NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9647/03

Paper 3 Free Response **18 September 2012**

2 hours

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

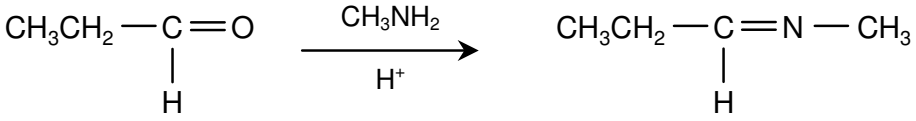
Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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.

Answer **any four** questions

1 Aldehydes and ketones react with primary amines in slightly acidic solution to form imines which have the C=N functional group. For example, propanal reacts with methylamine to give *N*-methyl-1-propanimine.



propanal — *N*-methyl-1-propanimine

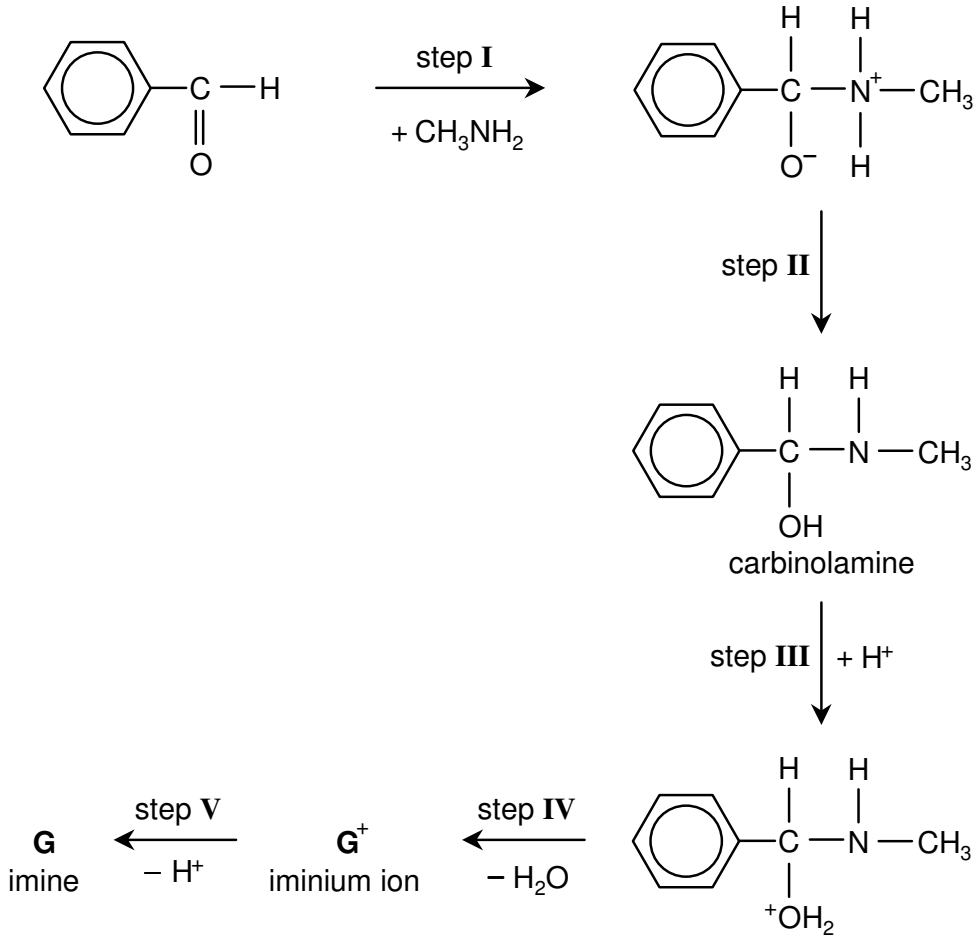
(a) Aldehydes and ketones also react with 2,4-dinitrophenylhydrazine (2,4-DNPH) to give compounds that are closely related to imines.

(i) Write a balanced equation for the reaction between benzaldehyde and 2,4-DNPH.

(ii) State what you would observe in the reaction with 2,4-DNPH. What is the type of reaction?

[4]

(b) The mechanism for the reaction between benzaldehyde and methylamine is shown below.



(i) What is the type of reaction in step **I**?

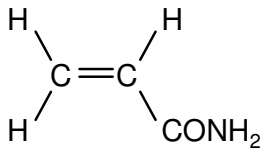
(ii) The positive charge on the iminium ion, $\mathbf{G}^+$, does **not** reside on a carbon atom. Suggest the structure of $\mathbf{G}^+$.

(iii) Write equations for step **I** and step **IV** to show the movement of electrons, using curved arrow notation. Show the lone pairs of electrons, if any, that are involved in each step.

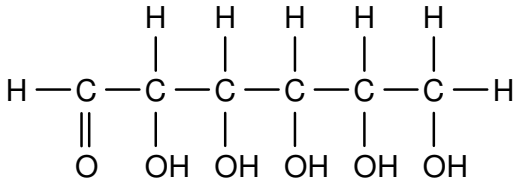
(iv) The maximum rate of formation of imines occurs at a pH of about 4.5. Explain why the rate is slow under very acidic conditions and under alkaline conditions.

[6]

(c) Acrylamide is a carcinogen. It is formed when potato chips are heated to above 120 °C. Its formation has been linked to the presence of glucose ($C_6H_{12}O_6$) and an α-amino acid **L** found in relatively high amounts in potato.



acrylamide



glucose

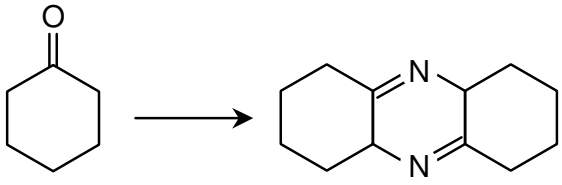
Glucose reacts with **L** to form an imine **M**. At high cooking temperatures, **M** decomposes to produce only three compounds in equimolar amounts: acrylamide, carbon dioxide and compound **N** ($C_6H_{13}NO_5$).

(i) Name the functional groups in acrylamide.

(ii) Deduce the structure of **L**. Show clearly how you obtained your answer.

[5]

(d) Suggest the reagents and conditions required to synthesise the following imine derivative. Identify all the intermediate compounds.



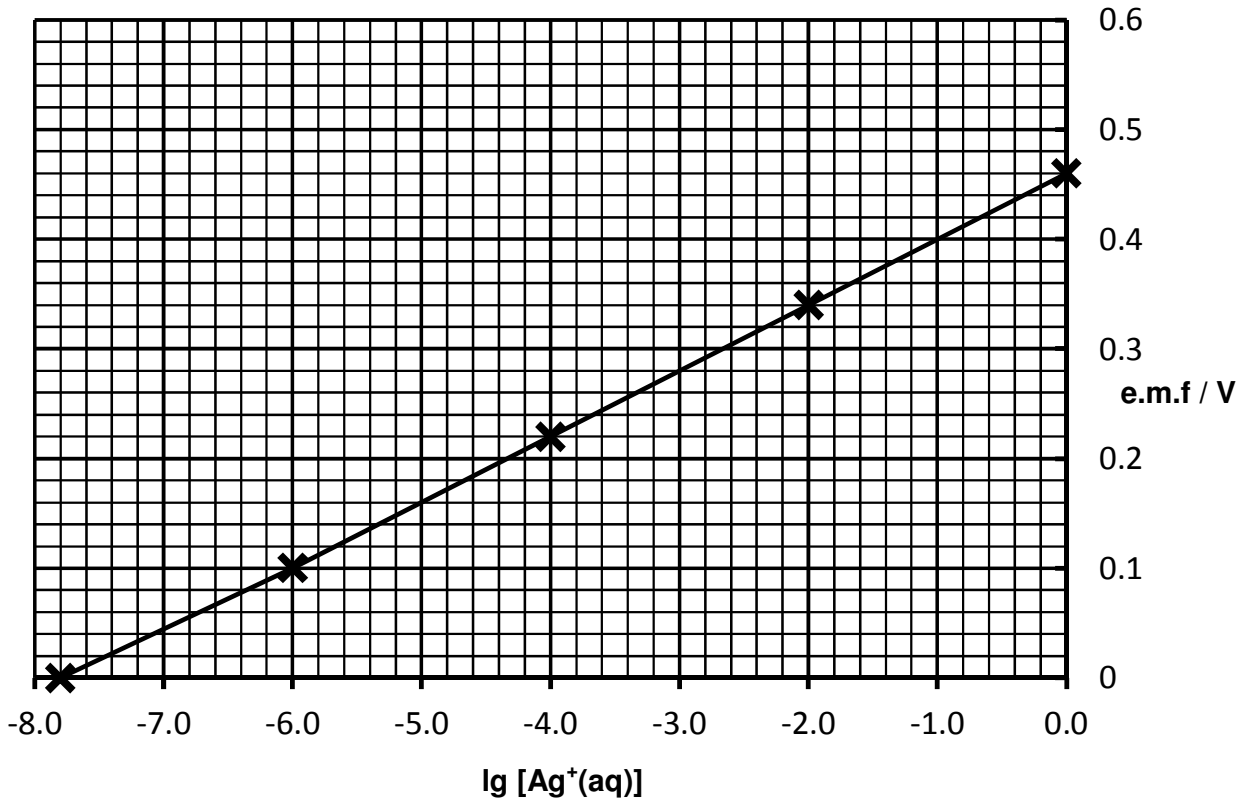
[5]

[Total: 20]

2 **(a)** A container holds a gaseous mixture of nitrogen and propane. The pressure in the container at 200 °C is 4.5 atm. At –40 °C, the propane completely condenses and the pressure drops to 1.5 atm. Calculate the mole fraction of propane in the original gaseous mixture. [3]

(b) The graph below shows the variation in electromotive force (e.m.f.) of the following electrochemical cell with lg [$Ag^+(aq)$] at 298 K.

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$



(i) Using the information from the graph, calculate the standard electrode potential of the half-cell, $Ag^+(aq) \mid Ag(s)$, at 298 K.

(ii) If the $Ag^+(aq)$ solution of the electrochemical cell is replaced by a saturated solution of silver bromate(V), $AgBrO_3$, in 0.1 mol dm^{-3} potassium bromate(V) and the e.m.f. of the cell measured at 298 K is +0.27 V, determine

(I) the concentration of $Ag^+(aq)$ ions in the saturated solution, and

(II) the solubility product of silver bromate(V) at 298 K.

[5]

(c) Solid silver nitrate was slowly dissolved in a solution **Q** containing ethanedioate, $C_2O_4^{2-}$, and chromate(VI), CrO_4^{2-}, ions of concentrations 2.50 x 10^{-2} mol dm^{-3} and 1.44 x 10^{-5} mol dm^{-3} respectively.

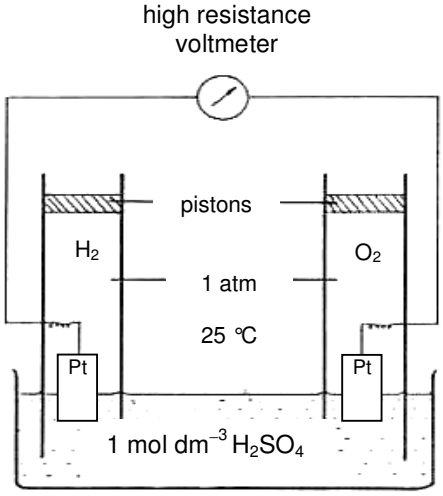
(i) When a permanent precipitate of silver ethanedioate first appeared, the concentration of silver ions in the solution was 2.10 x 10^{-5} mol dm^{-3}. Calculate the solubility product of silver ethanedioate.

(ii) The dissolving of solid silver nitrate in **Q** was continued until a permanent red precipitate of silver chromate(VI) first appeared. Calculate the concentrations of silver ions and ethanedioate ions at that instant.
(K_{sp} of silver chromate(VI) is 1.2 x 10^{-12} mol^3 dm^{-9}.)

(iii) What is the amount of silver ethanedioate precipitated from 1.00 dm^3 of the solution?

[7]

(d) An electrochemical cell containing an oxygen cathode and a hydrogen anode is shown below. The pistons above the gas chambers are frictionless.



(i) Write balanced equations for the half reactions and for the overall reaction in the cell.

(ii) How does the concentration of sulfuric acid affect the equilibria of the half reactions?

(iii) If weights are added to the pistons of both chambers, how would the reading of the voltmeter change? Explain your answer.

[5]

[Total: 20]

3 (a) (i) Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4 and $K_2Cr_2O_7$.
Suggest a reason why these reagents do not attack an alkane such as CH_4.

(ii) It is found by experiment that, during free-radical substitution of alkane, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

type of hydrogen atom	reaction	relative rate
primary	$RCH_3 \rightarrow RCH_2Cl$	1
secondary	$R_2CH_2 \rightarrow R_2CHCl$	7
tertiary	$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number and type of hydrogen atoms within the molecule, predict the relative ratio of the two possible products **J** and **K** from the monochlorination of 2-methylpropane. Explain your answer.

[3]

(b) Compounds **A** and **B** are amines with the same molecular formula. Both have a molecular mass of 73.0 and the following composition by mass: C, 65.8 % and H, 15.1 %.

Compound **A** has a pK_b of 3.23 and contains a tri-substituted N atom.

The pH of an aqueous solution of 0.0100 mol dm^{-3} of compound **B** is 11.5. When **B** undergoes free-radical substitution reaction, it only gives **one** mono-substituted organic product.

(i) Calculate the molecular formulae of compounds **A** and **B**.

(ii) Calculate the pK_b of compound **B**.

(iii) Suggest the structural formulae of compounds **A** and **B**.

(iv) State and explain the relative basicity of compounds **A** and **B**.

[7]

(c) **(i)** The hydrolysis of 2-bromo-2-methylpropane takes place as follows.

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$$

An experiment was conducted to determine the order of reaction with respect to 2-bromo-2-methylpropane. The following results were obtained.

time/s	19	28	50	69	154
$[(CH_3)_3COH]$/mol dm^{-3}	0.0030	0.0040	0.0060	0.0072	0.0095

It was found that the order of reaction with respect to 2-bromo-2-methylpropane is one and the half-life of the reaction is 34.5 s.

Using a non-graphical method, show that the concentration of 2-bromo-2-methylpropane at the start of the experiment is 0.0096 mol dm^{-3}.

(ii) Hence, deduce how long the reaction has proceeded when concentration of $(CH_3)_3COH$ obtained is 0.0084 mol dm^{-3}.

(iii) The following two mechanisms are both consistent with the reaction being overall first order.

mechanism **X** $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$

mechanism **Y**

$$(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + Br^- \quad \text{slow}$$
$$(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH + H^+ \quad \text{fast}$$

Explain why both mechanisms **X** and **Y** show overall first order kinetics.

(iv) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane increases when the temperature is increased. Explain this observation with the aid of a suitable diagram.

(v) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane is R at T ^oC. What is the new rate if temperature is increased to (T+50) ^oC?
Explain your answer.

[10]

[Total: 20]

4 This question is about thermal decomposition reactions of Group II compounds.

(a) A student investigates the thermal decomposition of some Group II nitrates. He separately heats equal amounts of the nitrates of magnesium, calcium and barium for one minute, passes the gases produced through aqueous sodium hydroxide and measures the volume of the remaining gas. The following table shows the results:

Element of nitrate	Mg	Ca	Ba
Volume of remaining gas / cm^3	90	19	9

(i) Explain the purpose of sodium hydroxide and identify the remaining gas.

(ii) Draw an appropriate experimental set-up that allows the student to perform the experiment and measure the volume of the remaining gas.

(iii) Using suitable data from the *Data Booklet*, explain the results obtained by the student.

(iv) Hence, estimate the volume of remaining gas produced after 1 min if the student were to heat zinc nitrate.

(v) The student heats a 10.0 g mixture of magnesium nitrate and calcium nitrate till no further changes. The volume of remaining gas produced was 780 cm^3 at room temperature. Calculate the mass of magnesium nitrate present.

[12]

(b) The decomposition of calcium carbonate is as follows.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In order to determine the enthalpy change of decomposition, two pieces of calcium carbonate were selected, each with a mass of 1.25 g. The first piece was placed in 20 cm^3 of excess dilute hydrochloric acid and the temperature rose by 2 °C. The second piece was heated strongly for ten minutes to decompose it thoroughly. It was then allowed to cool to room temperature before it was added to 20 cm^3 of dilute hydrochloric acid. The temperature rose by 26 °C. The two experiments were estimated to be 90% efficient.

(i) By using the information above and drawing a suitable energy cycle, calculate the enthalpy change of decomposition of calcium carbonate, in kJ mol^{-1}, to 3 significant figures.

When calcium carbonate is heated in a sealed tube at its thermal decomposition temperature, the reaction eventually reaches an equilibrium.

(ii) Given that ΔS = +161 J mol^{-1} K^{-1} and your answer in part **(i)**, calculate the thermal decomposition temperature, in K.

(iii) Hence sketch the graph of ΔG against T, labelling clearly the thermal decomposition temperature.

[8]

[Total: 20]

5 Iron is the sixth most abundant element in the Universe and the most common refractory element.

(a) Iron(III) oxide has a high melting point and is a good conductor of electricity when molten. Explain, in terms of its bonding and structure, why iron(III) oxide has these properties. [3]

(b) Samples of iron(III) oxide and iron(III) chloride are added, with stirring, to separate beakers of pure water. Suggest the pH value of the resulting solution in each beaker after stirring, giving a reason for your choice. Write equations for any reactions occurring. [4]

(c) Give the ion-electron equations for the electrode reactions in the electrolysis of aqueous iron(III) chloride using inert electrodes. [2]

(d) When water reacts with iron(III) ions, it acts as a *ligand* in the formation of the complex ion, $[Fe(H_2O)_6]^{3+}$ to give a coloured solution.

(i) Explain what is meant by the term *ligand*.

(ii) Explain why solutions containing iron(III) ions are coloured but those containing zinc ions are colourless.

[5]

(e) A solution contains a mixture of iron(III) and zinc ions. You are provided with NaOH(aq) and HNO_3(aq). You are to propose a series of test-tube experiments to separate the two cations so that each cation is present as its **aqueous** ions.

(i) Give a description of your proposed sequence of steps to separate the two cations, numbering each step.

(ii) With the aid of appropriate equations, explain the reactions involved.

[6]

[Total: 20]

[End of Paper]