



JURONG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

CLASS

EXAM
INDEX
NUMBER

CHEMISTRY

Paper 3 Free Response

9647/03

27 August 2012

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 working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.

Begin your answer to each new question on a fresh sheet of writing paper.
At the end of the examination, arrange the answers in numerical order and attach the cover sheet on top.

A *Data Booklet* is provided. Do not write anything on the *Data Booklet*.

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.

Answer any **four** questions.

1. *Use of the Data Booklet is relevant to the question.*

(a) Hydrogen can play an important role in the future by replacing the petroleum currently used in automobiles. For example, electric cars can be powered by hydrogen-oxygen fuel cells, with its hydrogen fuel kept at extremely high pressures in thick-walled storage tanks.

(i) State the half equations for the reactions occurring at each of the electrodes in a hydrogen-oxygen fuel cell operating under acidic conditions.

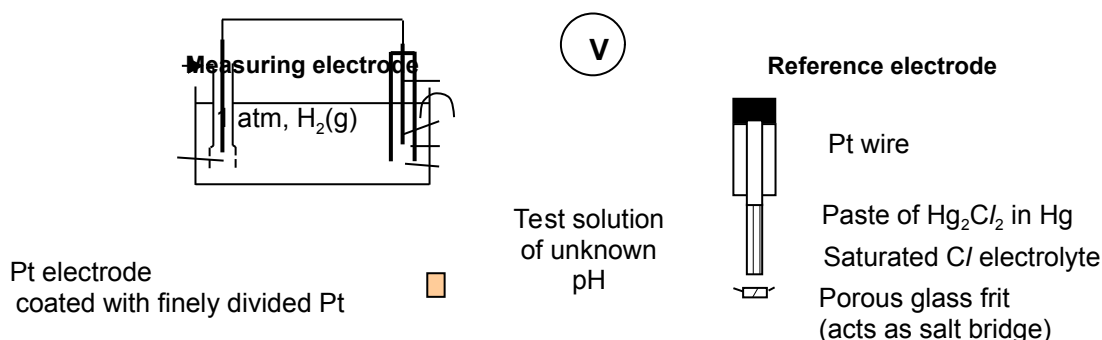
(ii) Describe one disadvantage of using a hydrogen-oxygen fuel cell over internal combustion engines in automobiles.

(iii) A quantity of hydrogen gas is confined in a chamber of constant volume. When the chamber is placed at a temperature of 20°C , the pressure of the gas is $3.29 \times 10^5 \text{ Pa}$.

What will be the pressure of the gas, in Pa, if the chamber is now placed in a water bath of boiling water to simulate the operating temperature of a certain automobile?

[5]

(b) A student designed an ion-specific probe to determine the concentration of H^+ ions in solution. He connected a hydrogen electrode to a calomel reference electrode, which comprises a paste of mercury(I) chloride and mercury in a saturated chloride electrolyte solution. The porous glass frit acts as a salt bridge.



The hydrogen electrode, sensitive to H^+ ion concentration, is the measuring electrode. Therefore, this galvanic cell acts as a pH meter.

When both electrodes are in contact with the test solution, an electric current flows through the wire and mercury(I) chloride reacts to form liquid mercury and chloride ion at the reference electrode.

Under standard conditions, the E_{cell}° of the pH meter is $+0.28 \text{ V}$.

(i) Construct the half equation for the reaction occurring at the reference electrode.

(ii) Hence write an overall balanced equation for the pH meter.

(iii) Explain why the cell potential would increase when the pH meter is placed in a solution of a higher pH.

[3]

1. (c) The student used his probe to analyse a sample of $0.104 \text{ mol dm}^{-3}$ solution of mandelic acid, Jurong Junior College 9647/P3/Prelim 2012

[Turn over]

a bitter almond extract that is used as antibacterial treatment or an oral antibiotic.

The student obtained a cell potential reading, E_{cell} , of +0.41 V.

- (i) The *Nerst equation* can be used to calculate the concentration of H^+ ions detected by the probe:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log_{10} \left(\frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{P_{\text{H}_2}} \right)$$

where n is the number of moles of electrons transferred in the overall reaction,

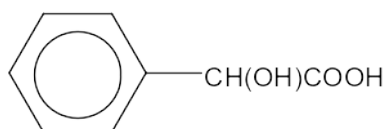
$[\text{H}^+]$ is the concentration of hydrogen ions detected

$[\text{Cl}^-]$ is the concentration of Cl^- ions at the cathode.

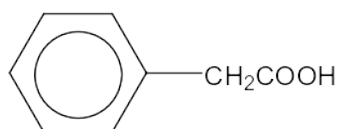
P_{H_2} is the pressure, in atm, of hydrogen gas passed into the probe,

Assuming that the concentration of Cl^- is constant at 1 mol dm^{-3} , use the *Nerst equation* to calculate the concentration of H^+ ions in the solution and the pH of the solution.

- (ii) Hence calculate the value of acid dissociation constant, K_a , of mandelic acid.
- (iii) How would you expect the value of K_a of mandelic acid to compare with that of phenylacetic acid? Explain your answer.

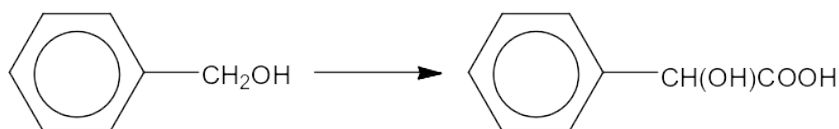


mandelic acid



phenylacetic acid

- (iv) Suggest a chemical test (stating reagents and observations) that would distinguish mandelic acid from phenylacetic acid.
- (v) Suggest a synthetic route to form mandelic acid from starting material phenylmethanol.



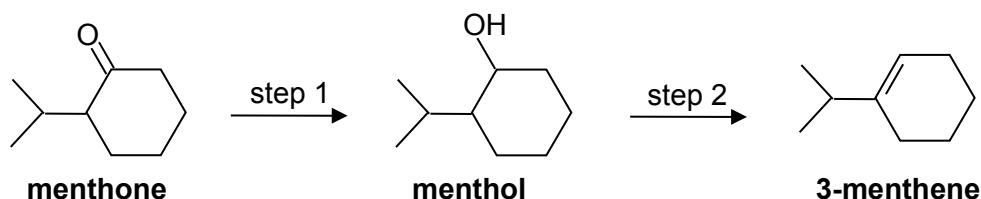
phenylmethanol

[12]

[Total: 20]

2. (a) Peppermint oil, also known as brandy mint and balm mint, is extracted from *mentha piperita* of the Labiatae family. Menthol and menthone are the two main components of peppermint oil.

Menthone can be reduced to menthol, which can be easily dehydrated to give 3-menthene as the major product.



Both menthone and menthol exhibit *stereoisomerism* but 3-menthene has no stereoisomer.

- (i) Which compound, menthone or menthol, is expected to be more volatile? Give your reasoning.
- (ii) Menthol is insoluble in water but is freely soluble in ethers and alcohols. Explain why menthol is insoluble in water.
- (iii) Suggest the reagents and conditions required for step 1 and step 2.
- (iv) An alkene **M** is also formed in step 2 in a much lower proportion than 3-menthene. Suggest the structure for **M** and give the organic product when **M** is heated with concentrated acidified $\text{KMnO}_4(\text{aq})$.
- (v) When $\text{HCl}(\text{g})$ is bubbled through a solution of 3-menthene, an addition reaction occurs via a 2-stage mechanism.
Suggest the mechanism of this reaction by means of a diagram. Include all whole or partial charges, and represent the movements of electron pairs by curly arrows.
- (vi) What do you understand by the term *stereoisomerism*? Explain why 3-menthene does not exhibit any stereoisomerism.

[12]

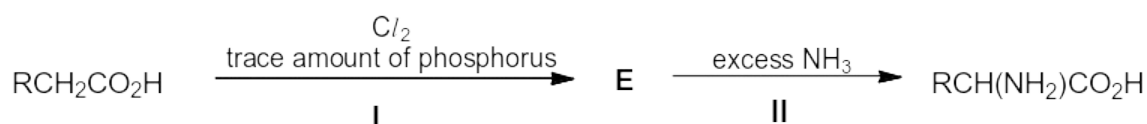
- (b) Magnesium nitrate is a hygroscopic salt. In air, it readily forms a hydrate with the formula $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Barium nitrate, however, does not form any hydrate in air. Both nitrates are soluble in water. Like all soluble barium compounds, barium nitrate is toxic by ingestion. Solutions of sulfate salts such as Epsom salt may be given as first aid for barium poisoning.
- (i) Suggest reason(s) why magnesium nitrate readily forms a hydrate whereas barium nitrate does not.
 - (ii) Describe what you would see when a sample of white crystals of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is heated in an open test-tube. Write a balanced equation for the reaction.
 - (iii) Explain why barium nitrate decomposes at a higher temperature than anhydrous magnesium nitrate.

2. (b) (iv) When water is added to the solid residue after barium nitrate has been heated, a colourless solution is obtained. When water is added to the solid residue after magnesium nitrate has been heated, a white suspension is obtained instead. Explain these observations.
- (v) Suggest how administering of Epsom salt solution, which contains magnesium sulfate, helps to treat barium poisoning.

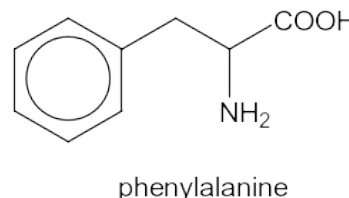
[8]

[Total: 20]

3. (a) Amino acids, such as alanine and phenylalanine, are essential building blocks for making proteins. They can be synthesised by a general 2-step reaction as exemplified below:



- (i) Suggest the structure of the intermediate organic compound **E**.
- (ii) What *type of reaction* is occurring in step I?
- (iii) Phenylalanine is found naturally in the breast milk of mammals. It is used in the manufacture of food and drink products and is sold as a nutritional supplement. Suggest the structural formula of the starting material needed to synthesise phenylalanine by the above 2-step reaction.



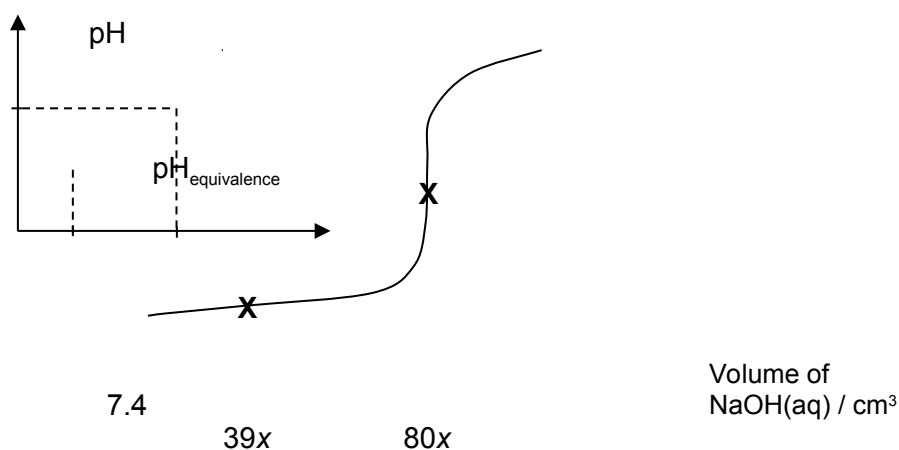
[3]

- (b) Solutions of amino acids are buffers important in maintaining optimal pH in our body. A food chemist needs to ensure that all infant manufactured food products containing phenylalanine and its salt, simulates the exact composition of human breast milk.

- (i) Draw the structural formula of the zwitterionic form of phenylalanine.

Hence suggest, with the aid of an equation, how phenylalanine behaves as a buffer when small amount of base is added.

- (ii) In order to investigate the composition of a buffer solution of pH 7.4 containing phenylalanine and its salt, the food chemist titrated a sample of this buffer solution with NaOH(aq) and obtained the titration curve below.



The buffer solution operates at its maximum capacity when $39x \text{ cm}^3$ of NaOH(aq) is added and the equivalence point is attained when $80x \text{ cm}^3$ of NaOH(aq) is added.

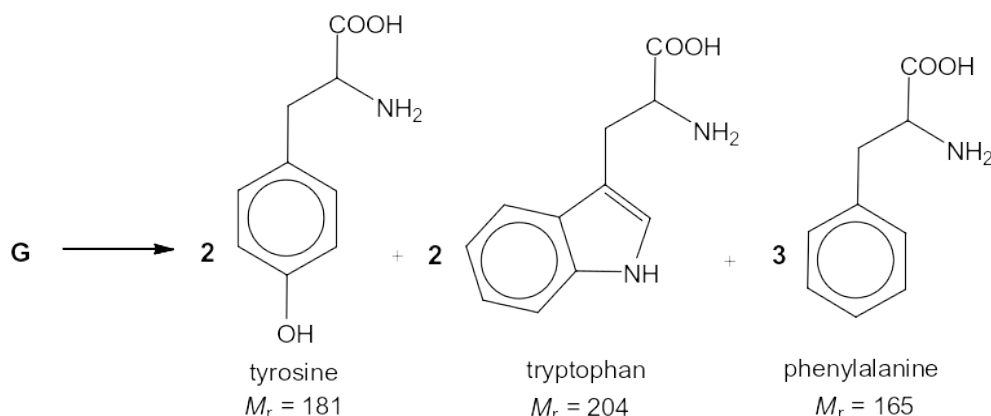
Show that the ratio of [phenylalanine] : [salt of phenylalanine] is 40 : 1 in the original sample of buffer solution.

- (iii) Hence determine the pH value at the maximum buffering capacity of the buffer containing phenylalanine and its salt.

[6]

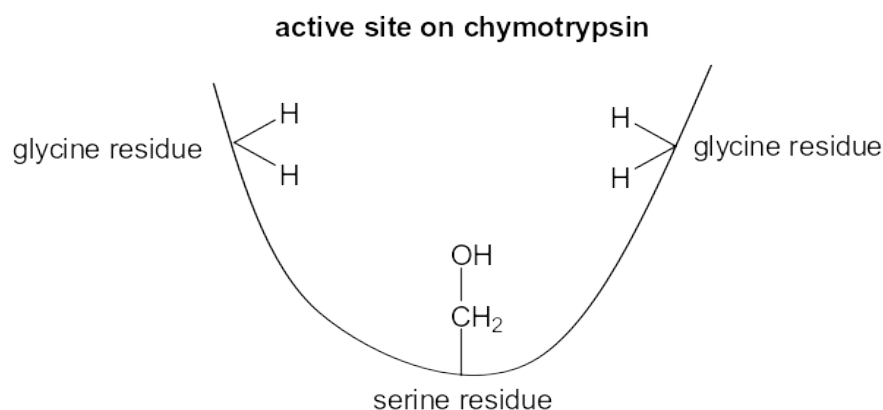
3. (c) Chymotrypsin is a digestive enzyme produced by the pancreas to aid digestion in the small intestine. -

- (i) A small peptide **G** was hydrolysed by chymotrypsin and gave three different amino acids according to the following reaction.



Calculate the M_r of peptide **G**.

- (ii) During the hydrolysis of peptide **G** by chymotrypsin, the tyrosine residue of peptide **G** must first bind to the active site on chymotrypsin. -



Copy this diagram onto your answer script and use it to illustrate how one tyrosine residue of peptide **G** can bind to the active site on chymotrypsin. Label the type(s) of interaction that could be involved.

- (iii) Vomiting is one of the immediate and observable effects of excessive alcohol consumption as the presence of alcohol inhibits the digestive activity of chymotrypsin.

Suggest how the consumption of alcohol inhibits the digestive activity of chymotrypsin.

[5]

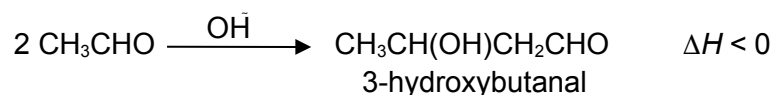
- (d) Compound **H**, an isomer of phenylalanine, with molecular formula $\text{C}_9\text{H}_{11}\text{NO}_2$, is a basic compound. When **H** is heated under reflux with NaOH(aq) followed by careful neutralisation, compound **J** and ethanol are formed. Compound **J** reacts with aqueous sodium carbonate and also dissolves in HCl(aq) . 0.10 mol of compound **J** reacts completely with 0.20 mol of aqueous bromine to give a white precipitate.

Suggest the structures of compounds **H** and **J** and explain all the reactions involved.

[6]

[Total: 20]

4. Under the influence of a dilute base or acid, two molecules of an aldehyde or a ketone may combine in a process known as aldol reaction. An example of an aldol reaction between ethanal molecules in dilute alkaline solution is shown below.



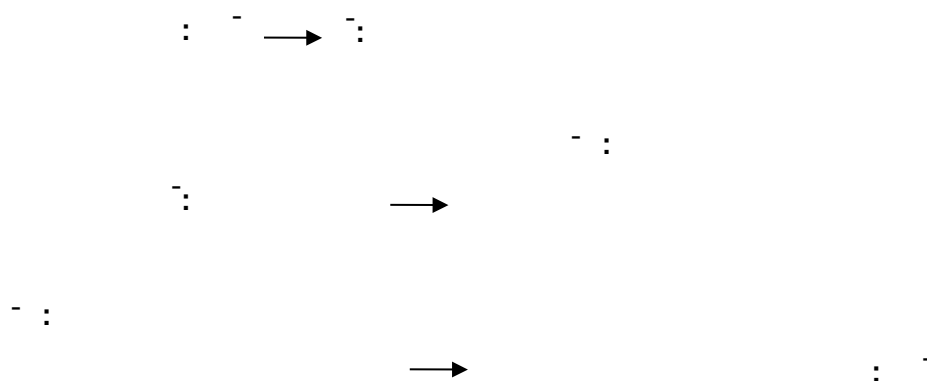
A chemist studied the kinetics of the above reaction at 298 K and obtained the following table of results.

experiment number	initial $[\text{CH}_3\text{CHO}]$ / mol dm^{-3}	initial $[\text{OH}^-]$ / mol dm^{-3}	initial rate / $\text{mol dm}^{-3} \text{s}^{-1}$
1	0.10	0.10	0.0110
2	0.10	0.15	0.0165
3	0.30	0.20	0.0660

- (a) (i) Use these data to deduce the order of reaction with respect to both ethanal and OH^- , showing how you arrived at your answers.
- (ii) Hence write the rate equation for the reaction and calculate the value of the rate constant, stating its units.
- (iii) The half-life of ethanal in experiment 1 is 9.0 s. Predict the half-life of ethanal in experiment 3.

[6]

- (b) The following three-step mechanism has been proposed for the reaction between ethanal molecules.



- (i) Using your answers in (a), predict which of the three steps is the rate-determining step. Explain your answer.
- (ii) Sketch a labelled energy profile diagram for the above proposed mechanism. You are only required to label the reactants, products and the activation energy of forward reaction on your diagram.

4. (b) (iii) Name the type of reaction occurring in Step 1.

(iv) Use a diagram to show how the product in Step 2 is formed. In your diagram, include all whole or partial charges, and represent the movements of electron pairs by curly arrows.

Hence explain why the overall reaction produces a racemic mixture of 3-hydroxybutanal.

[7]

(c) In a similar three-step mechanism mentioned in (b), one molecule of 3-hydroxybutanal can react further with one molecule of ethanal to give a mixture of products with six carbon atoms each.

Deduce the structural formula of **two** possible products from this reaction.

[2]

(d) The aldol reaction is a powerful means of forming carbon-carbon bonds and it combines simple molecules to give a more complex one. Copper(I) and copper(II) complexes have been developed successfully to catalyse some aldol reactions.

(i) Write the electronic configuration of copper(I) and copper(II) ions using the s,p,d,f notation.

(ii) Explain why complexes of copper(II) are usually coloured and those of copper(I) are colourless.

[5]

[Total: 20]

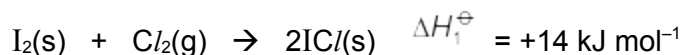
5. The halogens and their compounds are useful laboratory reagents.

(a) Iodine trichloride, ICl_3 , is a bright yellow solid formed by reaction of iodine and chlorine.

(i) Draw and suggest the shape of ICl_3 molecule. Include all lone pairs in your diagram.

(ii) Unlike ICl_3 , the compound FCl_3 does not exist. Suggest a reason for this difference.

(iii) Given the following enthalpy changes,



construct an energy cycle to calculate the standard enthalpy change of formation of solid iodine trichloride.

(iv) The standard entropy change of formation of solid iodine trichloride is $-225 \text{ J mol}^{-1} \text{ K}^{-1}$. Explain why the formation of solid iodine trichloride has a negative entropy change.

(v) Explain why the formation of solid iodine trichloride is spontaneous at low temperatures.

(vi) Predict whether the reaction is spontaneous at 298 K.

[10]

(b) Silver chloride and silver iodide are sparingly soluble in water at room temperature. Their solubility products at 298K are given below.

Silver halide	Solubility product, K_{sp}
AgCl	1.77×10^{-10}
AgI	8.52×10^{-17}

(i) Write an expression for the solubility product, K_{sp} , of silver iodide and hence calculate $[\text{Ag}^+(\text{aq})]$ in a saturated aqueous solution of silver iodide at 298K.

(ii) With the aid of relevant equations, suggest explanations for the following observations:

When aqueous silver nitrate is added to aqueous sodium chloride, a white precipitate is formed which is soluble in excess aqueous ammonia, giving a colourless solution.

When aqueous sodium iodide is added to the resultant solution, a yellow precipitate is formed immediately.

[5]

(c) Solid halides such as sodium bromide or sodium chloride are commonly used in situ with concentrated sulfuric acid to produce alkyl halides from alcohols.

(i) Describe what would be observed when concentrated sulfuric acid is added to separate portions of $\text{NaCl}(\text{s})$ and $\text{NaBr}(\text{s})$. Write an equation for **any** reaction that occurs and explain the differences in their reactions.

(ii) Suggest why sodium iodide is not used in situ with concentrated sulfuric acid to produce alkyl iodide from alcohol.

[5]

[Total: 20]

