H

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME **Answers**

CLASS

TUTOR'S NAME

CHEMISTRY

9647/02

Paper 2 Structured Questions

19 September 2011

2 hours

Candidates answer on the Question Paper.

Additional Materials: 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 **all** questions.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/12
2	/10
3	/12
4	/20
5	/18
Total	/72

This document consists of **19** printed pages and 1 blank page.

For Examiner's Use

1 Planning (P)

There are four colourless solutions, labelled as **A1, A2, B1** and **B2.** You are told that A1 and A2 could be 1.0 mol dm^{-3} H_2SO_4 or 2.0 mol dm^{-3} H_2SO_4. **B1** and **B2** are either 1.0 mol dm^{-3} NaOH or 1.0 mol dm^{-3} $Ba(OH)_2$.

You are required to plan a simple experiment to identify **A1, A2, B1 and B2**.

You are provided with 200 cm^3 **of each solution,**

a thermometer

polystyrene cup

common apparatus in the laboratory

No pH indicators are provided.

(a) Suggest how we can first identify $Ba(OH)_2$. Write an equation (with state symbols) to explain your answer.

Add a few drops of A1 (or A2) to 2 cm^3 of B1. Repeat this with B2. The solution which gives a white precipitate is $Ba(OH)_2$.

$Ba(OH)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2H_2O(l)$

[2]

(b) Write an equation for the reaction between sodium hydroxide and sulfuric acid.

$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

[1]

(c) Outline the steps you will take to determine the identities of **A1** and **A2**, using the sodium hydroxide solution.

Step 1: Using a measuring cylinder, add 20 cm^3 of A1 into the polystyrene cup provided and record its initial temperature. Using another measuring cylinder, measure 80 cm^3 of NaOH and record its initial temperature.

Step 2: Add the 80 cm^3 of NaOH into the polystyrene cup containing A1, stir with the thermometer and record the highest temperature reached. Rinse the cup.

Step 3: Repeat steps 1 and 2, this time replacing A1 with A2.

[Accept any specific volume suggested by student, but volume of NaOH should be 4 times of A2/A1 and total volume of mixture should be between 50-100 cm^3.]

[3]

(d) Let ΔT_1 be the temperature change for the reaction between **A1** and NaOH(aq) and ΔT_2 be the temperature change for the reaction between **A2** and NaOH(aq). Illustrate how the identities of **A1** and **A2** can be deduced from the temperature changes obtained in the procedure above.

$2NaOH\ (aq) + H_2SO_4\ (aq) \rightarrow Na_2SO_4\ (aq) + 2H_2O\ (l)$

n_{NaOH} used in both experiments = 1.0 x 80/1000 = 0.080 mol

For 1.0 mol dm–3 H_2SO_4, $n_{H_2SO_4}$ used = 1.0 x 20/1000 =0.020 mol

n(H_2O) formed = 2 x $n_{H_2SO_4}$ = 0.040 mol

For 2.0 mol dm–3 H_2SO_4, $n_{H_2SO_4}$ used = 2.0 x 20/1000 =0.040 mol

n(H_2O) formed = n_{NaOH} = 0.080 mol

Since number of moles of water formed in the two reactions are in the ratio of 1:2, temperature change for the two reactions is expected to be around 1:2.

If $\Delta T2 = 2\Delta T1$,

A2 is 2.0 mol dm–3 H_2SO_4 and A1 is 1.0 mol dm–3 H_2SO_4.

[Other methods are acceptable.]

[3]

(e) Define the term enthalpy change of neutralisation.

The enthalpy change when one mole of water is formed during the neutralisation of an acid and alkali under standard conditions.

[1]

(f) Do you expect the enthalpy change of reaction per mole of **acid** to be more exothermic, less exothermic or the same if

(i) hydrochloric acid was used instead of sulfuric acid? Explain your answer.

Enthalpy change of reaction per mole of acid will be **less exothermic**

Reason: **HCl is also a strong acid, and the amount of water formed per mole of acid would be less.**

(ii) ethanedioic acid was used instead of sulfuric acid? Explain your answer.

Enthalpy change of reaction per mole of acid will be **less exothermic**

Reason: **ethanedioic acid is a weak strong acid, and is only partially dissociated. Part of the energy is used dissociate ethanedioic acid completely before neutralisation occurs.**

[2]

[Total: 12]

2 Nitrobenzene may be made by reacting together concentrated nitric acid, concentrated sulfuric acid and benzene.

Data about these three compounds and nitrobenzene are given in the table.

Compound	Boiling point /^{o}C	Density /g cm^{-3}	Molar mass / g mol^{-1}	Solubility in water
Nitrobenzene	210	1.20	123.0	insoluble
Benzene	80.1	0.88	78.0	insoluble
Concentrated nitric acid	120	1.36	63.0	soluble
Concentrated sulfuric acid	337	1.84	98.0	soluble

Preparation of nitrobenzene

1 Place 35 cm^3 of concentrated nitric acid in a 500 cm^3 round bottomed flask, and add slowly 40 cm^3 of concentrated sulfuric acid, keeping the mixture cool during the addition by immersing the flask in cold water.

2 Place a thermometer in this nitrating mixture, and then add *very slowly* 29 cm^3 of benzene. This should be added about 3 cm^3 at a time, and the contents of the flask *thoroughly* mixed after each addition.

3 When all the benzene has been added, fit a reflux water condenser to the flask, and place the latter in a water bath, which is then maintained at 55-60^{o}C for 45 minutes.

(a) (i) What is the role of sulfuric acid in this reaction? Write a balanced equation when the two acids are mixed.

Sulfuric acid acts as a catalyst that generates the stronger electrophile NO_2^+

$2H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

(ii) For safety reasons, it is important to keep the mixture cool in step 1. Explain why the mixing of the acids is exothermic.

The hydration of the H^+ released by the sulfuric acid gives out heat.

[3]

(b) Suggest with reasoning, one more safety precaution you would take when carrying out the experiment.

Any of the following:

- **Concentrated sulfuric acid / Concentrated nitric acid is corrosive.**

  Wear gloves when handling it wear safety goggles or gloves when handling it

- **Nitrobenzene/benzene is carcinogenic or flammable, carry out the experiment in a fume cupboard**

[1]

(c) Calculate the mass of nitrobenzene formed from benzene, assuming a 70% yield.

given density of benzene $\rho = 0.88 = \frac{m}{V}$

mass of benzene used $= 29 \times 0.88 = 25.52 g$

$n_{Benzene} = \frac{25.52}{78.0} = 0.3272$ mol,

$n_{HNO_3} = \frac{35 \text{ x } 1.36}{63.0} = 0.7556$ mol $\therefore$ limiting reagent is Benzene.

assuming 70% yield, $n_{nitrobenzenehence} = \frac{70}{100} n_{benzene}$

$m_{nitrobenzenehence} = \left(\frac{70}{100} \times \frac{25.52}{78.0}\right) \times 123.0 = 28.17 = \underline{28.2 g}$

The preparation of organic compounds usually produces a mixture of the required compound and other impurities. The purification of nitrobenzene is described below.

Purification of impure nitrobenzene

4 After completion of heating, pour the contents of the flask into a large excess of cold water. Stir the mixture as vigorously as possible. Transfer the liquid to a separating funnel and separate the aqueous layer from the nitrobenzene.

5 Return the nitrobenzene to the separating funnel, and wash with an equal volume of dilute sodium carbonate solution, releasing the pressure as necessary.

6 Transfer the nitrobenzene into a small conical flask, and add some anhydrous granular potassium hydroxide. Shake until the liquid is completely clear.

7 Filter the nitrobenzene into a clean and dry distilling flask fitted with an air condenser. Distil the nitrobenzene carefully, by boiling over a suitable range.

(d) In step 4, the impure nitrobenzene is shaken with a large excess of cold water and the two layers are allowed to separate.

(i) Why is the mixture vigorously stirred with water?

The acids are more soluble in water, by vigorous stirring removes as much of the acid from the nitrobenzene into the aqueous layer as possible, hence purifying the nitrobenzene.

(ii) Will the nitrobenzene be the upper or lower layer? **Lower**

Explain your answer.

Nitrobenzene has a higher density than water.

[2]

(e) Suggest a reason for using potassium hydroxide as a drying agent, rather than the more conventional calcium chloride or sodium sulfate.

The use of KOH would also eliminate any traces of acid in the nitrobenzene.

[1]

(f) In step 7, distillation was carried out to purify the product. Suggest a suitable temperature range for the collection of the fraction.

From **207^{o}C** **to** **211** **^{o}C**

[1]

[total : 10]

3 Nitrogen monoxide, NO, is a by-product of the combustion of hydrocarbon fuels in internal combustion engines.

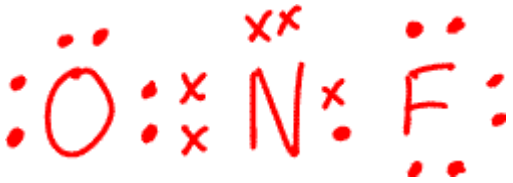
(a) The compound nitrosyl fluoride, ONF, can be produced from nitrogen monoxide and fluorine

$2NO(g) + F_2(g) \rightarrow 2ONF(g) \qquad \Delta H = (-)$

The rate equation for this reaction is rate = $k[NO][F_2]$

The mechanism has two steps. One of these steps produces ONF and the free radical F• in equimolar amounts.

(i) Draw dot-and-cross electron diagrams for nitrogen monoxide, NO, and nitrosyl fluoride, ONF.

NO	ONF
	

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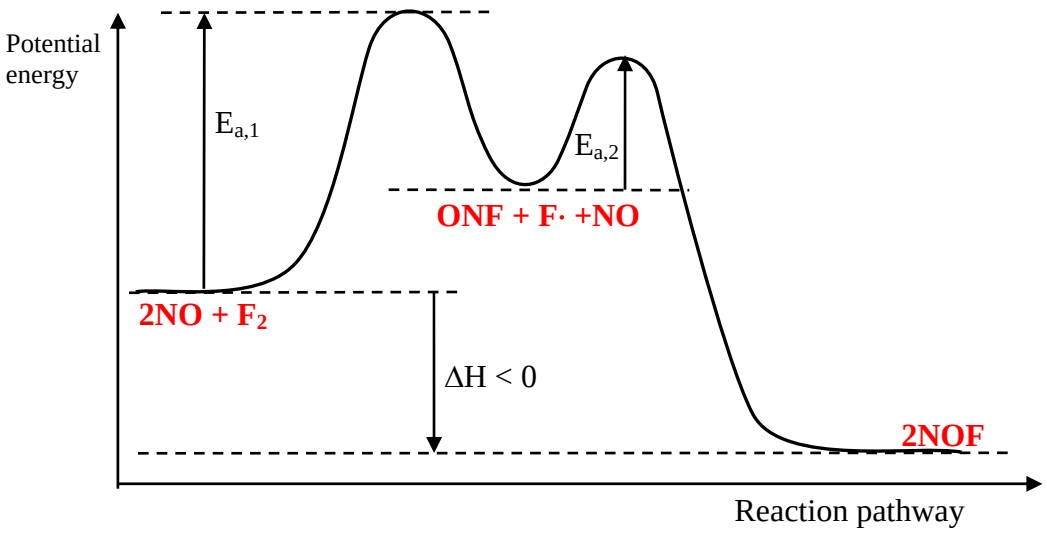
(ii) In the space below sketch the reaction pathway diagram for this reaction.



- ☐ **Labeling axis and diagrams correctly**
- ☐ **$E_{a1} > E_{a2}$ and exothermic reaction**

[4]

(b) One reaction which occurs in air polluted with nitrogen oxides is shown below.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Five experiments were carried out to find the relationship between the initial concentration of NO and of O_2, and the initial rate of formation of NO_2.

experiment	initial concentrations / mol dm^{-3}		initial rate of formation of NO_2 / mol dm^{-3} s^{-1}
	[NO]	$[O_2]$	
1	0.001	0.001	7×10^{-6}
2	0.001	0.002	14×10^{-6}
3	0.001	0.003	21×10^{-6}
4	0.002	0.003	84×10^{-6}
5	0.003	0.003	189×10^{-6}

(i) What is the order of the reaction with respect to each of the reactants?

NO **Second order**

O_2 **First order**

(ii) Hence suggest an equation for the rate-determining step.

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

(iii) Comment on why this rate-determining step is unusual.

This reaction involves the collision of three particles at the correct orientation and sufficient energy, which is statistically very highly unlikely.

(iv) The actual mechanism for the reaction between NO and O_2 is actually bimolecular. By considering the relative stabilities of the reactant molecules involved, suggest a more plausible mechanism for the reaction.

$2NO(g) \xrightarrow{fast} N_2O_2(g)$

$N_2O_2(g) + O_2(g) \longrightarrow 2NO_2$

[4]

(c) At 700 ^{o}C, nitrogen monoxide and hydrogen react as follows:

$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$

(i) Explain briefly why the initial reaction rate would be expected to increase by increasing each of the following:

the pressure,

When pressure is increased, the particles are brought closer together and hence frequency of collision of molecules increases. The frequency of effective collision also increases.

the temperature.

When temperature increases, the number of particles with energy greater than activation energy increases. The frequency of effective collision therefore increases.

(ii) Suggest, with reasons, whether you would expect the reaction between nitrogen monoxide and hydrogen to be endothermic or exothermic.

Exothermic.

The reaction involves forming of highly stable N_2 and H_2O molecules from highly unstable NO molecule.

[4]

[Total:12]

4 Iron is the fourth most common element in the Earth's crust. It has more than one oxidation state and many of its compounds are coloured.

(a) What do you understand by the terms *transition element*, *ligand* and *complex ion*?

A transition element: **is a d–block element which forms at least one stable ion with a partially filled d orbital.**

A complex ion: **is a species that contains a central metal atom/ion surrounded by molecules or anions (known as ligands) which forms coordinate bonds to the metal centre.**

A ligand: **is a molecule or anion with at least one lone pair of electrons that it can use to form a coordination bond to the central metal atom/ion in a complex ion.**

[3]

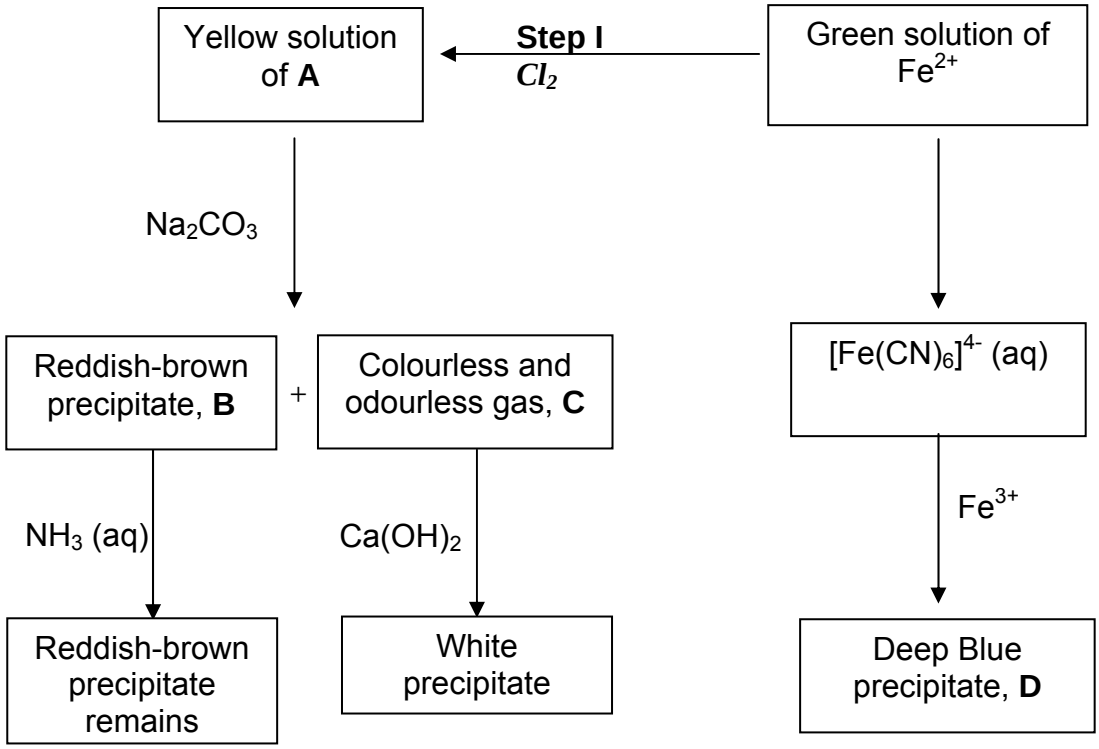
(b) Explain why so many transition element complexes are coloured.

- **In the complexes, the ligands cause the 3d orbitals to split into two energy levels.**
- **d-electrons in the lower energy level absorb energy in the visible spectrum and becomes excited to a vacant and higher energy d-orbital.**
- **The unabsorbed complementary wavelengths are emitted.**
- **Such d-d electron transitions are responsible for the colour of the compounds.**

[2]

(c) 'Blueprints', the detailed plans for architectural or engineering projects, were made in the 19th century by forming the insoluble complex 'Prussian Blue' on sensitised paper. Prussian Blue is the name given to the deep blue precipitate formed by adding a solution of $Fe^{3+}(aq)$ to a solution of $[Fe(CN)_6]^{4-}(aq)$.

The following diagram shows the reactions of iron and its compounds.



(i) A reddish-brown precipitate is seen when sodium carbonate is added to the aqueous solution of **A**. This precipitate is insoluble upon the addition of aqueous ammonia. Suggest the identity of the cation in **A**.

A: **$[Fe(H_2O)_6]^{3+}$**

(ii) Identify **B**, **C** and **D**

B: **$Fe(OH)_3$**

C: **CO_2**

D: **$Fe_4[Fe(CN)_6]_3$ or $Fe_3[Fe(CN)_6]_2$**

(iii) With the use of relevant equations, explain why gas **C** is formed when Na_2CO_3 is added to solution **A**.

Fe^{3+} has high charge density due to its high charge. It is able to polarize the O-H bond in the water ligand, causing hydrogen ion to be released.

$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$

$CO_3^{2-} + 2H_3O^+ \rightarrow CO_2 + 3H_2O$

(iv) By quoting and using relevant $E^{\ominus}$ values from the *Data Booklet*, explain why in **Step I** when chlorine gas is bubbled into the solution containing $Fe^{2+}(aq)$, the solution turned from green to yellow. When the experiment was repeated using iodine, no such observation was seen.

$Cl_2 + 2e \rightleftharpoons 2Cl$ $\quad E^{\ominus} = +1.36$ V

$I_2 + 2e \rightleftharpoons 2I^-$ $\quad E^{\ominus} = +0.54$ V

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $\quad E^{\ominus} = +0.77$ V

$E^{\ominus}$ values for chlorine is more positive, indicating chlorine is a stronger oxidising agent than iodine hence it's able to oxidise green Fe^{2+} to yellow Fe^{3+}

Reaction between Cl_2 and Fe^{2+};

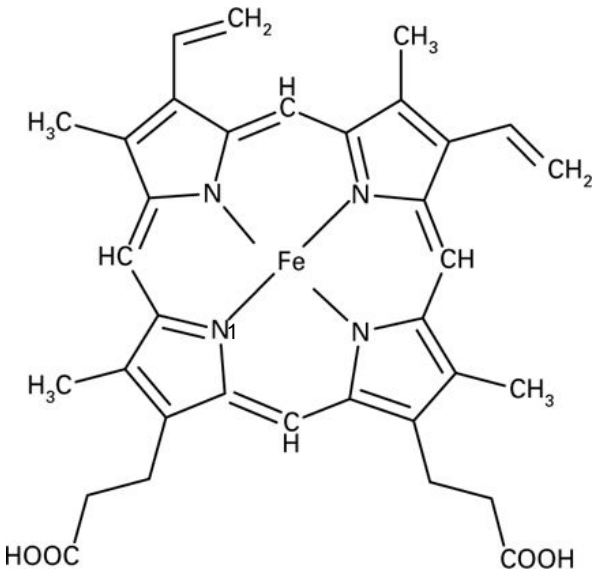
$E^{\ominus}_{cell} = +1.36 - 0.77 = +0.59$ V $> 0 \Rightarrow$ reaction is feasible

There is no reaction between I_2 and Fe^{2+};

$E^{\ominus}_{cell} = +0.54 - 0.77 = -0.23$V $< 0 \Rightarrow$ reaction is not feasible

[9]

(d) Iron is essential in almost all organisms. An important biological complex containing iron is haemoglobin. The diagram below shows the structure of a haemoglobin molecule.



(i) What is the role of haemoglobin in the body?

Oxygen carrier

(ii) State the type of hybridisation for the nitrogen atom labelled, N_1 in the diagram given.

(iii) State the type of bond that the nitrogen atom labelled, N_1 forms with the Fe ion in the diagram given.

(ii) sp^2, (iii) dative/co-ordinate bond

(iv) Name one other poison that can affect haemoglobin in the same way as carbon monoxide.

NaCN / KCN) / HCN

[4]

(e) A nail of mass 1.50 g was dissolved in an excess of dilute sulfuric acid to form 100 cm^3 of solution. A 25 cm^3 sample of the solution required 8.0 x 10^{-4} mol of manganate (VII) for complete oxidation.

By assuming that, in dissolving in sulfuric acid, the iron in the nail was converted entirely into Fe^{2+} (aq), calculate

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(i) the number of moles of Fe^{2+} produced from the nail.

$n(Fe^{2+})$ from nail = $8.0 \times 10^{-4} \times 5 \times \frac{100}{25} = 0.016$ mol

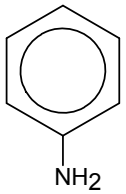
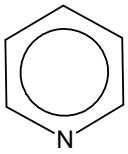
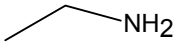
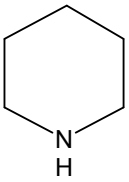
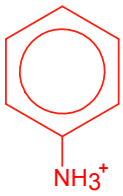
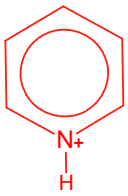
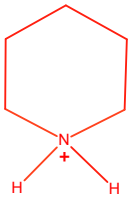
(ii) the percentage of iron in the nail.

% by mass of iron in nail = $\frac{0.016 \times 55.8}{1.50} \times 100\% = 59.5\%$

[2]

[Total: 20]

5 Values of the base dissociation constants, pK_b for some weak bases are given below.

Compound	Phenylamine, $C_6H_5NH_2$	Pyridine, C_5H_5N	Ethylamine, $CH_3CH_2NH_2$	Piperidine, $C_5H_{10}NH$
Formula				
pK_b	9.42	8.75	3.19	2.89
(iii) Structural formula of ions formed after reaction with HCl (aq)				

(a) (i) Which is the weakest base? **Phenylamine**

(ii) Explain in terms of molecular structures, why piperidine and phenylamine have significantly different pK_b values.

Piperidine is a stronger base than phenylamine.

In **piperidine**,

an electron donating alkyl group increases the electron density on the nitrogen atom

In **phenylamine**,

the lone pair of electrons on the nitrogen atom is **delocalised over the benzene ring**.

The lone pair of electrons of nitrogen in piperidine is **more available** for bonding with a proton compared to that of phenylamine

OR The lone pair of electrons of nitrogen in phenylamine is **less available** for bonding with a proton compared to that of piperidine.

(iii) Draw the structures of the ions formed when each of the bases are reacted with aqueous hydrochloric acid in the table above.

(iv) Calculate the pH of 0.100 moldm^{-3} of phenylamine.

$$\left[OH^-\right] = \sqrt{K_b c} = \sqrt{(10^{-9.42}) \times 0.10}$$

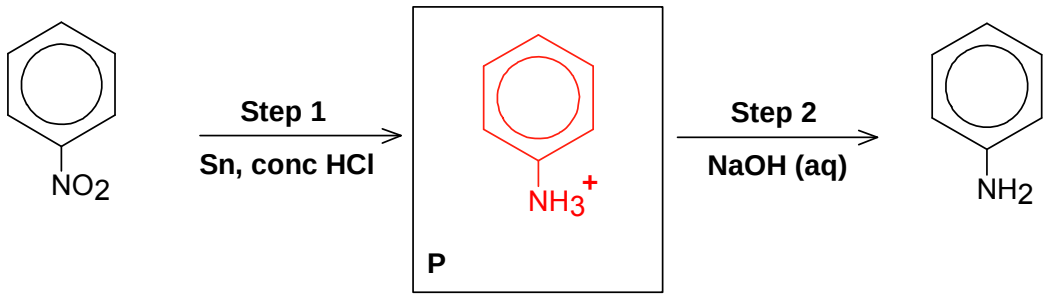
$$pOH = -lg\left[OH^-\right] = 5.21$$

$$pH = 14 - pOH = 8.79 = \underline{8.8}$$

[8]

(b) Phenylamine can be synthesised from nitrobenzene in a two-step process shown.

(i) Write the formula of the intermediate **P** in the blank.



(ii) State the bases (pyridine, ethylamine and piperidine) that could be used in place of sodium hydroxide in step 2. Explain your answer.

All of the bases are stronger bases than phenylamine, and hence they will all be able displace phenylamine from its salt.

[2]

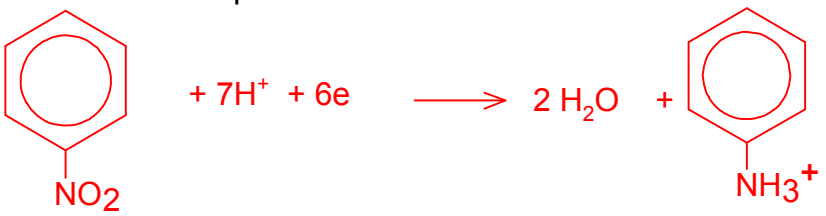
In the redox reaction in step 1, tin reacts with hydrochloric acid to generate tin (II) ions which acts as a reducing agent. In reducing nitrobenzene, tin (II) ions are oxidized to tin (IV) ions.

(iii) Write an equation to show the reaction between tin and hydrochloric acid.

$Sn + 2HCl \longrightarrow Sn^{2+} + 2Cl^{-} + H_2$

(iv) By means of balanced half-equations, write an equation to show the redox reaction for step 1.

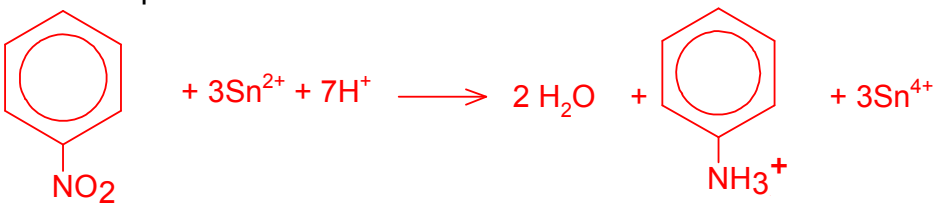
reduction half-equation :



oxidation half-equation : $Sn^{2+} \rightarrow Sn^{4+} + 2e$

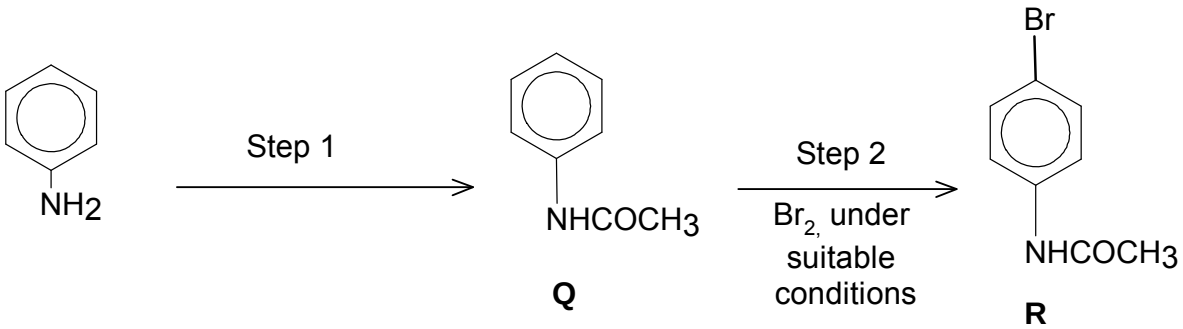
[1] for **both** half-equations correct

Overall equation:



[3]

(c) Phenylamine undergoes the following reaction scheme.

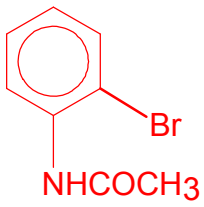


(i) Suggest the reagents and conditions for step 1.

CH_3COCl, room temperature

[1]

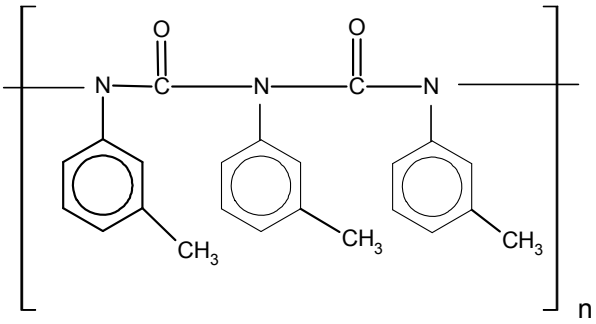
(ii) Another possible product besides **R** is formed. Suggest its structual formula.



[1]

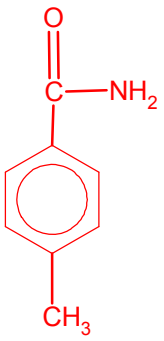
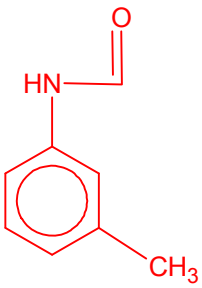
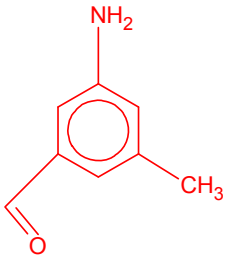
(iii) Intermediate **Q** has three other isomers, **X**, **Y** and **Z**. Identify the other isomers given the following information:

- Isomer **X** gives ammonia on reaction with hot aqueous sodium hydroxide. On reaction with hot acidified potassium manganate (VII), 1,4-dibenzoic acid is formed.
- Isomer **Y** gives methanoic acid on reaction with hot aqueous hydrochloric acid.
- Isomer **Y** can be used to form the following polymer:

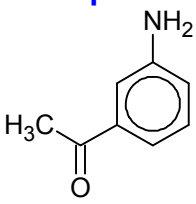


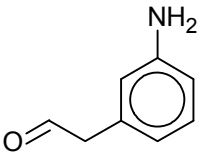
- Both **X** and **Y** do not react with aquoeus bromine, but reacts with bromine in the presence of iron (III) bromide.
- Isomer **Z** does not give methanoic acid nor ammonia on hydrolysis.
- 1 mol of Z reacts with 3 mol of aqueous bromine to give a substituted product.

Suggest structures for **X**, **Y** and **Z**.

X	**Y**	**Z**
		

Other possible answers:





[total : 18]

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