



HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

**CANDIDATE
NAME**

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CT GROUP

15S

**CENTRE
NUMBER**

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**INDEX
NUMBER**

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CHEMISTRY

9647/02

Paper 2 Structured Questions

30 August 2016

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

- 1) Write your **name**, **CT group**, **centre number** and **index number** clearly in the spaces at the top of this page.
- 2) Answer **all** questions in the spaces provided in this Question Paper.

INFORMATION FOR CANDIDATES

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

A Data Booklet is provided.

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

You may use a calculator.

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

For Examiner's Use	
1	/ 12
2	/ 17
3	/ 14
4	/ 13
5	/ 16
Deductions	
Total	/ 72

Calculator Model:

1 Planning (P)

An electrochemical cell is a device that produces an electric current as a result of redox reactions. Any spontaneous redox reaction can be harnessed to produce electrical energy under the right conditions. Electrons are generated at one electrode and driven towards the other by electromotive force, also known as the cell potential, measured in volts.

The Gibbs' Free Energy equation is given as $\Delta G = \Delta H - T\Delta S$. ΔG may be obtained from the cell potential of an electrochemical cell by the relationship:

$$\Delta G = -nFE$$

where n = number of moles of electrons transferred in the reaction

F = Faraday's constant

E = cell potential

By constructing an electrochemical cell, the cell potential can be measured over a range of temperatures. The entropy change of a reaction can then be determined by plotting a suitable linear graph using the data obtained.

- (a) (i) Write an ionic equation for the reaction between Cu and Fe^{3+} . You should include state symbols in your equation.

.....[1]

- (ii) Predict the sign of ΔS for the above reaction. Explain your answer.

.....
.....[1]

- (b) Using the information given above, you are required to write a plan for determining the entropy change for the redox reaction between Cu and Fe^{3+} . You will measure the cell potential over a 30 °C range of temperature.

You are also required to explain how the data you obtain from this experiment may be used to determine the entropy change of the reaction.

You may assume that the values of ΔH and ΔS are constant over this measured temperature change.

You may also assume that you are provided with:

0.20 mol dm⁻³ aqueous FeCl_3

0.10 mol dm⁻³ aqueous CuSO_4

0.50 mol dm⁻³ aqueous H_2SO_4

solid hydrated iron(II) sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

common electrodes

the apparatus normally found in a school or college laboratory.

- a fully-labelled diagram of the set-up of the electrochemical cell you would use to monitor how cell potential varies with temperature;
- details for the preparation of 100 cm³ of 0.20 mol dm⁻³ aqueous acidified FeSO₄;
- details of the appropriate quantities and concentrations of solutions used;
- the temperatures at which the experiments would be carried out;
- an outline of how the results would be obtained;
- a sketch of the graph you would expect to obtain;
- how the data obtained from the graph would be used to determine the entropy change for the reaction.

[illegible]

- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10

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[10]

[Total: 12]

- 2 (a) The transition metals form many complexes. Two examples of complexes formed by Fe^{3+} are $[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$.

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These complexes contain the ligands, H_2O , SCN^- , and CN^- , in which the "donor atom" for dative bonding are O, S and C respectively.

- (i) Explain why the atomic radius of oxygen (0.066 nm) is smaller than that of carbon (0.077 nm).

.....

[2]

- (ii) Explain why the atomic radius of sulfur (0.104 nm) is larger than those of oxygen and carbon.

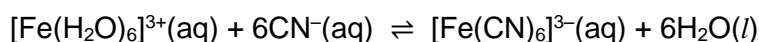
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[1]

- (b) When water ligands in an aqua complex are replaced by other ligands, the equilibrium constant for the reaction is called the stability constant, K_{stab} , of the new complex.

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For example,



$$K_{\text{stab}} = \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}] [\text{CN}^{-}]^6}$$

The K_{stab} value is an indication of the stability of a complex ion with reference to the aqua complex. The table below lists the K_{stab} values of some iron complexes.

complex	K_{stab}
$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	1×10^2
$[\text{Fe}(\text{CN})_6]^{3-}$	1×10^{31}
$[\text{Fe}(\text{CN})_6]^{4-}$	1×10^{24}
$[\text{Fe}(\text{edta})]^{-}$	1×10^{25}
$[\text{Fe}(\text{edta})]^{2-}$	2×10^{14}



- (i) State the colour of the solution obtained when aqueous potassium thiocyanate, KSCN, is added to aqueous Fe^{3+} .

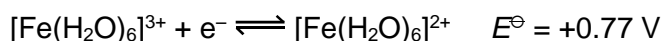
.....[1]

- (ii) Suggest why the colour you stated in (b)(i) is not obtained when aqueous KSCN is added to aqueous $[\text{Fe}(\text{CN})_6]^{3-}$.

.....

[1]

- (iii) Predict whether edta would make the reduction potential for the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ system higher or lower than +0.77 V. Explain your answer.



.....

[1]

(c) A series of tests was conducted as follow:

- I When concentrated hydrochloric acid was added to dissolve black copper(II) oxide, a yellow solution was obtained.
- II Dilution of this yellow solution with water changed its colour to green and then blue.
- III When aqueous ammonia was then added, a pale blue precipitate formed which dissolved in excess aqueous ammonia to give a dark blue solution.

(i) Identify the copper-containing species formed in each test.

Test	Identity of copper-containing species
I	Yellow solution:
II	Blue solution:
III	Pale blue precipitate: Dark blue solution:

[2]

(ii) Write equations to illustrate the ligand exchange reactions in forming the blue solution in Test II:

.....

the dark blue solution in Test III:

..... [2]

(d) Aluminium is extracted from molten aluminium oxide, Al_2O_3 , by electrolysis.

(i) With reference to E^\ominus data from the *Data Booklet*, explain why an aqueous solution of Al^{3+} (from a soluble aluminium salt) would be unsuitable as the electrolyte.

.....

.....

.....[1]

In the industry, Al_2O_3 is dissolved in molten cryolite, Na_3AlF_6 to lower the melting point of Al_2O_3 . The molten mixture is then electrolysed using graphite electrodes.

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- (ii) The electrode reactions are very complicated. In one simplified study, some scientists say that, in molten cryolite, Al_2O_3 ionises into Al^{3+} ions and AlO_2^- ions.

At the cathode, Al^{3+} is converted to Al metal: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

At the anode, AlO_2^- is converted to Al_2O_3 and oxygen gas.

Write an equation for the anode reaction.

..... [1]

- (iii) A typical cell operates at 10^4 A. Calculate the time, in hours, needed to produce 1 tonne of aluminium. (1 tonne = 1000 kg)

[2]

- (e) A saturated solution of XeF_2 ($M_r = 169$) in water at 0°C contains 25.0 g dm^{-3} of XeF_2 . The solution is a strong oxidising agent, quantitatively oxidising another solution containing $0.150 \text{ mol dm}^{-3}$ of a Cr(III) salt. XeF_2 is reduced to Xe in the reaction.

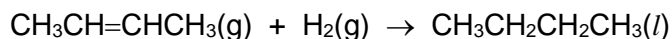
In an experiment, 15.20 cm^3 of the XeF_2 solution is required to completely react with 10.0 cm^3 of the Cr(III) solution.

Determine the oxidation state of Cr after the reaction.

[3]

[Total: 17]

- 3 The hydrogenation of but-2-ene is shown in the equation below



- (a) Describe the changes in bond angle and the type of hybridisation involved at the site of the hydrogenation reaction.

.....

[2]

- (b) Under certain conditions, but-2-ene gives alcohol **A**, $\text{C}_4\text{H}_{10}\text{O}$, which exists as a liquid at room temperature.

- (i) State the reagents and conditions required in this reaction. Draw the displayed formula of alcohol **A** formed in this reaction.

Reagents and conditions:

A:

[2]

- (ii) Explain, in terms of structure and bonding, the difference in the physical state of but-2-ene and alcohol **A** at room temperature. Draw a diagram to illustrate your answer for alcohol **A**.

.....

Diagram:

[3]

- (iii) Ester **C** is used in synthetic fruit flavours. Alcohol **A** reacts with compound **B** at room temperature to give a good yield of ester **C** with relative molecular mass of 116.

Draw the structures of compounds **B** and **C**.

B:

C:

[2]

- (c) (i) In a separate reaction, butane is treated with a small quantity of bromine in the presence of ultraviolet light to give 1-bromobutane and 2-bromobutane. It is found experimentally that the hydrogen atom is substituted by bromine at different rates, as shown in the table below.

Type of H atom	Relative rate of substitution
Primary hydrogen	1
Secondary hydrogen	4.5

Using this information, and considering the number and types of hydrogen within butane, determine the mole ratio of the two monobrominated products.

.....

[2]

- (ii) Name and outline the mechanism for the formation of 2-bromobutane in this reaction.

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[3]

[Total: 14]

- 4 (a) Using relevant data from the *Data Booklet*, describe and explain how the thermal stability of the hydrogen halides varies down Group VII.

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[2]

- (b) In the laboratory, three bottles each containing one of the following reagents were mixed up:

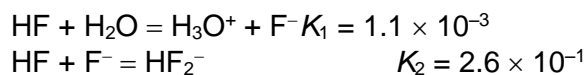
NaI(aq), KBr(aq) and KCl(aq).

Describe chemical test(s), which does **not** involve silver nitrate, that could distinguish and identify the contents of each bottle.

.....

[3]

- (c) HF behaves as a medium-strength acid and dissociates only partially in aqueous solutions as shown below. K_1 and K_2 represent the numerical values of the respective equilibrium constants.



- (i) Write the overall equation for the reaction of liquid HF with H_2O to form HF_2^- and calculate the numerical value of the equilibrium constant for this reaction.

[2]

- (ii) The dissociation equilibrium of a solute in a solvent can be significantly shifted by the addition of a suitable substance into the solution. Suggest an inorganic reagent which can be added to increase the dissociation of HF in water. Explain your choice.

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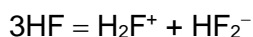
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.....[2]

- (d) Similar to water, pure liquid hydrogen fluoride also undergoes auto-ionisation according to the following equilibrium:



The ionic product of HF is $8.0 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$.

- (i) Draw the structures of both the cationic and anionic species in liquid HF. Label the types of bonding within the anionic species.

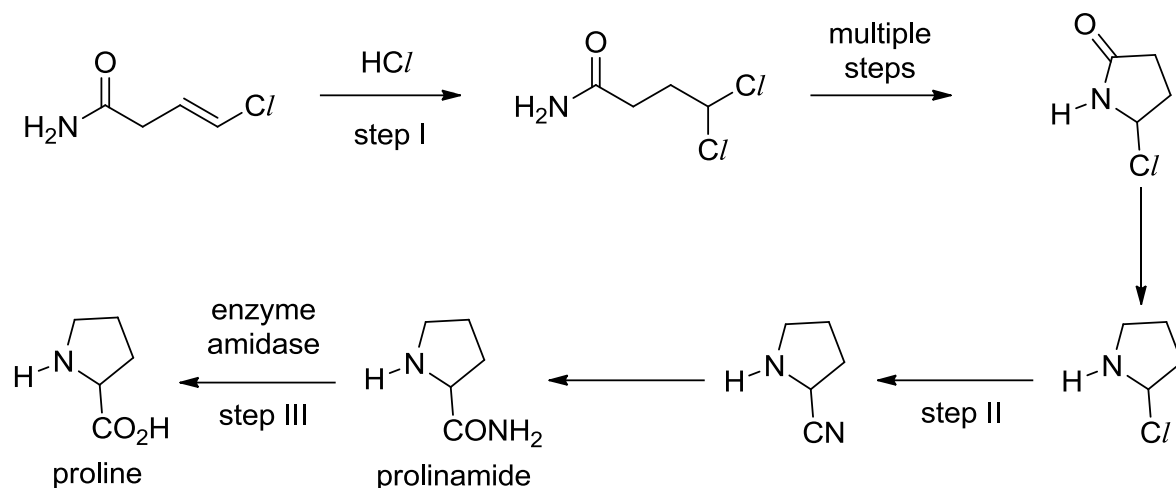
[2]

- (ii) Calculate the fraction of H_2F^+ in liquid HF (density = 1.002 g cm^{-3}), supposing that only these three species are present in the system.

[2]

[Total: 13]

- 5 The following reaction scheme is proposed for the synthesis of the amino acid proline.



- (a) (i) Draw structures of two possible intermediates formed in step I. Hence, explain why the yield of the product in step I is low.

.....

.....

.....[2]

- (ii) With the aid of a sketch of the Boltzmann distribution, explain how an increase in temperature affects the rate of reaction in step II.



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.....[3]

- (iii) It was found that only 50% of prolinamide synthesised by the method above could be converted to proline by enzyme amidase in step III. Suggest an explanation for this observation.

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[1]

- (b) The enzyme amidase used in step III contains amino acids listed in the following table.

name	abbreviation	structural formula
aspartic acid	asp	$\text{HO}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
asparagine	asn	$\text{H}_2\text{NCOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
cysteine	cys	$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
glycine	gly	$\text{CH}_2(\text{NH}_2)\text{CO}_2\text{H}$
isoleucine	ile	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
lysine	lys	$\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
phenylalanine	phe	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$
serine	ser	$\text{HOCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$

- (i) There are three pK_a values associated with aspartic acid: 2.1, 3.7 and 9.8. In the boxes below, draw the structures of the major species present in solutions of aspartic acid at pH 3 and pH 8.

pH 3	pH 8
------	------

[2]

- (ii) Complete the following table by indicating the type of interaction between each pair of amino acid residues that stabilises the tertiary structure of enzyme amidase at pH 7.

amino acid residue 1	amino acid residue 2	type of interaction
aspartic acid	lysine	
isoleucine	phenylalanine	
serine	asparagine	

[2]

- (iii) Explain how mercury ion, $\text{Hg}^{2+}(\text{aq})$, affects the activity of the enzyme amidase through denaturation.

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.....

.....[2]

- (c) A section of the polypeptide chain in enzyme amidase was partially hydrolysed and the following peptide fragments are produced.

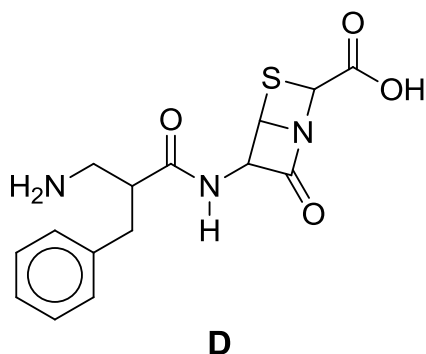
lys-gly, asp-lys-ser, cys-asn-phe, gly-cys-asn, ser-phe-lys

State the **smallest** possible sequence of amino acids in this section of the polypeptide chain using the 3-letter abbreviations.

.....[1]

- (d) A scientist extracted a new compound **D** from microorganisms. He proposed the following structure for **D**.

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- (i) **D** was postulated to be synthesised from amino acids.

Identify from the list in (b), **two** α -amino acids that could be used in the synthesis.

.....[1]

- (ii) Assuming that the S–C bond is inert, draw the organic products if **D** was heated in aqueous H_2SO_4 .

[2]

[Total: 16]