NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

CLASS

TUTOR'S NAME

CHEMISTRY

9746/03

Paper 3 Free Response

10 September 2008

2 hours

Additional Materials: Answer Paper
Data Booklet
Graph Paper

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.

This document consists of **10** printed pages and **2** blank pages.

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Answer any **four** questions.

1 Some organic and inorganic compounds are classified under a category called 'Non-Existent Compounds'. They are called non-existent because so far chemists had been unable to synthesise them. Some of the reasons why these compounds are unstable are:

- unfavourable bond energy terms
- a redox incompatibility of the ions making up the compound
- inability of the element concerned to provided orbitals of suitable energy for effective bond-forming overlap with neighbouring atoms
- reaction occurring between the ions

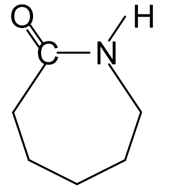
For the following cases, suggest an explanation for each observation. You may use data from the *Data Booklet* to assist you in your answers. Give relevant equations to support your answers.

(a) Both phosphorus and nitrogen are elements in Group V of the Periodic Table. PCl_5 can be formed but not NCl_5. [3]

(b) It is possible to find $MnCl_2$ in the laboratory but impossible to get $MnCl_3$. [3]

(c) When aqueous sodium carbonate is added to aqueous aluminium chloride, a colourless gas is liberated and the precipitate formed is not aluminium carbonate, $Al_2(CO_3)_3$. [5]

(d) Caprolactum, a monomer of the polymer nylon 6, exists as an alicyclic ring structure and not as 6-aminohexanoic acid, a straight chain aliphatic structure as most monomers do.

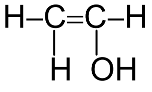


Caprolactum

$H_2NCH_2CH_2CH_2CH_2CH_2CO_2H$

6-aminohexanoic acid [4]

(e) Hydration of ethyne, H–C≡C–H, should produce ethenol,

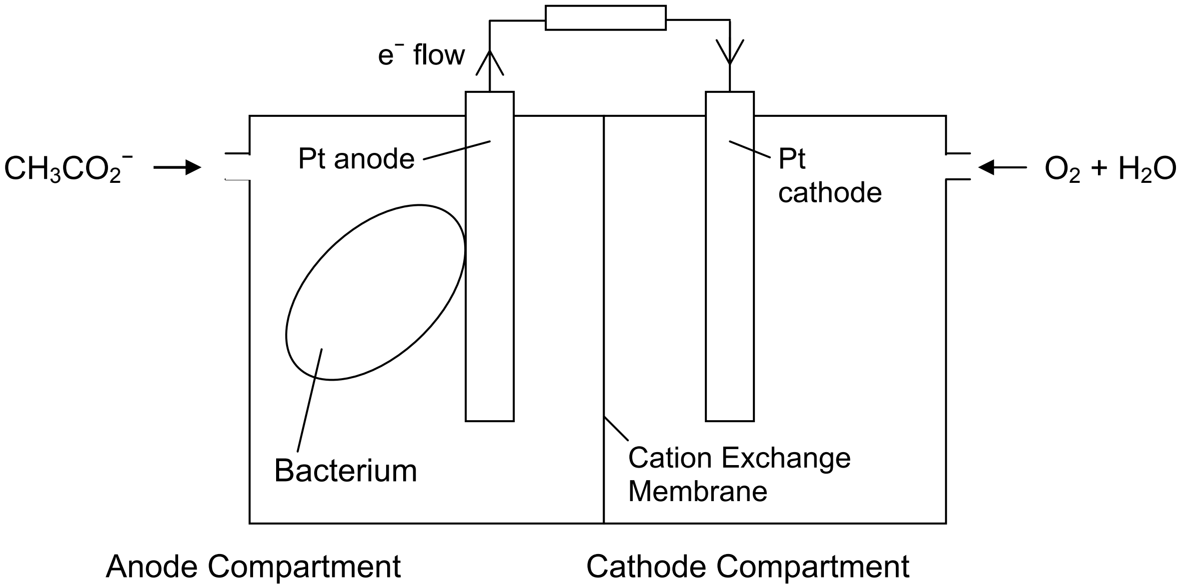


$H\!-\!\underset{H}{C}\!=\!\underset{OH}{C}\!-\!H$

but, instead, it produces ethanal, CH_3CHO. [5]

[Total: 20]

2 A current research in alternative sources of renewable energy is in the area of Microbial Fuel Cell (MFC). MFCs convert chemical energy directly into electricity using bacteria as catalyst.



An MFC consist of an anode compartment and a cathode compartment separated by a cation exchange membrane which allows only cations to pass through.
The bacteria live in the anode compartment and feed on organic substrates, such as ethanoate ion, $CH_3CO_2^-$ that is continuously introduced. The bacteria will convert the substrate into hydrogen carbonate ions, HCO_3^-, protons and electrons. The HCO_3^- ions and protons will pass into the anode electrolyte while the electrons will be transferred to the anode. The flow of electrons through the external circuit can be harnessed to do electrical work.
At the cathode, oxygen in the cathode electrolyte is reduced to form water.

(a) **(i)** Write ionic equations for the reactions occurring at the anode and cathode.

(ii) Suggest, with reasoning, the function of the cation exchange membrane.

[3]

(b) Under standard conditions, the reduction potential for the $HCO_3^-/CH_3CO_2^-$ system is +0.19 V when measured against the standard hydrogen electrode.

(i) Draw a labeled diagram to show how the standard electrode potential of the $HCO_3^-/CH_3CO_2^-$ system could be measured.

(ii) Calculate the standard cell potential that can be obtained in the MFC.

[4]

(c) A current of 0.50 A is produced when the MFC is in operation. Calculate the mass of $CH_3CO_2^-$ processed by the MFC in one hour. [2]

(d) In actual MFCs, the anode electrolyte contains a mixture of sodium dihydrogen phosphate, NaH_2PO_4 and sodium hydrogenphosphate, Na_2HPO_4 to help maintain the pH at 7. This solution can be obtained by dissolving phosphorus (V) oxide, P_4O_{10} in water followed by careful addition of aqueous sodium hydroxide.

In an experimental setup, solid P_4O_{10} was dissolved in 50 cm^3 of distilled water and added to 50 cm^3 of 0.224 mol dm^{-3} aqueous sodium hydroxide. The resulting solution was used as the anode electrolyte.

(i) Write equations for the above reactions.

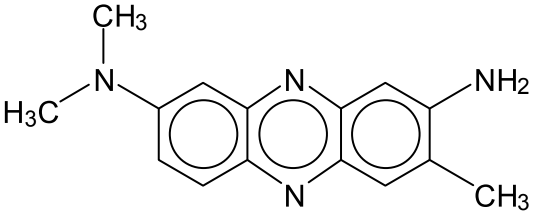
(ii) Explain with the help of equations the roles of NaH_2PO_4 and Na_2HPO_4.

(iii) The acid dissociation constant, K_a of $H_2PO_4^-$ is 6.2 x 10^{-8} mol dm^{-3}. Determine the ratio of the amount of HPO_4^{2-} to $H_2PO_4^-$ in 100 cm^3 of anode electrolyte.

(iv) Using your answer in **(d)(iii)**, calculate the mass of P_4O_{10} dissolved in the 50 cm^3 of distilled water.

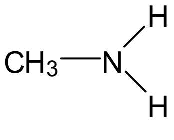
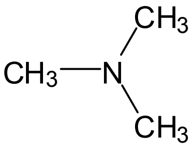
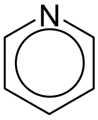
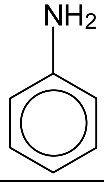
[7]

(e) Chemical mediators are used in MFCs to help in the transfer of electrons. One such mediator is the compound neutral red.



Neutral Red

In order to understand the relative basicity of the various nitrogen groups on neutral red, a comparison is done with similar nitrogeneous bases.
The pK_b values of these relevant bases are given below.

Methylamine	Trimethylamine	Pyridine	Phenylamine
			
3.34	4.19	8.75	9.37

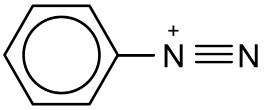
(i) Explain the relative basicity of
- methylamine and trimethylamine,
- pyridine and phenylamine

(ii) Rank the four nitrogen groups on neutral red in order of increasing basicity.

[4]

[Total: 20]

3 Arenediazonium ions have the general formula ArN_2^+, where Ar represents an aryl group. The benzenediazonium ion is an example of an arenediazonium ion.



benzenediazonium ion

Aqueous solutions of arenediazonium salts are stable at low temperatures.

(a) Warming an aqueous solution of a benzenediazonium salt produces phenol and nitrogen gas.

$$C_6H_5N_2^+(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + H^+(aq)$$

The reaction is first order with respect to benzenediazonium ion.

In an experiment to determine the rate constant for the reaction at 48°C, 100 cm^3 of a 0.00800 $mol\ dm^{-3}$ solution of benzenediazonium chloride was warmed to 48°C. The volume of nitrogen gas evolved was measured at 48°C and 101 kPa over a 40 min time interval. The following results were obtained.

Time / min	Volume of N_2 / cm^3
0	0.0
3	3.5
6	6.3
10	9.5
15	12.5
22	15.4
30	17.6
40	19.2

(i) Calculate the maximum volume of N_2 (at 48°C and 101 kPa) that can be obtained if the reaction goes to completion.

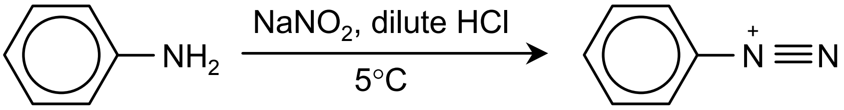
(ii) What do you understand by the terms *order of reaction* and *rate constant*?

(iii) Confirm that the reaction is first order with respect to benzenediazonium ion.

(iv) Write an expression for the rate equation and determine the half-life and rate constant.

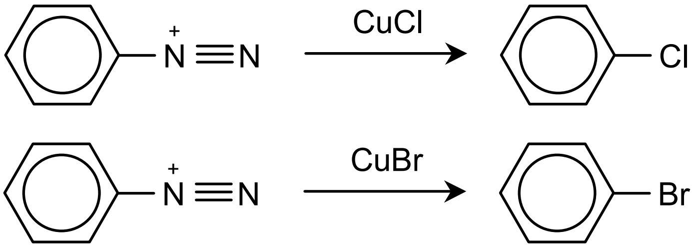
[11]

(b) Arenediazonium ions are formed by the reaction of a primary aromatic amine with sodium nitrite and dilute hydrochloric acid at 5°C. The process is called diazotisation. The diazotisation of phenylamine yields benzenediazonium ion.

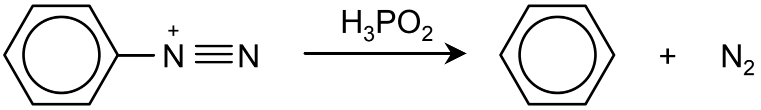


Arenediazonium ions are useful intermediates in the synthesis of many substituted aromatic compounds. This is because the diazonium group can be replaced with many other atoms or groups such as OH, Cl, Br and H.

In the Sandmeyer reaction, the arenediazonium ions are reacted with copper(I) chloride and copper(I) bromide to replace the diazonium group with Cl and Br respectively.

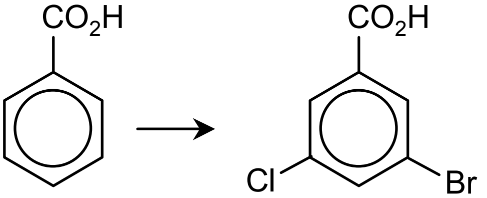


Deamination can be carried out using phosphinic acid, H_3PO_2.



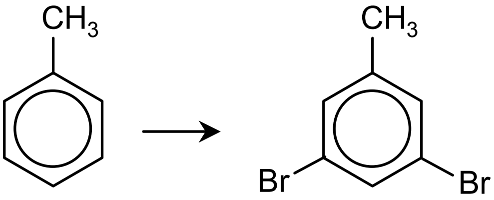
Compounds **P** and **Q** shown below can be synthesised from their respective starting materials using arenediazonium ion as an intermediate at some stage of each synthesis. Suggest the reagents and conditions required for each transformation. In each case, identify all the intermediate compounds.

(i)



P

(ii)



Q

[9]

[Total: 20]

4 This question involves chlorine and some of its compounds.

(a) Describe the reactions that occur when chlorine is passed into aqueous sodium hydroxide at room temperature and the mixture is then heated.

Write equations for the reactions involved. [3]

(b) When chlorine is bubbled through a solution of iodine in hot aqueous sodium hydroxide, the two halogens react in the $Cl_2 : I_2$ ratio of 7 : 1, forming a white precipitate **A** and a solution of sodium chloride. **A** has the following composition by mass:

Na, 16.9%; I, 46.7%; H, 1.1%; O, 35.3%

(i) Calculate the empirical formula of **A**.

(ii) Construct a balanced equation for the above reaction.

(iii) State the oxidation number of iodine in **A**.

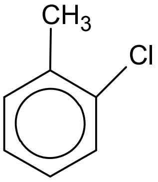
[4]

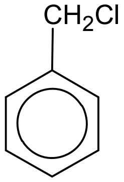
(c) Describe a simple chemical test which would enable you to distinguish the following pairs of compounds.

For each test, state the reagents, and conditions, and state what would be observed with **each** compound.

(i) $CCl_3CH_2COCH_3$ $CCl_3COCH_2CH_3$

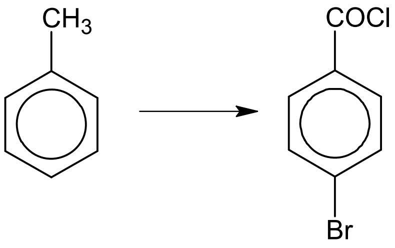
(ii)





[4]

(d) 4-bromobenzoyl chloride can be synthesized from methylbenzene via multi-step transformation.



Suggest reagents and conditions for each step and draw the structural formulae of the intermediates formed. [5]

(e) Compound **A**, $C_5H_{10}Cl_2$, is a chiral compound which reacts with warm aqueous potassium hydroxide to form compound **B**.

Oxidation of **B** produced a compound that does not react with 2,4-dinitrophenylhydrazine. **B** gives a negative tri-iodomethane test. When **B** is added to excess concentrated sulphuric acid at 170 °C, compound **C,** C_5H_8 is formed.

On reacting **C** with acidified potassium manganate(VII), compound **D,** $C_3H_4O_3$ is formed.

Draw the structural formulae of compounds **A** to **D**. [4]

[Total: 20]

5 Compounds, especially organic compounds, exhibit many types of isomerism e.g. structural isomerism, geometric isomerism, optical isomerism..

(a) The cis-trans interconversion of but-2-ene isomers does not occur spontaneously, but it can be made to happen by treating the alkene with a strong acid catalyst.

$$\text{cis-but-2-ene(g)} \rightleftharpoons \text{trans-but-2-ene(g)}$$

(i) Given that the K_p of the above equilibrium is 3.4, calculate the fraction of trans-but-2-ene present at equilibrium.

(ii) The hydrogenation of butene is given by

$$C_4H_8(g) + H_2(g) \rightarrow C_4H_{10}(g)$$

However, hydrogenation of the two isomers gives different enthalpy changes:

enthalpy change of hydrogenation of cis-but-2-ene = – 120 kJ mol^{-1} and
enthalpy change of hydrogenation of trans-but-2-ene = – 116 kJ mol^{-1}

Calculate the enthalpy change for the cis-trans interconversion of but-2-ene.

(iii) Hence, predict an approximate value of ΔG for the cis-trans interconversion of but-2-ene, showing your reasoning.

(iv) The reaction between but-2-ene and Cl_2 gas, in the presence of sunlight, produces two mono-chlorinated isomers **A** and **B**.

- Draw the structural formula of isomers **A** and **B**.
- Outline the mechanism required to produce either **A** or **B**

[6]

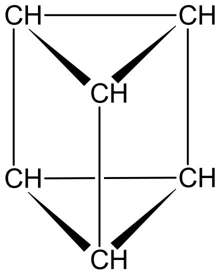
(b) The following data show the enthalpy change of combustion data of some organic compounds.

Substance	**ΔH_c / kJ mol^{-1}**
Benzene	– 3268
Cyclohexene	– 3754
Cyclohexane	– 3920
Hydrogen	– 286

(i) By drawing energy level diagrams which incorporates the above enthalpy values, calculate the enthalpy change of hydrogenation of cyclohexene and that of benzene.

(ii) What conclusion can you draw about the structure of benzene compared with that of cyclohexene?

(iii) In 1869, Albert Ladenburg proposed the following as a possible structure for benzene.



Draw structures of three possible isomers of dibromobenzene based on the proposed Ladenburg structure of benzene.

(iv) The enthalpy change of hydrogenation of cyclohexa-1,3-diene is less exothermic than that of cyclohexa-1,4-diene. With help from your answer in part **(i)**, estimate the two values, explaining your answer.

[8]

(c) Acid, **X**, has the structural formula $CH_3CHC\mathit{l}CH_2CH_2CHC\mathit{l}COOH$ and pK_a value of 2.31.

(i) One mole of acid **X** reacts exactly with 3 moles of hot ethanolic KOH. During the reaction, a mixture of six isomers is formed. Draw the structural formulae of all six isomers that are formed.

(ii) Calculate the pH of the solution formed when 20.0 cm^3 of 1.5 mol dm^{-3} of **X** is added to 40.0 cm^3 of 0.75 $moldm^{-3}$ of dilute KOH.

[6]

[Total: 20]

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