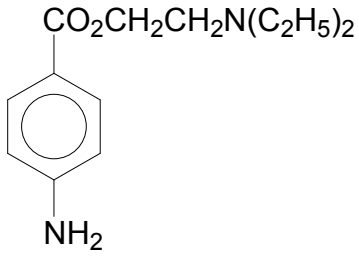
[3]

(d) Haem can be represented schematically as shown below. Briefly explain how the haemoglobin carries oxygen and why carbon monoxide is toxic to the human body.



[2]
[Total: 20]

5 **(a)** When an organic compound **G** is heated with acidified potassium manganate (VII), the purple colour is decolourised and compound **H** is obtained.
When phosphorus pentachloride is added to **H**, white fumes are observed and compound **J** is formed.
J is heated with tin in concentrated hydrochloric acid, followed by aqueous sodium hydroxide to form compound **K**.
K reacts with $(C_2H_5)_2NCH_2CH_2OH$ to form procaine which has the following structure:



Procaine

Identify compounds **G**, **H**, **J** and **K** and explain the reactions involved.

[7]

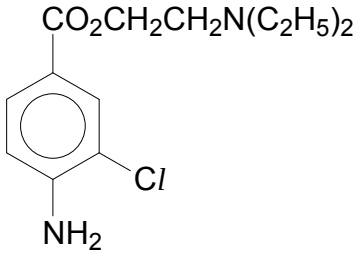
(b) Draw the structure of the compound(s) formed when procaine reacts with:

(i) Hot, dilute hydrochloric acid

(ii) Aqueous bromine

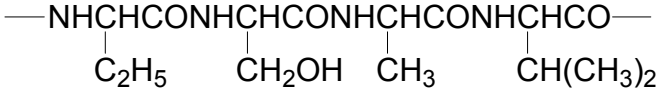
[3]

(c) Compound **M** has the following structure:



State and explain whether procaine or compound **M** is more basic. **[2]**

(d) The diagram below shows the structure, at pH 7, of a fragment of a protein which contains 4 amino acids **P**, **Q**, **R** and **S** in the following sequence:

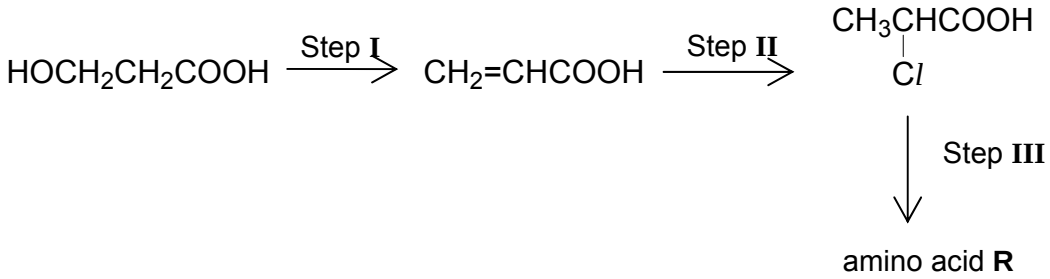


(i) Draw the structures of the amino acids **Q** and **R** when this protein is hydrolysed.

(ii) State the interactions in amino acids **Q** and **R** that could be involved in the maintenance of the tertiary structure of proteins.

[2]

(e) Amino acid **R** can be obtained via the following route:



(i) Name the types of reactions as well as the reagents and conditions needed for Steps **I**, **II** and **III.**

(ii) Outline the mechanism involved in Step **III**.

[6]
[Total: 20]

-END OF PAPER-

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