Index No.	Name	Form Class	Tutorial Class	Subject Tutor

ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY **9729/02**
Higher 2

Paper 2 Structured Questions **15 August 2017**
2 hours

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.

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.

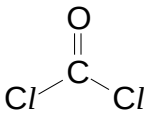
1 A range of different chemicals - chlorine, phosgene and mustard "gas" - were used as weapons throughout World War I.

Their melting and boiling points are tabulated below.

Gas	Melting point / ^{0}C	Boiling point / ^{0}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'.



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.

$$COCl_2 + 2H_2O \rightarrow H_2CO_3 + 2HCl$$

[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?

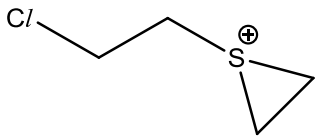
It is actually a liquid at room temperature because its melting point is lower than room temperature and its boiling point is higher than room temperature.

[1]

1 (b) The structural formula of mustard "gas" is C*l*$CH_2CH_2SCH_2CH_2$C*l*.

Unlike alkyl halides, mustard "gas" reacts instantly with water to form hemi-mustard, C*l*$CH_2CH_2SCH_2CH_2OH$.

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



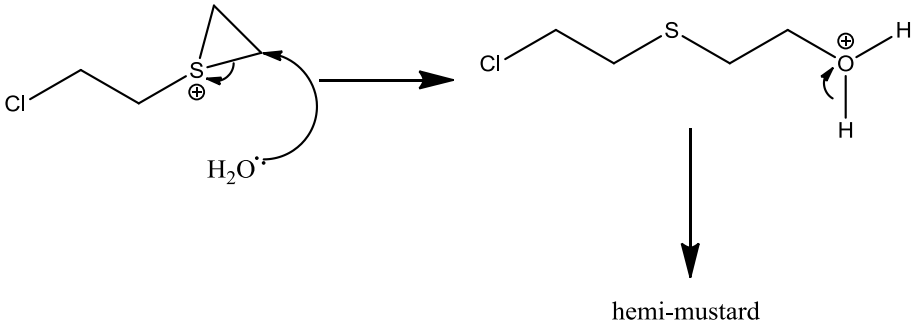
How does this intermediate make the hydrolysis of mustard "gas" easier than that of alkyl halides?

The presence of angle/ring strain in this intermediate makes it more susceptible to nucleophilic attack than the mustard gas molecule itself.

[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.

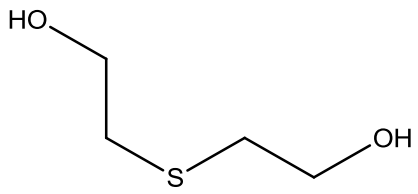
Use electron arrows to show how the intermediate in **b(ii)** is converted into hemi-mustard.



[2]

1 (b) (iv) Hemi-mustard can be further attacked by water to form **J**, $C_4H_{10}SO_2$.

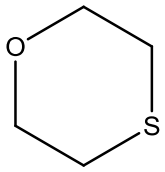
Draw the structure of **J**.



[1]

(v) On reaction with concentrated sulfuric acid at 140 ^oC, hemi-mustard can be converted into **K**, C_4H_8SO, which does not decolourise bromine.

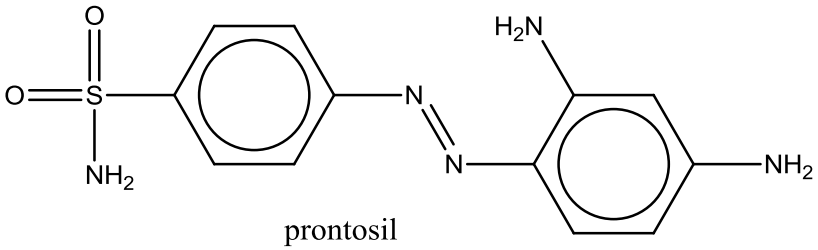
Draw the structure of **K**.



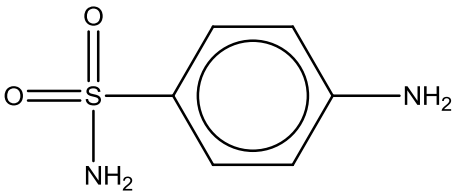
[1]

[Total: 7 marks]

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



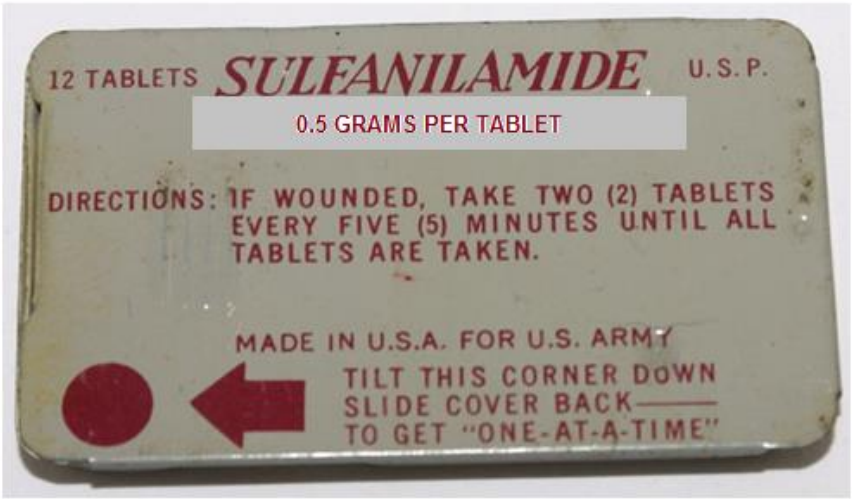
prontosil



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.

Yes.
Mass of drug in 30 kits = 30(12)0.5 g < 6.5(70) g

[1]

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.

Reductase

[1]

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

1,2,4-triaminobenzene or benzene-1,2,4-triamine

[1]

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

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

Sulfanilamide is not very soluble in water due to limited hydrogen bonding due to the presence of benzene / hydrophobic nature of benzene.

However, in acid, sulfanilamide is a base / will be protonated by acid / becomes ionic, so interactions with water change from hydrogen bonding to the more favorable / stronger ion-dipole interactions.

[2]

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 cm^3 graduated flask. A 25.0 cm^3 aliquot was transferred into a conical flask, in which 25.0 cm^3 of 0.0200 mol dm^{-3} $KBrO_3$ was added. About 10 g of solid KBr was then added.

BrO_3^- reacts with bromide according to the equation:

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

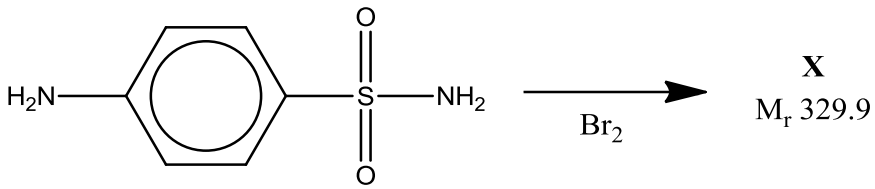
(d) **(i)** Calculate the amount of Br_2 formed.

Amount of Br_2 = 3 * (25.0 * 0.0200 / 1000) = 0.00150 mol

[1]

The bromine formed then reacts with the sulfanilamide to form **X**.

Note that the following equation is not balanced.



sulfanilamide
M_r 172.1

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

The A_r of bromine is 79.9 to the nearest 1 dp.

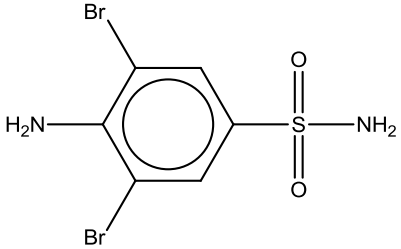
Observing the 0.9 in the M_r of **X**, we can conclude there are two bromine atoms in **X**.

Or

329.9 + 2 – (172.1) = 159.8 = 2(79.9)

[1]

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



[1]

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 cm^3 of 0.0900 mol dm^{-3} $Na_2S_2O_3$.

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

Calculate the amount of bromine which reacted with the KI.

Amt of iodine = 0.5 * (18.00 * 0.0900 / 1000) = 8.10×10^{-4} mol = amount of bromine reacted with KI.

[1]

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

Amt of bromine reacted with sulfanilamide
$= (1.50 \times 10^{-3}) - (8.10 \times 10^{-4}) = 6.90 \times 10^{-4}$ mol

amt of sulfanilamide which reacted with the bromine $= 3.45 \times 10^{-4}$ mol

[2]

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

Mass of sulfanilamide in sample = $3.45 \times 10^{-4} \times 4 \times 172 = 0.2374$ g

Percentage mass of sulfanilamide in sample = $\frac{0.2374\ g}{0.350 g} \times 100\% = 67.8\%$

[2]

[Total: 13 marks]

3 Hydrazine (N_2H_4) 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.

$$NH_2Cl\,(g) + NH_3\,(g) \rightleftharpoons HCl\,(g) + N_2H_4\,(g)$$

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

T / K	298	304	503
K_c	1.525×10^6	1.230×10^5	2.201×10^4

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

1.230×10^5

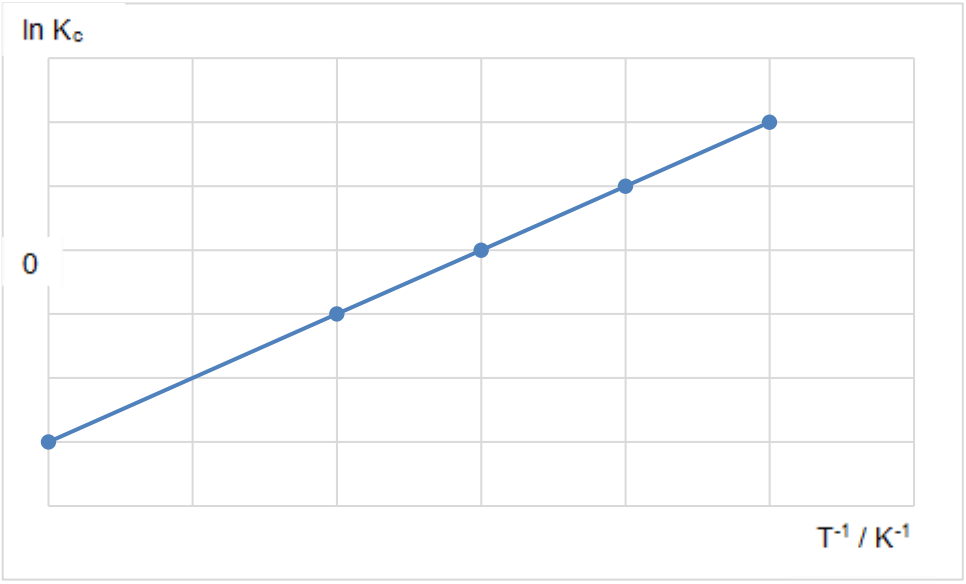
As the unit of K_c is dimensionless OR there are equal amounts of gaseous reactants and products in the equation, the value of K_c is the same as the value of K_p.

[2]

(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 $\frac{1}{T}$ as the x-axis.



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

Read off the y-intercept and then multiply it by R

[1]

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	HC*l* (g)	N_2H_4 (g)	NH_2Cl (g)	NH_3 (g)
Standard molar entropy / J mol^{-1} K^{-1}	187	239	201	193

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

Standard entropy change
$= \sum S\,(products) - \sum S\,(reactants)$
= 187 + 239 – (201+193)
= + 32 J mol^{-1} K^{-1}

[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.

$$\mathrm{R \ln K_c} = \frac{1}{\mathrm{T}}(-\Delta \mathrm{H}) + \Delta S$$

8.31 ln (1.525 * 10^6) = (1/298)(-ΔH) + 32

ΔH = - 25.7 kJ mol^{-1}

[1]

(c) The pK_a and pK_b values of the two reactants – monochloramine (NH_2Cl) and ammonia - are tabulated below.

Product	NH_2Cl	NH_3
pK_a	14	32.5
pK_b	15	4.75

Explain these differences as much as you can.

NH_2Cl has an C*l* atom which is more electronegative than H in NH_3.

The presence of the more electronegative chlorine atom in NH_2Cl compared to hydrogen in NH_3 causes the lone pair on the nitrogen in monochloramine to be less available than the lone pair in ammonia. Hence, monochloramine is the weaker base as shown by the bigger pK_b.

The presence of the more electronegative chlorine atom in NH_2Cl compared to hydrogen in NH_3 causes the conjugate base of monochloramine to be more stable than the conjugate base of ammonia. Hence monochloramine is the stronger acid as shown by the bigger pK_a.

[2]

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.

In alkaline medium, concentration of H^+ will be lower, thus backward reaction is favoured.

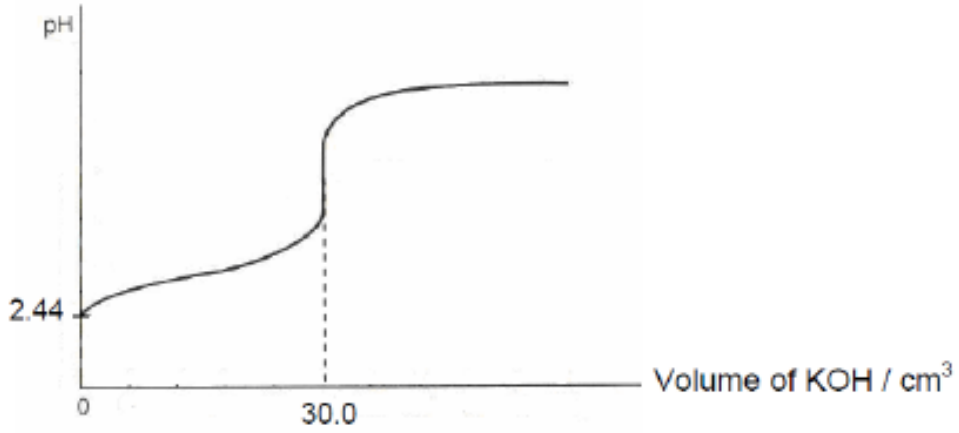
The tendency of monochloramine to be reduced decreases, and hence the reduction potential decreases.

[2]

[Total: 9 marks]

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

When a 20.0 cm^3 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}.

Amount of KOH
= 30.0/1000 * 0.05

Concentration of ethanoic acid solution
= (30.0/1000 * 0.05) / (20.0/1000) = 0.0750 M (shown)

[1]

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

If ethanoic acid were a strong acid where dissociation is complete (100%), $[H^+]$ = 0.0750 M, pH = – log (0.0750) = 1.12

However, it is a weak acid where dissociation is partial, the $[H^+]$ dissociated is low, the actual pH would be higher than 1.12.

OR

$[H^+] = 10^{-2.44} = 0.003631$ M < 0.0750M, dissociation of acid is not complete, it is a weak acid.

[2]

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

$[H^+] = 0.003631$ M
$K_a = (0.003631)^2 / (0.0750 - 0.003631) = 1.85 \times 10^{-4}$ M

[2]

(iv) Calculate the value of the pH after 15.00 cm^3 of aqueous potassium hydroxide has been added.

When 15.00 cm^3 of KOH is added, half of the weak acid would have reacted. It is a maximum buffering capacity.

$pH = pK_a = 3.73$

[1]

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

Hydrolysis of conjugate base:

$$CH_3CO_2^- (aq) + H_2O (l) \rightleftharpoons CH_3CO_2H (aq) + HO^- (aq)$$

[1]

(b) (i) Solution **A** was prepared by adding 10.00 cm^3 of the potassium hydroxide solution to 25.0 cm^3 of the ethanoic acid solution.

Calculate the pH of solution **A**.

Amt of ethanoic acid remaining = $\frac{25 \times 0.0750}{1000} - \frac{10 \times 0.0500}{1000} = 0.001375$ mol
Amt of ethanoate = 0.0005
$pH = pK_a + \lg (\frac{[salt]}{[acid]})$
$= - \lg (1.85 \times 10^{-4}) + \lg (0.0005/0.001375) = 3.29$

[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.

Solution **A** is buffer as there are large reservoirs of ethanoic acid (weak acid) and ethanoate ions (conjugate base).

When a small amount of acid is added,

$$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$$

The formation of CH_3CO_2H is insignificant compared to the large reservoir of CH_3CO_2H. Hence, the pH does not decrease significantly.

When a small amount of base is added,

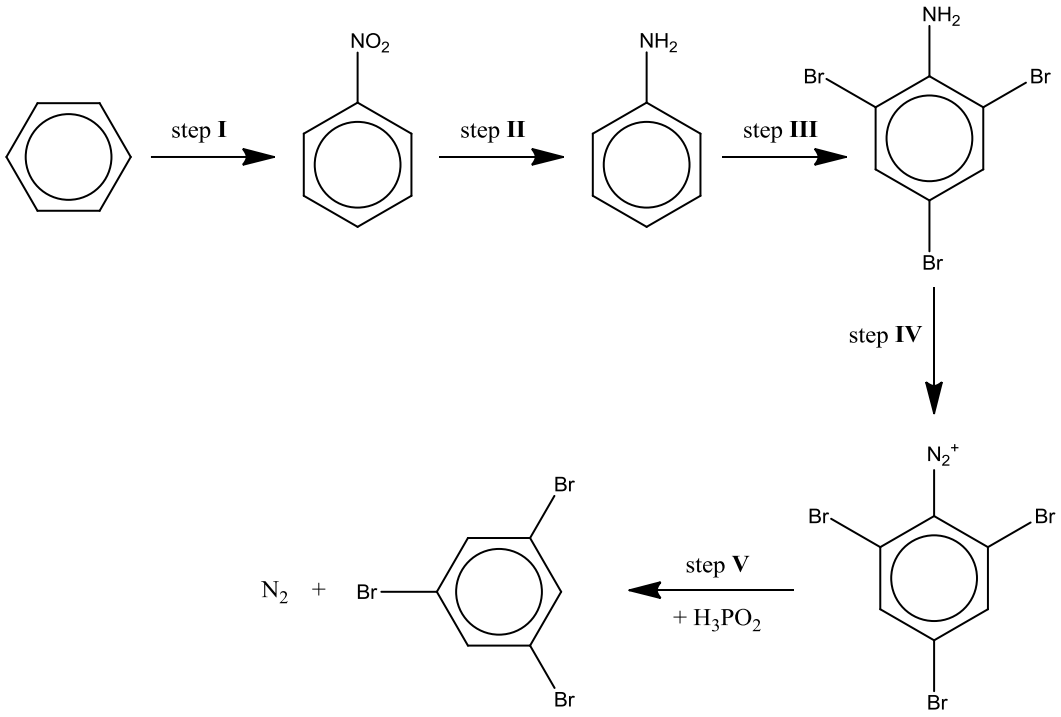
$$CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$$

The formation of $CH_3CO_2^-$ is insignificant compared to the large reservoir of $CH_3CO_2^-$. Hence, the pH does not increase significantly.

[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.**

step **I** : Conc. HNO_3, conc. H_2SO_4, 55 -60 ^{0}C
step **II** : Sn, conc HC*l* , heat under reflux

[2]

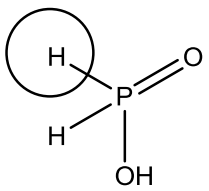
(b) By examining the positions of the bromine atoms, suggest why 1,3,5-tribromobenzene cannot be made directly from benzene with bromine.

Bromine is a 2,4-director.

[1]

(c) Phosphinic acid, H_3PO_2, 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.

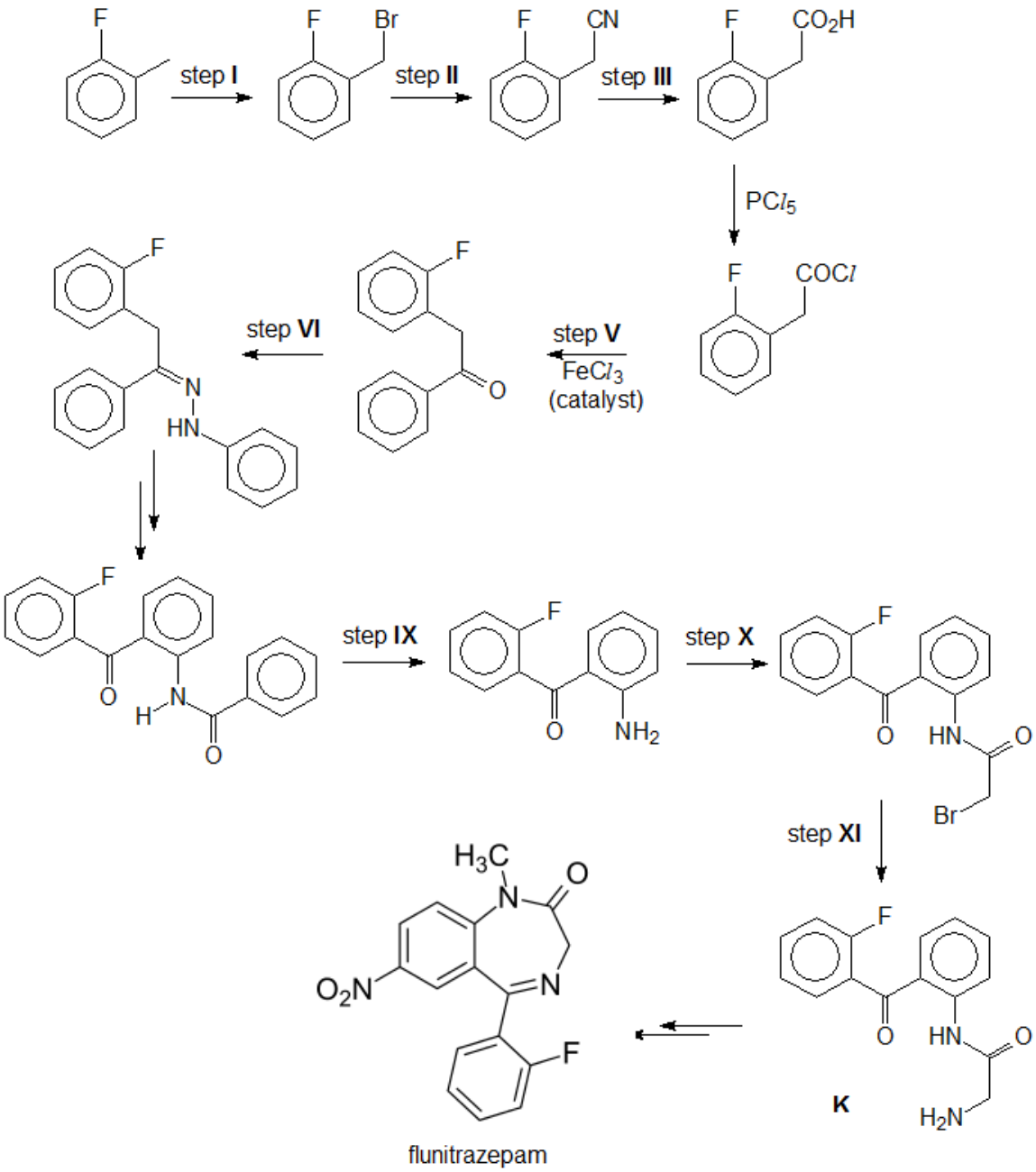


[2]

[Total: 5 marks]

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

Study the synthetic route to flunitrazepam shown below.

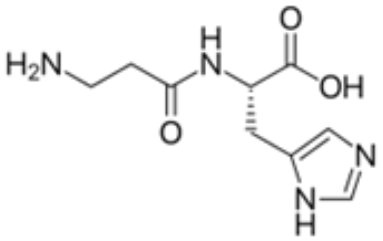


6 (a) Fill in the table below with the appropriate reagents and conditions.

Step	Reagents and conditions
I	Limited Br_2, UV or high temp
II	KCN, ethanol, heat under reflux
III	H_2SO_4 (aq) (or HCl), heat under reflux
V	Benzene
VI	Phenylhydrazine ($C_6H_5NHNH_2$)
XI	excess ammonia, ethanol, heat in sealed tube. Or concentrated ammonia, heat at high pressure

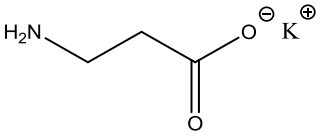
[6]

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.

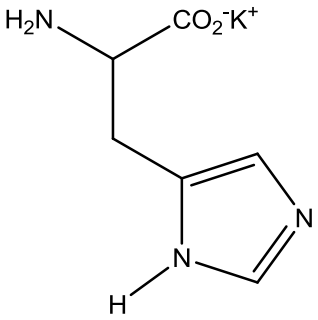


carnosine

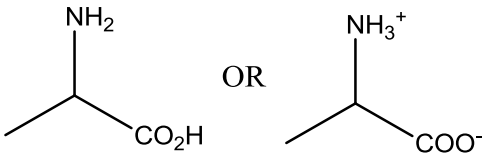
(i) One of the products is β–alanine (structure shown below) when carnosine is hydrolysed with hot KOH (aq).



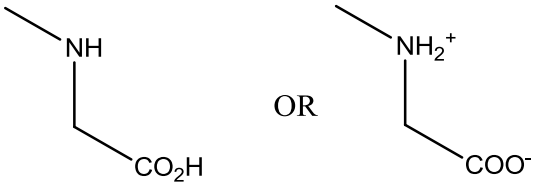
Draw the structural formula of the other product.



(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:

$$7S_8\,(g) \rightleftharpoons 8S_7\,(g)$$

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

$K_c = [S_7]^8 / [S_8]^7$

[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 dm^3 of solvent.

Amount of S_7 = 0.005 / (7 X 32.1) = 2.23 X 10^{-5} mol
Amount of S_8 = 0.98 / (8 X 32.1) = 3.82 X 10^{-3} mol

[2]

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

$K_c = \frac{(2.23\times10^{-5})^8}{(3.82\times10^{-3})^7}$ = 5.15 X 10^{-21} mol dm^{-3}

[1]

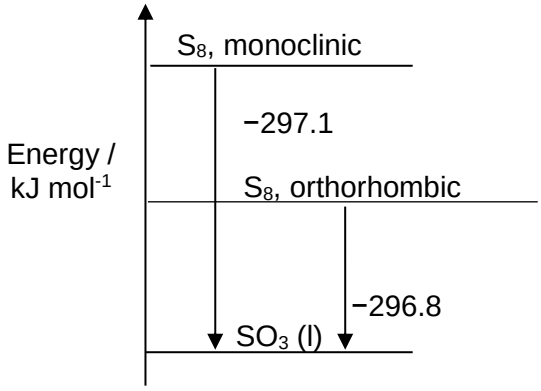
(b) In the solid phase, S_8 crystallises in two well-known allotropic forms: orthorhombic and monoclinic.

Both combust in excess oxygen to form liquid SO_3. The standard enthalpy changes of combustion of these two forms are as follows:

ΔH_c (S_8, orthorhombic) = −296.8 kJ mol^{-1}
ΔH_c (S_8, monoclinic) = −297.1 kJ mol^{-1}

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

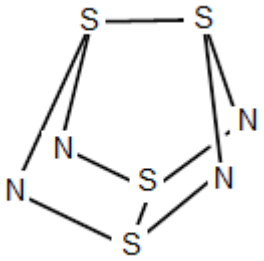
Orthorhombic [1]



[2]

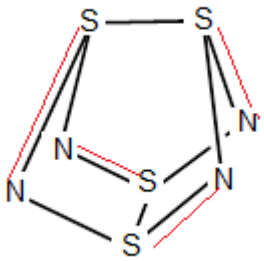
7 (c) Sulfur also forms an interesting cage-like compound with nitrogen, S_4N_4.

(i) There are π bonds in S_4N_4 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.

An increase in entropy with the formation of gas.

[1]

(iii) The skeletal equation is as such:

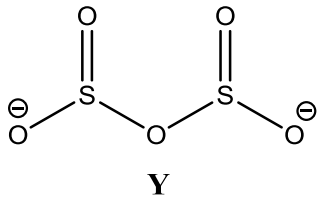
$$S_4N_4 + OH^- + H_2O \rightarrow S_2O_3^{2-} + S_3O_6^{2-} + NH_3$$

Balance the ionic equation.

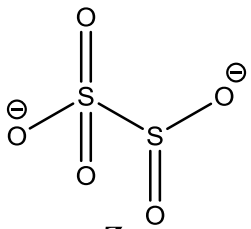
$$2S_4N_4 + 6OH^- + 9H_2O \rightarrow S_2O_3^{2-} + 2S_3O_6^{2-} + 8NH_3$$

[1]

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



Y



Z

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

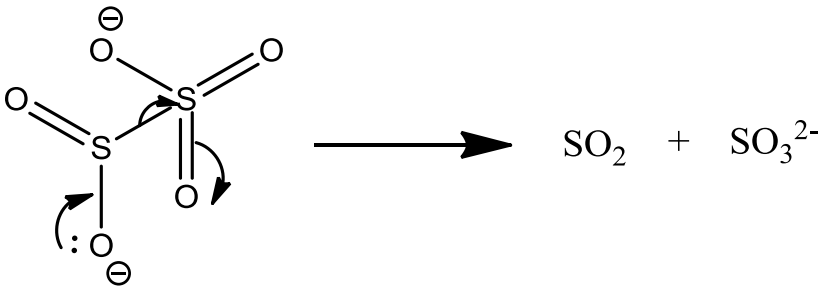
ΔH_{atom}**Y** = 4(S-O) + 2(S=O) = 4(360) + 2(500) = + 2440 kJ mol^{-1}

ΔH_{atom} **Z =** 2(S-O) + 2(S=O) + (S-S) = 2(360) + 3(500) + 264
= + 2484 kJ mol^{-1}

Z is the more stable one.

[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.

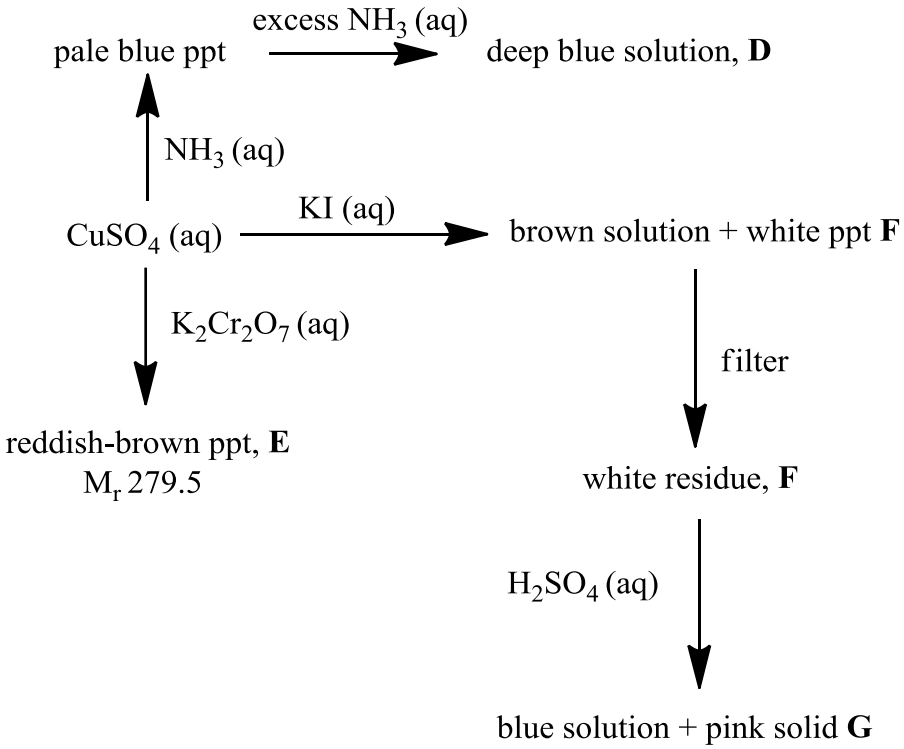
K^+ has the lower polarising power due to its lower charge density as compared to Na^+.

Hence, the covalent bonds in the metabisulfite ion in $K_2S_2O_5$ is weakened to the lesser extent. [1]

[2]

[Total: 14 marks]

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



Identify **D**, **E**, **F** and **G**.

D: $Cu(NH_3)_4(H_2O)_2^{2+}$ or $Cu(NH_3)_4^{2+}$ **F**: CuI or Cu_2I_2

E: $CuCr_2O_7$ **G**: Cu

[4]

(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: $[CoBr(NH_3)_4]^{2+}$ or $[Co(H_2O)Br(NH_3)_4]^{2+}$
L: $[CoSO_4(NH_3)_4]^{+}$ or $[Co(H_2O)SO_4(NH_3)_4]^{+}$

[2]

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

Different ligands will split the energy of the d orbitals by different extents, hence visible light of different wavelengths will be absorbed, leading to different colours.

[1]

[Total: 7 marks]

END OF PAPER