

September 2015

2 hours

Higher 2

CHEMI	STRY		9647/02
CLASS		INDEX NUMBER	
CANDIDATE NAME			

Paper 2 Structured Questions

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page. Write in dark blue or black pen in the spaces provided. 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 **all** questions.

A Data Booklet is provided. Do not write anything on it.

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.

For Examiner's Use		
1	/ 12	
2	/ 7	
3	/ 23	
4	/ 17	
5	/ 13	

1 Planning (P)

Cobalt(III) complex salts played a critical role in early studies of the structures of octahedral transition metal complexes.

One such complex salt is the nitrate salt of pentaammineaquacobalt(III), $[Co(NH_3)_5(H_2O)](NO_3)_3$, which is prepared from cobalt(II) nitrate, $Co(NO_3)_2$.

 $2HNO_3(aq) + 2Co(NO_3)_2(s) + H_2O_2(aq) + 10NH_3(aq) \longrightarrow 2[Co(NH_3)_5(H_2O)](NO_3)_3(s)$

1.45 g of solid $Co(NO_3)_2$ is added to 45 cm³ of concentrated ammonia.

This is followed by the addition of 25 cm³ of hydrogen peroxide solution. A rapid increase in the concentration of hydrogen peroxide in the reaction mixture can result in hydrogen peroxide undergoing self-decomposition.

Subsequently, 30 cm³ of concentrated nitric acid is added. The initial reaction may be highly exothermic.

Once the reaction is completed, a 100 cm³ crude mixture is obtained.

The product, $[Co(NH_3)_5(H_2O)](NO_3)_3$, is precipitated from the crude mixture to separate it from any unreacted $Co(NO_3)_2$. This is done by adding an approximately equal volume of a suitable solvent to the crude mixture.

The table below shows the respective solubilities of $Co(NO_3)_2$ and $[Co(NH_3)_5(H_2O)](NO_3)_3$ in three possible solvents.

Soluto	Solubility / g per 100 g of solvent			
Solute	Water	Ethanol	Hexane	
Co(NO ₃) ₂	10.2	9.5	0.9	
[Co(NH ₃) ₅ (H ₂ O)](NO ₃) ₃	10.5	2.1	1.1	

The precipitated $[Co(NH_3)_5(H_2O)](NO_3)_3$ is subsequently purified by recrystallisation from a given solution of ammonium nitrate as a solvent.

(a) Explain the role of H_2O_2 in the reaction.

[1]

2

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		For Examiner's Use
	[10]	
(c)	Identify one potential safety hazard in this experiment and state how you would minimise this risk.	
	[1]	
	[Total: 12]	

- For Examiner's Use
- 2 (a) Organic compounds containing the —NCO functional group are known as isocyanates. They are useful starting materials for making polyurethane polymers. One example of an isocyanate is 1,2-diisocyanatocyclopentane.



(i) State the hybridisation of C atom in the -NCO functional group. [1] (ii) The bond length of C=O in 1,2-diisocyanatocyclopentane is 118 pm whereas the bond length of C=O in CH₃COCH₃ is 123 pm. Explain the difference in bond lengths of C=O. [2] (iii) 1,2-diisocyanatocyclopentane can exist as a pair of stereoisomers as shown below. State the type of stereoisomerism present. NCO ŅСС Type of stereoisomerism: [1] total (iv) Hence, state the number of stereoisomers present for 1,3-diisocyanatocyclopentane. NCO OCN Total number of stereoisomers: [1] (b) Cyanate ions, NCO⁻, are ambidentate ligands in which either the nitrogen or oxygen atoms can act as donor atoms which form dative bonds with a metal ion such as Ag⁺. An example is the formation of [Ag(NCO)₂]⁻ or [Ag(OCN)₂]⁻ complex ions.

The structure of the cyanate ligand is shown below:



Draw the displayed formulae of the $[Ag(NCO)_2]^-$ and $[Ag(OCN)_2]^-$ complex ions. State the bond angle with respect to the donor atoms clearly in the structure.

 $[Ag(NCO)_2]^-$

Bond angle (Ag–N–C):

[Ag(OCN)₂]⁻

Bond angle (Ag–O–C):

[2]

[Total: 7]

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- 8
- 3 This question looks into the impact of natural occurrences and anthropogenic events on environmental conditions.
 - (a) Volcanic emissions contain gases which include H₂O, HF, HC*l*, HBr, BrO and SO₂. These gases affect the composition of the surrounding air around the volcanoes.
 - (i) Gaseous HC*l* and HBr have been found to exist only for a short time in the atmosphere.

Suggest a possible reason for this observation.

(ii) With reference to the reactions with concentrated H₂SO₄, compare the reducing powers of HC*l* and HBr and write equations for the reactions, where appropriate.

.....

3



(b) Emissions from the combustion of petroleum have devastating results in the urban atmosphere. Nitrogen oxides, emitted by car engines, are components of photochemical smog.

At 298 K, N_2 and O_2 in air do not react at a significant rate. However, a car engine produces about 2.5 g of NO per kilometre because the reaction shown below occurs much more quickly at the high temperatures that exist in the engine.

 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(i) Give a reason why the reaction takes place slowly at 298 K. [1] At 298 K, the value of K_p for the above reaction is 5.0 x 10⁻³¹ while at 1500 K, (ii) its value is 1.0×10^{-5} . Use this information to explain whether the formation of NO is endothermic or exothermic. [1] (iii) The reaction is only thermodynamically feasible at high temperatures. By considering the chemical equation and your answer to b(ii), explain clearly what information can be deduced about the ΔS^{\ominus} of the reaction. _____ [2]

When exposed to the open atmosphere, NO reacts rapidly with O_3 to form NO_2 .

(iv) Draw a dot-and-cross diagram for NO₂.

For Examiner's Use (v) Ozone depletion in the stratosphere involves the following reactions:

 $\begin{array}{ccc} \mathsf{NO} + \mathsf{O}_3 & \longrightarrow & \mathsf{NO}_2 + \mathsf{O}_2 \\ \mathsf{NO}_2 + \mathsf{O} & \longrightarrow & \mathsf{NO} + \mathsf{O}_2 \end{array}$

By considering the structures of NO and NO₂, explain how the above reactions cause rapid and extensive depletion of ozone.

.....

- (vi) Ethene plays a role in the chemistry of photochemical smog according to the following steps.
 - Step 1: Ethene reacts with a hydroxyl radical, •OH, to form 2-hydroxyethyl radical, •CH₂CH₂OH.
 - Step 2: The 2-hydroxyethyl radical reacts with O_2 to form $\bullet O_2CH_2CH_2OH$.
 - Step 3: $\bullet O_2 CH_2 CH_2 OH$ reacts with NO to generate NO₂.

Draw the mechanism for steps 1 and 2. Use curly arrows (\uparrow) to indicate the movement of single electrons and show structural formulae for all compounds so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•).

Step 1:

Step 2:

[2]

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[1]

- For Examiner's Use
- (c) Mustard gas, C₄H₈SCl₂ is a man-made chlorinated gas which was used in chemical warfare during World War I. It is now used in the treatment of Hodgkin's disease.

It can be prepared according to the following reaction:

 $SCl_2(g) + 2CH_2 = CH_2(g) \rightleftharpoons C_4H_8SCl_2(g)$

At 20 °C, a 5 dm³-flask was filled with 0.258 mol SC l_2 and 0.592 mol CH₂=CH₂ and the flask was subsequently sealed. At equilibrium, 0.522 mol CH₂=CH₂ was left.

(i) By calculating the amounts of SCl_2 and $C_4H_8SCl_2$, determine the total amount of gas at equilibrium.

(ii) Assuming that the gases behave ideally, show that the total pressure at equilibrium was 3.80×10^5 Pa.

[2]

		1
(iii)	Hence, calculate the equilibrium constant, K_{p} , for the reaction, giving its units.	E>

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	[2]
(iv)	The same equilibrium system was studied in a larger flask at the same temperature. State, with reasons, how
	 the position of equilibrium, and the K_p value will change compared to the original system.
•	
	[3]

(v) SCl_2 and $CH_2=CH_2$ react to form mustard gas, $C_4H_8SCl_2$, as shown in the reaction scheme below.



Step 2:

$$\begin{array}{ccc} H & H \\ H - C - C - H + CH_2 = CH_2 \longrightarrow C_4H_8SCl_2 \\ I & I \\ Cl & S - Cl \end{array}$$

Suggest the type of reaction for Step 1.

.....[1]

(vi) Draw the structure of $C_4H_8SCl_2$, given that it is a symmetrical molecule.

[1]

[Total: 23]

For Examiner's (a) The figure below shows a reaction sequence starting from nitrobenzene. Use Step 1 NO₂ NH_2 Br_2 Br₂(aq) AlBr₃ room heat temperature Α В (i) Suggest reagents and conditions for Step 1. [2] (ii) Draw the structures of compounds A and B formed in the reaction scheme above. [2] In the bromination of nitrobenzene, a Lewis acid is used to generate the electrophile. $AlBr_3 + Br_2 \longrightarrow AlBr_4^- + Br^+$ A Lewis acid is an electron-pair acceptor. (iii) From the equation above, identify the Lewis acid used to generate the electrophile. [1] (iv) Explain why the species you have chosen in (a)(iii) is able to act as a Lewis acid. [1]

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- (v) Explain why the bromination of phenylamine, C₆H₅NH₂, is possible with the mild conditions shown in the reaction scheme.
- (b) (i) Outline the mechanism of the nitration of benzene, using a mixture of concentrated nitric acid and sulfuric acid as the nitrating agent. Indicate the rate-determining step and draw the formula of the organic intermediate.

17

enthalpy

(ii) Given that the nitration of benzene is exothermic, sketch the reaction pathway diagram of the reaction using the axes below, labelling significant points on the diagram.

Use

reaction coordinate

[2]

(c) To study the mechanism of nitration of benzene, every hydrogen atom on benzene is replaced by its isotope, deuterium, to form C₆D₆. A C–D bond has higher bond dissociation energy than a C–H bond.

If the rate-determining step involves the breaking of a C–H bond, replacing the C–H bond with a C–D bond will change the rate constant, k, of the reaction. This is known as the deuterium isotope effect.

Deuterium isotope effect = $\frac{k_H}{k_D}$ k_H = rate constant for nitration of C₆H₆ k_D = rate constant for nitration of C₆D₆

- If $\frac{k_H}{k_D}$ = 1, it is said that the deuterium isotope effect is absent.
- If $\frac{k_H}{k_D} >> 1$, it is said that the deuterium isotope effect is present.
- (i) With reference to your answer in (b)(i), predict with a reason if the deuterium isotope effect will be present in the nitration of benzene.

[1]

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The bromination of propanone

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

is believed to occur via the following mechanism:

Step	$1 \qquad \begin{array}{c} O \\ \parallel \\ -C \\ -C \\ -C \\ + \\ + \\ + \\ + \\ + \\ - \\ -C \\ -C$
Step	$2 \qquad \begin{array}{c} \stackrel{+}{} OH & OH \\ \stackrel{ }{\longrightarrow} CH_3 \stackrel{-}{\longrightarrow} CH_3 \stackrel{ }{\longrightarrow} CH_2 + H^+ \end{array}$
Step	³ $\overset{OH}{\underset{+}{\overset{+}{\operatorname{CH}_3-\operatorname{C}=\operatorname{CH}_2}}$ + Br ₂ \longrightarrow $\overset{OH}{\underset{+}{\overset{+}{\operatorname{CH}_3-\operatorname{C}-\operatorname{CH}_2\operatorname{Br}}}$ + Br ⁻
Step	4 $CH_3 - CH_2Br \longrightarrow CH_3 - CH_2Br + H^+$
Wher $\frac{k_H}{k_D} \approx$	n deuterated acetone, CD_3COCD_3 undergoes the same bromination reaction, 6.
(ii)	Deduce the rate-determining step in the reaction mechanism.
	[1]
(iii)	Hence, write the rate equation for the reaction.
	[1]
(iv)	The iodination of propanone occurs via a similar mechanism. Predict whether the rate of iodination of propanone depends on the concentration of iodine.
	[1]
	[Total: 17]

5	(a)	State	e the full electronic configuration of the Cu ²⁺ ion.	For Examiner's Use
	(b)	Copp aque	[1] per forms many coloured compounds. Explain the origin of the blue colour of eous Cu ²⁺ .	
			[3]	
	(c)	A gr reac	een solution, D , contains a mixture of 2 cations and undergoes the following tions. One cation has a charge of 2+ while the other has a charge of 3+.	
		gree solutic	$\begin{array}{c} \text{And} & \underset{\text{on } \mathbf{D}}{\overset{\text{NH}_3(\text{aq})}{\longrightarrow}} & \underset{\text{and red-brown ppt.}}{\text{mixture of blue ppt.}} & \underset{\text{followed by filtration}}{\overset{\text{NH}_3(\text{aq})}{\overset{\text{in excess,}}{\longrightarrow}} & \underset{\text{deep blue filtrate } \mathbf{E}}{\overset{\text{NH}_3(\text{aq})}{\overset{\text{in excess,}}{\longrightarrow}}} & \underset{\text{followed by filtration}}{\overset{\text{NH}_3(\text{aq})}{\longrightarrow}} & \underset{\text{followed } \mathbf{F}}{\overset{\text{NH}_3(\text{aq})}{\longrightarrow}} & \underset{\text{followed } \mathbf{F}}{\overset{\text{followed } \mathbf{F}}{\longrightarrow}} & f$	
		(i)	State the formula of the complex ion present in E.	
		(ii)	[1] State the formula of compound F .	
			[1]	
		(iii)	A pale blue precipitate is observed when dilute sulfuric acid is added dropwise to the deep blue filtrate E . Write an ionic equation for this observation.	
			[1]	

(d) Copper(II) oxide is produced on a large scale in the process of extracting copper from its ores.

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(i) By using the information below and the *Data Booklet,* construct a labelled energy level diagram to determine the lattice energy of copper(II) oxide.

enthalpy change of formation of copper(II) oxide	–155 kJ mol ^{–1}
enthalpy change of atomisation of copper	+339 kJ mol ⁻¹
first electron affinity of oxygen	–141 kJ mol ^{–1}
second electron affinity of oxygen	+790 kJ mol ⁻¹

Energy / kJ mol⁻¹



(ii) When concentrated hydrochloric acid is added to solid copper(II) oxide, the black CuO dissolves to form a dark yellow solution. When water is subsequently added in excess, a blue solution is formed.

Explain the colour changes in terms of ligand exchange reactions.

[2]

[Total: 13]

- END OF PAPER -