HWA CHONG INSTITUTION
JC2 Preliminary Examinations
Higher 2

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

CHEMISTRY

9647/03

Paper 3 Free Response

13 September 2011

2 hours

Candidates answer on separate paper

Additional Materials: Answer Paper

Data Booklet

INSTRUCTIONS TO CANDIDATES

Write your name and class on all the work you hand in.

Write in dark blue or black pen.

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.

Begin each question on a **new** piece of paper.

A Data Booklet is provided.

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

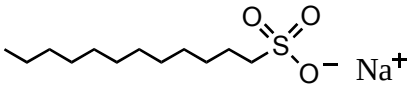
The number of marks is given in brackets [ ] at the end of each question or part question.

At the end of the examination, fasten all your work securely together.

Write down the **question numbers** for the questions that you have attempted on the **cover page** provided.

Answer any **four** questions.

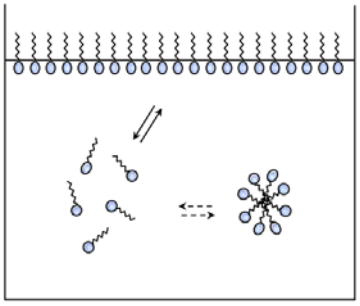
1 **(a)** The primary ingredient of a shampoo is a surfactant. A surfactant is an *amphiphilic* molecule, that is, it contains both a discrete polar portion and a well-defined non-polar fragment. A common surfactant used in shampoos is sodium lauryl sulfate.



sodium lauryl sulfate

simplified representation

When a surfactant is added to water, the molecules orientate themselves on the water's surface as shown in the diagram below. When even more surfactants are added, the surfactant molecules will group together in three-dimensional spherical clusters, with the hydrocarbon chains filling the interior of the cluster and the ionic ends composing the outer surface. These molecular conglomerations are known as *micelles*.



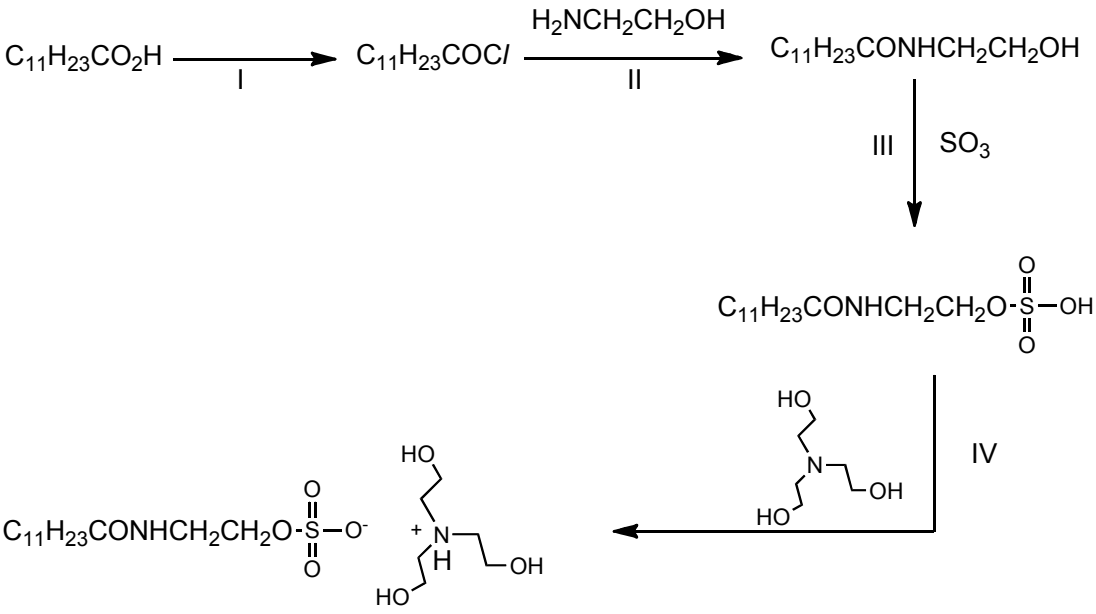
(i) By identifying all favorable interactions, explain the molecular orientation of the surfactant molecules at the surface of the water.

(ii) Explain how micelles help to remove grease from hair.

[3]

(b) Many shampoos, particularly those targeted for babies and children, claim to cause no eye irritation or sting. Compound **A** has been shown to be slightly effective as a "no-tears" formulation.

The reaction scheme below outlines the synthesis of compound **A**.



A

(i) State the reagent and condition needed for step **I**.

(ii) State the type of reaction in step **IV**.

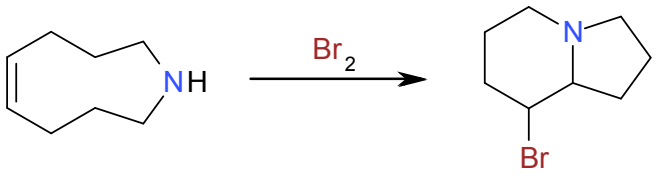
(iii) Step **II** in the above reaction scheme is not satisfactory. Identify the problem arising from the use of the reagent $H_2NCH_2CH_2OH$ in the attempt to synthesize $C_{11}H_{23}CONHCH_2CH_2OH$.

(iv) The reagent in step **II**, $H_2NCH_2CH_2OH$, can be synthesized from chloroethane in 3 steps. Give the reagents and conditions for each step, as well as the structures of the intermediates formed.

[6]

(c) The bicyclic product **B** is a precursor for the synthesis of certain types of novel non-ionic surfactants that help to improve the solubility, foaming action and conditioning action of a shampoo formulation.

Describe the mechanism for the formation of the bicyclic product **B** formed in the following reaction.



B

[4]

(d) SO_3 in step **III** is manufactured from the reaction between SO_2 and O_2, in the presence of V_2O_5, in the Contact Process as shown below:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) When a 2:1 mixture of SO_2 and O_2 was allowed to reach equilibrium at 800 K and a total equilibrium pressure of 8 atm, the partial pressure of SO_2 was found to be 0.150 atm.

Write an expression for K_p and calculate its value at 800 K.

(ii) State the role of V_2O_5 and describe its mode of action in the above reaction.

[7]

[Total: 20]

2 **(a)** The most common fuel used in engines today is gasoline, which is made up of hydrocarbons containing between 4 to 10 carbon atoms. Another common petroleum-derived fuel is diesel oil, which is made up of hydrocarbons containing 12 or more carbon atoms.

The fuel ignition process in a gasoline and diesel engine are very different for the following reasons. Gasoline is highly flammable and exposure to a spark will cause an explosion. However, diesel oil cannot be ignited even if a lighted match is thrown into a container of the fuel.

Using your knowledge of chemical bonding, explain why gasoline and diesel oil have such different combustion characteristics.

[2]

(b) The problems associated with the internal combustion engine led to a quest to produce 'cleaner' fuels. Hydrogen gas is touted as the cleanest fuel since the only product is water.

One of the methods of producing hydrogen fuel is to convert an ethanol-water-oxygen mixture to hydrogen at the surface of a suitable catalyst. Carbon dioxide is the only other product.

The efficiency of this process is measured by the number of hydrogen molecules that may be produced per molecule of ethanol.

(i) Write an equation, including state symbols, for the conversion of the ethanol-water-oxygen mixture to hydrogen gas.

(ii) Predict and explain the sign of the entropy change for this reaction.

(iii) State and explain **two** advantages of using ethanol in preference to methanol in the production of hydrogen by this process.

[5]

(c) The efficiency of a fuel is dependent on the heat produced on combustion of the fuel as well as its expansion ratio.

The heat produced in the combustion causes rapid expansion of the gaseous products which then moves the pistons in the engine and does useful work. The expansion ratio of a fuel is the volume increase that accompanies the combustion of that fuel.

(i) Write equations, including state symbols, for the combustion of hydrogen and ethanol in the engine respectively to give gaseous products.

(ii) Using relevant data from the *Data Booklet*, calculate the enthalpy change of combustion for hydrogen and ethanol respectively.

(iii) Hence deduce whether hydrogen gas or ethanol is the more efficient fuel.

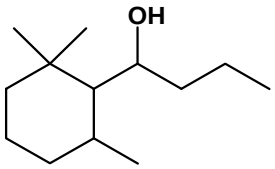
[5]

(d) The distinctive scent of rose oil comes mainly from a family of closely related chemicals called the rose ketones. Compounds **C**, **D** and **E** belong to this family.

C and **D** have the same molecular formula, $C_{13}H_{20}O$, while **E** has molecular formula, $C_{13}H_{18}O$. **C** can exist as a pair of enantiomers, but **D** and **E** do not show any optical activity.

1 mol of **C** and **D** each reacts with 2 mol of liquid bromine at room temperature. 1 mol of **E**, however, reacts with 3 mol of liquid bromine.

C, **D** and **E** react with hydrogen in the presence of nickel to give the same compound, $C_{13}H_{26}O$:



C and **D** each undergo oxidative cleavage with acidified $KMnO_4$ to give ethanoic acid as one of the two organic products. In addition, **C** also gives compound $C_{10}H_{14}O_4$, while **D** gives compound $C_{11}H_{16}O_5$ respectively.

E, on the other hand, gives three organic products on reaction with $KMnO_4$: ethanoic acid, CH_3COCO_2H and compound **F**, $C_8H_{10}O_6$. 1 mol of **F** reacts with 1 mol of Na_2CO_3 to produce CO_2 gas. 1 mol of **F** also reacts with 2 mol of HCN under cold conditions in the presence of trace base.

Deduce the structures of compounds **C**, **D**, **E**, and **F**, giving explanations of the reactions that occurred.

[8]
[Total: 20]

3 **(a)** State **two** properties that are unique to enzymes.

[2]

(b) An example of a copper-containing enzyme is superoxide dismutase (SOD). It aids in the disproportionation of the strongly oxidising superoxide ion, O_2^- to oxygen and hydrogen peroxide, thereby protecting the body from harm.

$$2O_2^- + 2H^+ \xrightarrow{\text{SOD}} O_2 + H_2O_2$$

(i) The activity of SOD hinges on the active site Cu^{2+} ion which can be reduced to Cu^+.

By referring to the following $E^\ominus$ data, suggest a mechanism for the catalysis of the disproportionation of O_2^- by SOD.

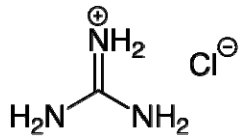
You may represent the oxidised and reduced forms of the enzyme as $SOD–Cu^{2+}$ and $SOD–Cu^+$.

	$E^\ominus$ / V
$O_2 + e^- \rightleftharpoons O_2^-$	–0.33
$O_2^- + e^- + 2H^+ \rightleftharpoons H_2O_2$	+0.89
$SOD–Cu^{2+} + e^- \rightleftharpoons SOD–Cu^+$	+0.42

(ii) The secondary structure of SOD is composed mainly of beta pleated sheets, as well as some regions of alpha helices.

With the aid of a diagram, describe **one** form of the secondary structure of the enzyme.

(iii) Guanidinium chloride is known to be one of the strongest denaturants of proteins.

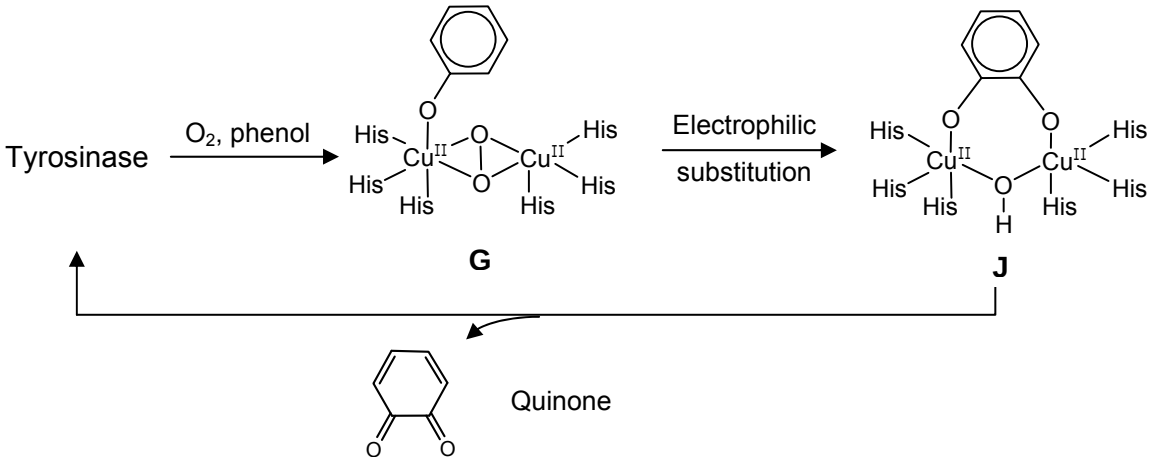


Guanidinium chloride

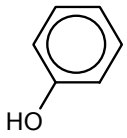
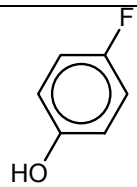
By referring to the primary, secondary and tertiary structures of the enzyme, suggest how the guanidinium cation can bring about denaturation of SOD. You may find that including suitable sketches or diagrams will help you in your answers.

[11]

(c) Another copper–containing enzyme is tyrosinase which catalyses the oxidation of phenols to quinones. **G** and **J** are two intermediate species in the catalytic cycle of tyrosinase. The conversion of **G** to **J** involves an electrophilic substitution mechanism.

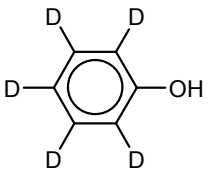


(i) Experiments were conducted using different phenol substrates and the relative rates of reactions are shown below.

Phenol substrate	 **I**	 **II**
Relative rate	7.9	0.02

Give a reason to account for the different relative rates of reactions.

(ii) In the phenol substrate **III** below, the hydrogen atoms on the phenyl ring are replaced with deuterium (D = $^{2}_{1}H$). The bond dissociation energy of the C–D bond is greater than that of the C–H bond.

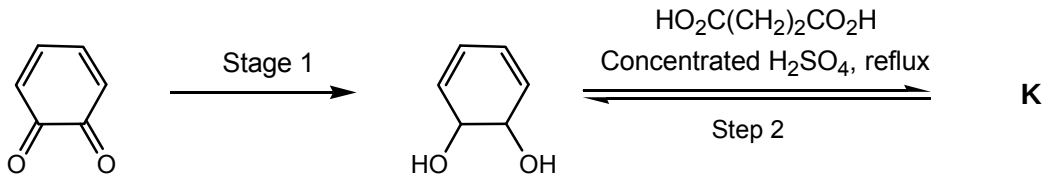


III

Predict and explain how the relative rate of reaction for substrate **III** would compare to that of substrate **I**.

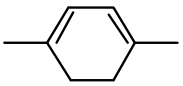
[2]

(d) The quinone product from the above reaction can undergo the following reaction.



(i) State the reagents and conditions needed for Stage 1.

(ii) Draw a possible structure for product **K**.

(iii) Suggest, in no more than 3 steps, how $HO_2C(CH_2)_2CO_2H$ can be obtained from  .

Identify the reagents and conditions for each step, and draw the structural formulae of all the intermediates.

[5]
[Total: 20]

4 In the atmosphere, nitrogen monoxide reacts with ozone as shown in the following equation.

$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

(a) NO_2 is considered to be an air pollutant. State one undesirable consequence of the presence of NO_2 in the atmosphere.

[1]

(b) The reaction does not take place in a single step. Experimentally it has been found that in mixtures of NO and O_3, free O atoms are present. No other short-lived intermediates can be detected.

The rate equation for the reaction was also found to be Rate = k [NO][O_3].

Outline the simplest mechanism consistent with the above observations, indicating the rate determining step.

[2]

(c) When NO and O_3, both at an initial concentration of 1.0×10^{-6} mol dm^{-3} were mixed together at 25 ˚C, [NO_2] varies with time, as shown in the table below.

Time / s	**[NO_2] / mol dm^{-3}**
0.05	0.50×10^{-6}
0.10	0.69×10^{-6}
0.15	0.77×10^{-6}
0.20	0.82×10^{-6}
0.25	0.85×10^{-6}
0.30	0.87×10^{-6}

(i) How is [O_3] related to [NO] during the course of the reaction?

(ii) The rate at a particular time can be approximated using rate = $\frac{\Delta[NO_2]}{\Delta t}$.

Use the information given in the table to produce data suitable for plotting a **straight line graph** to confirm that the reaction shows overall second order kinetics.

(iii) Plot the graph and use it to determine the rate constant k.

[8]

(d) NO_2 gas can also be formed from the dissociation of N_2O_4.

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g) \qquad \Delta H > 0$$

colourless brown

The equilibrium is reached fairly quickly in the gas phase.

(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm^3 flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the apparent relative molecular mass of the gaseous mixture in the flask, and hence the percentage dissociation of N_2O_4 at 27 °C.

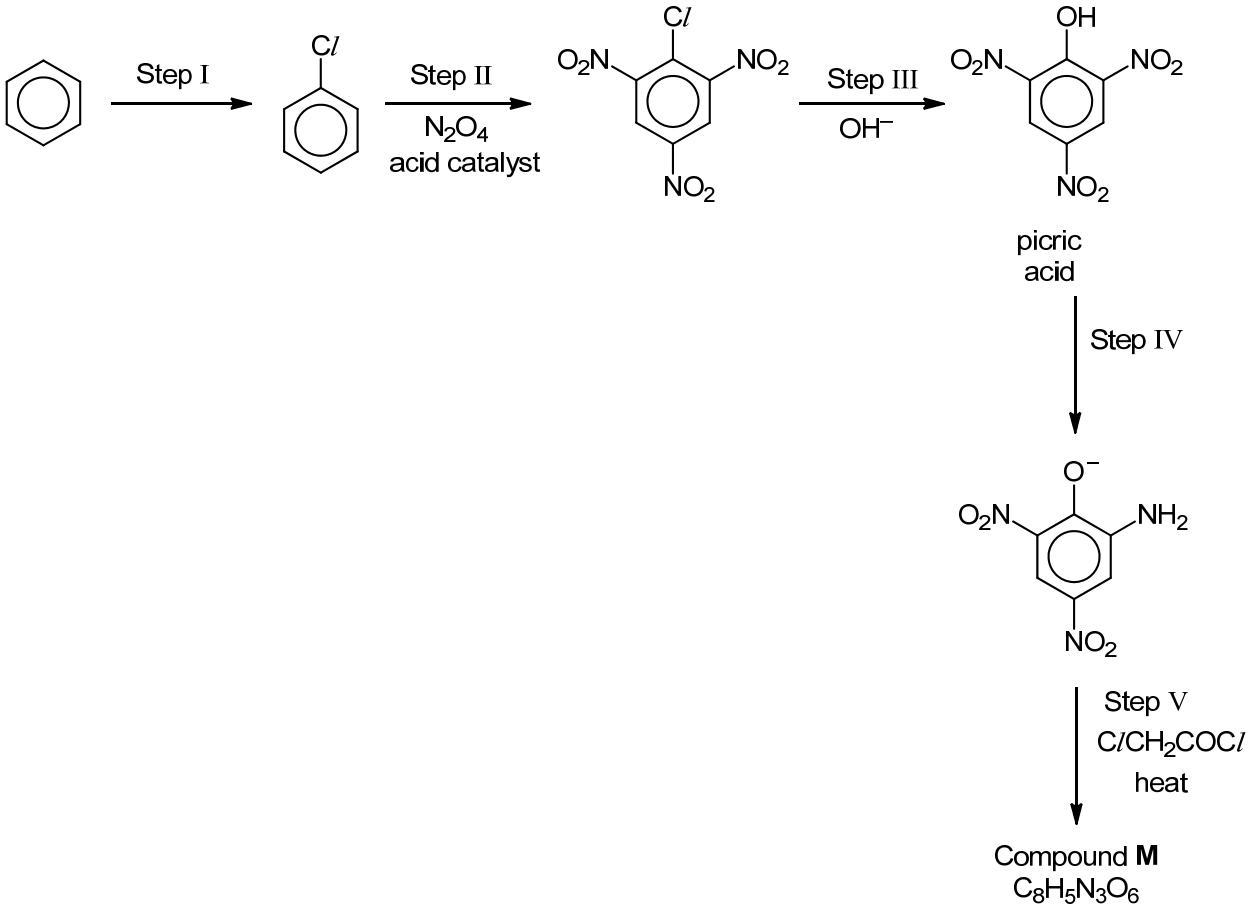
(ii) Describe and explain what you would observe when the stoppered flask is then placed into a basin of boiling water.

[5]

This question continues overleaf – part (e).

(e) N_2O_4 can be used to nitrate aromatic hydrocarbons in the presence of acid catalysts. Nitro compounds are of particular interest due to their potential use as explosives.

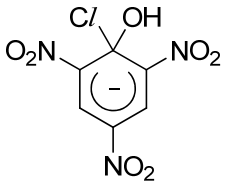
One such compound is picric acid. Under suitable conditions, picric acid can be formed from 2,4,6-trinitrochlorobenzene, as shown in Step **III**.



(i) State the reagents and conditions for Step **I**.

(ii) Suggest the type of reaction that occurs in Step **III**.

(iii) The reaction in Step **III** involves the formation of an anionic intermediate:



Suggest a reason why this anion intermediate can be formed.

(iv) State the reagents and conditions for Step **IV**.

(v) Deduce a structure of compound **M**.

[5]
[Total: 20]

5 **(a)** **(i)** Write the full electronic configuration of Cr^{3+} and explain why chromium is a transition element.

(ii) Explain why zinc commonly forms compounds of only one oxidation state.

(iii) When zinc metal is added to a chromium (III) chloride solution, effervescence of hydrogen is observed. Write two equations to account for this observation.

(iv) By quoting and using relevant $E^{\ominus}$ values from the *Data Booklet*, explain why the blue solution, containing $Cr^{2+}(aq)$, obtained by dissolving chromium metal in dilute sulfuric acid ***slowly*** turns green even in the absence of air.

(v) A 1.00 g sample of a dark red liquid, containing only Cr, O and C*l*, was dissolved in sufficient aqueous sodium hydroxide to produce exactly 100 cm^3 of a yellow solution.

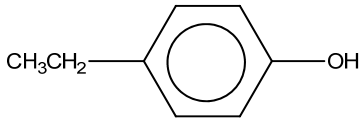
A 50.0 cm^3 portion of the yellow solution was then acidified and the resultant orange solution titrated against silver nitrate until precipitation of the white solid product was just complete. After filtration, this white solid was washed and dried and weighed 0.925 g.

The yellow solution was further tested by pipetting 10.0 cm^3 portions, acidifying to produce the orange solution and then adding an excess of aqueous potassium iodide. The iodine formed required 19.5 cm^3 of 0.100 mol dm^{-3} sodium thiosulfate for complete reaction.

Deduce the empirical formula of the dark red liquid, showing your working clearly.

[12]

(b) The compound 4-ethylphenol, **P**, and chlorinated products derived from it have useful antiseptic properties.



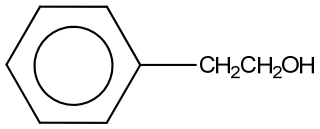
P

Under certain conditions, compound **P** reacts with chlorine to give compound **Q**, $C_8H_8CI_2O$.

(i) Compound **Q** reacts with NaOH (aq), followed by acidification, to give **R**, $C_8H_{10}O_3$, which immediately loses water to give **T**, $C_8H_8O_2$. Compound **T** is insoluble in water but it dissolves in NaOH (aq). It reacts positively with both 2,4-dinitrophenylhydrazine and alkaline aqueous iodine.

Deduce the structures of compounds **Q**, **R** and **T**. Explain the chemistry of the reactions described.

(ii) The compound 2-phenylethanol, **V**, is an isomer of **P**. Compound **V** is responsible for the fragrance of roses.



V

Describe a simple chemical test by which **P** can be distinguished from **V.** You should state the reagents and conditions for the test, and describe how each of the isomers behaves.

[8]
[Total: 20]