Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE DEPARTMENT OF CHEMISTRY Preliminary Examination

CHEMISTRY Higher 2

Paper 2 Structured Questions

Candidates answer on the Question Paper Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, index number, form class, tutorial class and subject tutor's name 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, glue or correction fluid.

Answer **all** questions. A Data Booklet is provided.

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.

For Examiner's Use		
Question no.	Marks	
1	/7	
2	/ 13	
3	/ 9	
4	/ 11	
5	/ 5	
6	/ 9	
7	/ 14	
8	/7	
TOTAL	/ 75	

This document consists of **21** printed pages, including this cover page.

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ANGLO-CHINESE JUNIOR COLLEGE Department of Chemistry

[Turn over

9729/02

2 hours

15 August 2017

For more than two millenia human ingenuity has turned natural and synthetic poisons into weapons of war. World War I was especially hailed by historians as the "Chemists' War" because it was the first war in which chemical weapons were used on such an enormous scale, even on civilians. Chemicals were used to bring widespread destruction and death. It set the precedence for World War II. On the bright side, chemicals were used to save millions of soldiers' lives in World War II.

Question 1 examines how chemical weapons were used to kill in World War I, while Question 2 examines the use of chemicals as medicine in the battlefields of World War II.

1 A range of different chemicals - chlorine, phosgene and mustard "gas" - were used as weapons throughout World War I.

Their melting and boiling points are tabulated below.

Gas	Melting point / °C	Boiling point / °C
chlorine	-101.5	-34.0
phosgene	-118	8.3
mustard "gas"	14.4	217.0

Chlorine was first used on a large scale by the German forces at Ypres in April 1915. It reacts with water in the lungs to form hydrochloric acid, which can quickly lead to death. At lower concentrations, it can cause coughing, vomiting, and irritation to the eyes.

(a) Phosgene is a colourless gas, with an odour likened to that of 'musty hay'.

$$Cl \subset Cl$$
 phosgene

Phosgene is known to react violently with water to give hydrochloric acid and carbonic acid. Give the equation of the reaction between phosgene and water.

[1]

- (b) The Germans introduced another chemical weapon mustard "gas". It was fired into enemy positions by cannons.
 - (i) How is the name mustard "gas" misleading?

[1]

Unlike alkyl halides, mustard "gas" reacts instantly with water to form hemi-mustard, $C_1CH_2CH_2SCH_2CH_2OH$.

(ii) The following intermediate is thought to be formed by mustard "gas" itself via an intramolecular nucleophilic substitution before the attack of water.



How does this intermediate make the hydrolysis of mustard "gas" easier than that of alkyl halides?

[1]

(iii) The conversion of the intermediate in **b(ii)** to hemi-mustard involves two steps, the first involving the attack by water and the second involving deprotonation.

Use curly arrows to show how the intermediate in **b(ii)** is converted into hemimustard. 1 (b) (iv) Hemi-mustard can be further attacked by water to form J, $C_4H_{10}SO_2$.

Draw the structure of **J**.

[1]

(v) On reaction with concentrated sulfuric acid at 140 $^{\circ}$ C, hemi-mustard can be converted into K, C₄H₈SO, which does not decolourise bromine.

Draw the structure of **K**.

[1]

[Total: 7 marks]

2 (a) Prontosil and sulfanilamide are anti-bacterial drugs.



sulfanilamide

These two drugs saved many soldiers in World War II.

The photo below is that of a **sulfanilamide kit** issued by the United States Army to its soldiers during World War II.



One source states that the maximum daily dosage of sulfanilamide is 6.5 g per kg of patient. An average US army soldier may be assumed to weigh about 70 kg.

Sulfanilamide has many side-effects – itching, headache, diarrhoea, pale skin, vomiting, dizziness, fatigue.

Is it safe for a wounded US army soldier to consume as many as 30 **kits** worth of tablets in a single day? Justify with calculations.

2 (b) Prontosil was found to be active in *vivo* (in human bodies) while sulfanilamide was found to be active both in *vivo* and in *vitro* (in bacterial cultures grown in petri dishes).

It was later proven that intestinal enzymes break down prontosil to sulfanilamide in the human intestine – in this reaction, the oxidation states of certain nitrogen atoms are altered.

There are a few classes of enzymes as listed below.

Transferases catalyse group transfer reactions.

Hydrolases catalyse reactions that involve hydrolysis.

Ligases are used in catalysis where two substrates are litigated and the formation of carbon-carbon, carbon-sulfide, carbon-nitrogen, and carbon-oxygen bonds due to condensation reactions.

Reductases catalyse reduction reactions.

Oxidases catalyse oxidation reactions.

(i) Suggest the type of intestinal enzyme which catalyses the conversion of prontosil to sulfanilamide.

[1]

[1]

(ii) Name the side-product in the conversion of prontosil to sulfanilamide.

To analyse the sulfanilamide content in a pill, it was dissolved in HCl (aq).

(c) Sulfanilamide is not very soluble in water. Explain why sulfanilamide is not soluble in water but is soluble in HC*l* (aq).

2 A 0.350 g sample of an antibiotic powder containing sulfanilamide was dissolved to form an aqueous solution.

The solution was diluted and made up to the mark in a 100 cm³ graduated flask. A 25.0 cm³ aliquot was transferred into a conical flask, in which 25.0 cm³ of 0.0200 mol dm⁻³ KBrO₃ was added. About 10 g of solid KBr was then added.

 BrO_{3} reacts with bromide according to the equation:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

(d) (i) Calculate the amount of Br₂ formed.

[1]

The bromine formed then reacts with the sulfanilamide to form **X**. Note that the following equation is not balanced.



(ii) By comparing the M_r of sulfanilamide and **X**, show that **X** is a dibrominated compound.

[1]

(iii) Draw the structure of **X**, ignoring the directing effects of the $-SO_2NH_2$ group.

2 (e) After ten minutes, an excess of KI was added.

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

The liberated iodine was then titrated with 18.00 cm³ of 0.0900 mol dm⁻³ Na₂S₂O₃.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^{-}$$

Calculate the amount of bromine which reacted with the KI.

[1]

(f) Using your answers to (d) and (e), calculate the amount of sulfanilamide which reacted with the bromine.

(g) Hence, calculate the percentage mass of sulfanilamide in the sample.

[2]

[2]

[Total: 13 marks]

3 Hydrazine (N₂H₄) was first used as rocket fuel in World War II, and has since been used as a propellent for maneuvering spacecraft, as it decomposes rapidly and exothermically into hydrogen gas and nitrogen gas.

Hydrazine may be produced industrially by the Olin-Rashig process from NH_2Cl and ammonia.

$$NH_2Cl(g) + NH_3(g) \longrightarrow HCl(g) + N_2H_4(g)$$

The values of K_c are tabulated below with the corresponding temperatures.

T/K	298	304	503
Kc	1.525 × 10 ⁶	1.230 × 10⁵	2.201 × 10 ⁴

(a) State the value of K_p at 304 K. Justify your answer.

(b) By manipulating the relationship of $K_c=~e^{\frac{-\Delta G}{RT}}$, we obtain

$$R \ln K_{c} = \frac{1}{T} (-\Delta H) + \Delta S.$$

The graph below was plotted with ln K_c as the y-axis and $\frac{1}{\tau}$ as the x-axis.



(i) Describe how you would obtain the value of ΔS from the above graph.

[2]

3 (b) (ii) Another way to find the standard entropy change of a reaction is to consider the standard molar entropies of the species involved.

Species	HCl (g)	N ₂ H ₄ (g)	NH ₂ Cl (g)	NH₃ (g)
Standard molar entropy / J mol ⁻¹ K ⁻¹	187	239	201	193

Calculate the standard entropy change of the Olin-Rashig process.

[1]

(iii) Hence, using your answer to **b(ii)** and the equation in **(b)**, calculate the standard enthalpy change of the Olin-Rashig reaction, including its units.

[1]

(c) The pK_a and pK_b values of the two reactants – monochloramine (NH₂Cl) and ammonia - are tabulated below.

Product	NH ₂ C <i>l</i>	NH_3
pKa	14	32.5
рК _ь	15	4.75

Explain these differences as much as you can.

3 (d) Monochloramine is an oxidising agent.

 $NH_2Cl + 2H^+ + 2e \rightarrow NH_4Cl$

The reduction potentials of the above half-reaction is +1.45 V. However, in alkaline medium, the reduction potential is +0.74 V. Explain the difference between these two reduction potentials.

[2] [Total: 9 marks]

4 (a) Ethanoic acid, a weak monobasic acid, is the main component in vinegar.

When a 20.0 cm³ sample of vinegar was titrated against 0.05 mol dm⁻³ aqueous potassium hydroxide using a pH meter, the following graph was obtained.



(i) Show that the concentration of the ethanoic acid solution is 0.0750 mol dm⁻³.

[1]

(ii) Hence use your answer and the initial pH to show that ethanoic acid is a weak acid.

4 (a) (iii) Show that the acid dissociation constant of ethanoic acid has a numerical value of 1.85×10^{-4} .

[2]

(iv) Calculate the value of the pH after 15.00 cm³ of aqueous potassium hydroxide has been added.

[1]

(v) Write a suitable chemical equation, with state symbols, to explain why the equivalence pH is above 7.

[1]

(b) (i) Solution A was prepared by adding 10.00 cm³ of the potassium hydroxide solution to 25.0 cm³ of the ethanoic acid solution.

Calculate the pH of solution **A**.

[2]

(ii) When a small amount of acid or base is added to solution **A**, its pH remained relatively constant. Explain, with the aid of equations, why this is so.

[2]

[Total: 11 marks]

5 Study the synthetic route from benzene to 1,3,5-tribromobenzene, shown below.



(a) State the reagents and conditions used in steps I and II.

[2]

(b) By examining the positions of the bromine atoms, suggest why 1,3,5-tribromobenzene cannot be made directly from benzene with bromine.

[1]

(c) Phosphinic acid, H₃PO₂, is used in step V. Only one out of its three hydrogen atoms is acidic. A non-acidic hydrogen substituted on the benzene to liberate nitrogen gas.

Draw the structure of phosphinic acid and circle the hydrogen atom which substitutes on the benzene.

[2]

[Total: 5 marks]

6 (a) Flunitrazepam is a drug used in the short-term treatment of insomnia and as a premedication in surgical procedures and for inducing anaesthesia.

Study the synthetic route to flunitrazepam shown below.



6 (a) Fill in the table below with the appropriate reagents and conditions.

Step	Reagents and conditions
I	
II	
III	
V	
VI	
XI	

[6]

6 (b) Carnosine is a dipeptide health supplement. It first appeared in the mainstream health community around a decade ago in the form of supplements, eye-drops and skin creams.



(i) One of the products is β -alanine (structure shown below) when carnosine is hydrolysed with hot KOH (aq).



Draw the structural formula of the other product.

(ii) α -alanine is one of the twenty essential amino acids. It is a constitutional isomer of β -alanine. Unlike β -alanine, it is chiral. Draw the skeletal formula of α -alanine.

(iii) Sarcosine is another constitutional isomer of β -alanine. It is an α -amino acid, just like α -alanine. Draw the structural formula of sarcosine.

[3]

[Total: 9 marks]

- 7 Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is the form of S_8 . In the gas phase, all ring sizes from S_3 to S_{12} have been detected.
 - (a) In the gas phase, the different ring sizes are in equilibrium. The equation for the equilibrium between $S_7(g)$ and $S_8(g)$ is given below:

7S₈(g) ____ 8S₇(g)

(i) Give the expression for the equilibrium constant, K_c , for the reaction between S_7 and S_8 as written above.

[1]

When dissolved in an organic solvent, S_6 , S_7 and S_8 were all detected in equilibrium in the following proportions by mass:

Allotrope	S_6	S ₇	S ₈
% by mass	1.5	0.5	98.0

(ii) Calculate the amount of S_7 and S_8 at equilibrium when 1.00 g of sulfur is dissolved in 1.00 dm³ of solvent.

[2]

(iii) Calculate the value of the equilibrium constant in (i).

[1]

(b) In the solid phase, S₈ crystallises in two well-known allotropic forms: orthorhombic and monoclinic. Both combust in excess oxygen to form liquid SO₃. The standard enthalpy changes of combustion of these two forms are as follows:

 ΔH_c (S₈, orthorhombic) = -296.8 kJ mol⁻¹ ΔH_c (S₈, monoclinic) = -297.1 kJ mol⁻¹

Draw an energy level diagram to conclude which is the more stable form.

- 7 (c) Sulfur also forms an interesting cage-like compound with nitrogen, S_4N_4 .
 - (i) There are π bonds in S₄N₄ which are alternating.



The π bonds are omitted in the structural formula shown above.

Fill in the missing π bonds onto the structural formula above.

[1]

 S_4N_4 reacts with hot NaOH(aq) to give thiosulfate ($S_2O_3^{2-}$)and trithionate ($S_3O_6^{2-}$) in 1:2 ratio. Ammonia is the gaseous side-product.

(ii) Suggest what makes this reaction spontaneous.

[1]

(iii) The skeletal equation is as such:

$$S_4N_4 + OH^- + H_2O \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + NH_3$$

Balance the ionic equation.

[1]

7 (d) There are two possible structures of the metabisulfite ion $(S_2O_5^{2-})$, as shown below.



(i) Using appropriate values from the Data Booklet, calculate the enthalpy changes of atomisation of **Y** and **Z**. Hence deduce which is more stable.

[2]

(ii) Metabisulfite (structure **Z**) decomposes to SO_2 and sulfite (SO_3^{2-}) in a single step. Draw curly arrows to show the electron movement in this decomposition.

[1]

7 (d) (iii) Potassium metabisulfite, $K_2S_2O_5$, is a white crystalline powder.

It is chemically very similar to sodium metabisulfite, $Na_2S_2O_5$, with which it is sometimes used interchangeably. Potassium metabisulfite is generally preferred out of the two as a food preservative as it does not contribute sodium to the diet.

Explain why potassium metabisulfite decomposes at a higher temperature on heating than sodium metabisulfite.

[2]

[Total: 14 marks]

8 (a) Copper(II) sulfate can undergo a series of reactions as shown in the reaction scheme below.



(b) Ionisation isomerism is a special type of constitutional isomerism in which the isomers form different ions in solution.

There is a pair of cobalt(III) ionisation isomers, **K** and **L**. They have molecular formula $CoBrSO_4(NH_3)_4$. **K** is red while **L** is dark violet.

On addition of aqueous barium nitrate, only **K** gave a white precipitate. On addition of aqueous silver nitrate, only **L** gave an off-white precipitate.

(i) Give the structural formulae of the cations in **K** and **L**.

K:

L:

[2]

(ii) Explain briefly why K and L exhibit different colours.

[1]

[Total: 7 marks]

END OF PAPER

9729/02/Prelim/2017