

NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE
NAME

CLASS

TUTOR'S
NAME

CHEMISTRY

Paper 2 Structured

9729/02

11 September 2018

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.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
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	/24
2	/11
3	/9
4	/13
5	/18
Total	/75

Answer **all** questions in the spaces provided.

- 1(a)** An unknown sample was found to contain the anions, Cl^- , ClO_3^- and NO_3^- . A student weighed a sample into a beaker and recorded the following data.

mass of beaker and sample / g	68.962
mass of empty beaker / g	67.620

The sample was dissolved and diluted in a 250 cm^3 volumetric flask to obtain solution **L**.

In **experiment 1**, a 50 cm^3 portion of solution **L** was reacted with excess silver nitrate solution. The AgCl precipitated was transferred onto a dry filter paper and was placed under an infra-red lamp. The dry AgCl precipitate was weighed and the following data was obtained.

Experiment 1

mass of dry filter paper and AgCl / g	0.737
mass of dry filter paper / g	0.620

In **experiment 2**, a gas was bubbled into another 50 cm^3 portion of solution **L** to convert ClO_3^- to Cl^- before the addition of excess silver nitrate solution. The AgCl precipitated was also dried and weighed. The following data was obtained.

Experiment 2

mass of dry filter paper and AgCl / g	0.799
mass of dry filter paper / g	0.651

- (i) Write the half equation for the reduction of ClO_3^- to Cl^- .

..... [1]

- (ii) Determine the mass of Cl^- in 50 cm^3 of solution **L**.

[1]

- (iii) Determine the mass of Cl^- converted from ClO_3^- in **experiment 2**.

[2]

- (iv) Hence, determine the percentage mass of ClO_3^- in the unknown sample.

[3]

- (v) The $E^\circ (\text{ClO}_3^-/\text{Cl}^-)$ has a value of +1.47 V. From the list of standard electrode potentials in the *Data Booklet*, identify a gas that would reduce ClO_3^- to Cl^- . Explain your answer.

.....
.....
.....
..... [2]

- (b) (i) An aqueous solution of HCl has a density of 1.15 g cm^{-3} and is 30% by mass of HCl.

Calculate the concentration in mol dm^{-3} of this solution of HCl.

[2]

- (ii) Calculate the volume of this solution required to prepare 5 dm^3 of 0.20 mol dm^{-3} HCl by dilution with water.

[1]

- (c) The gelatin silver process is the photographic process used with black-and-white films. The following information pertains to the process of taking photographs and developing films.

Taking photographs

- A 35 mm cartridge of black-and-white print film contains a long strip of plastic that has layered coatings on each side.
- On the front side of the film, the layers are made of gelatin which contain grains of silver chloride crystals.
- When the shutter of the camera is opened for a fraction of a second to allow the film to be exposed to light, these crystals undergo decomposition thereby producing an image on the film.

Developing films

- After the photographs have been taken, the film is developed in a dark room under a light source that emits low energy light.
- Firstly, the film is soaked in water before adding phenidone. Phenidone makes the image more visible by reacting with the exposed silver chloride crystals to produce silver atoms and two other by-products.
- This reaction can only proceed at high pH.
- After some time, the reaction will then be quenched.
- Finally, the film will be soaked in ammonium thiosulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_3$, which is used as a fixer to make the image permanent and light resistant. This is done through the reaction between the unexposed silver chloride crystals and the fixer.

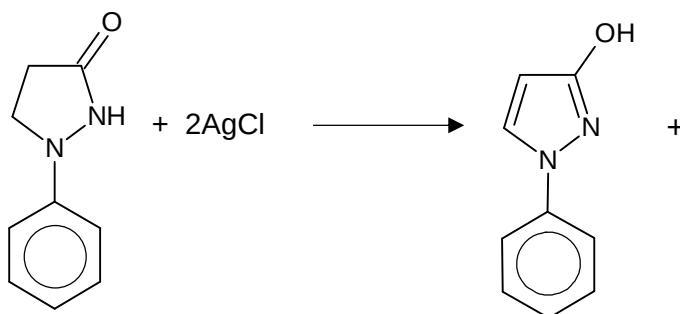
- (i) Write the balanced equation for the decomposition of silver chloride crystals when it is exposed to light.

..... [1]

- (ii) Suggest a suitable colour of the light source that is used in a dark room.

..... [1]

- (iii) Complete the equation for the reaction between the developing agent, phenidone, and the exposed silver chloride crystals. Hence, state the role of phenidone in this reaction.



phenidone

role of phenidone [2]

- (iv) Suggest a suitable reagent, other than excess cold water, that can be used to quench the development of the film. Explain.

.....

 [2]

- (v) When the non-exposed silver chloride crystals react with the fixer, $(\text{NH}_4)_2\text{S}_2\text{O}_3$, a silver complex compound **M** is formed together with a chloride salt, **N**. Both **M** and **N** have the same cation. The silver-containing complex ion has a coordination number of 2 and is chlorine-free.

Suggest the formulae of compounds **M** and **N**.

compound **M**: compound **N**: [2]

- (vi) State the shape of the silver-containing ion in compound **M**.

..... [1]

- (vii) Complete the electronic configuration of silver in compound **M**. Hence, deduce the colour of compound **M**.

compound **M** [Ar]3d¹⁰4s²

 [2]

- (viii) Explain why the fixer, $(\text{NH}_4)_2\text{S}_2\text{O}_3$, is able to make the image permanent and light resistant on the film.

.....

 [1]

[Total: 24]

2 Dinitrogen tetroxide, commonly referred to as nitrogen tetroxide, is the chemical compound N_2O_4 . It is a useful reagent in chemical synthesis.

(a) Colourless N_2O_4 readily dissociates to form brown NO_2 and the following equilibrium is reached fairly quickly in the gaseous phase.



(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm³ flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the value of K_p at 27 °C.

[3]

(ii) Describe and explain what you would observe when the stoppered flask is placed into a basin of boiling water.

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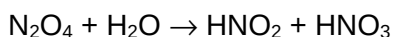
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..... [1]

- (b)** N_2O_4 is also used in the large scale manufacture of nitric acid. It reacts with water to give both nitrous acid and nitric acid.



The two acids have different acid strengths. To determine the acid strength of the two acids, two separate solutions containing 0.10 mol dm^{-3} of each acid were prepared. The pH was found to be 2.17 and 1.00 for the solutions containing nitrous acid and nitric acid respectively.

- (i)** Use the data provided to prove nitrous acid is a weak acid and hence, determine its K_a value.

[2]

- (ii)** Suggest a reason why nitrous acid is a weaker acid than nitric acid.

.....

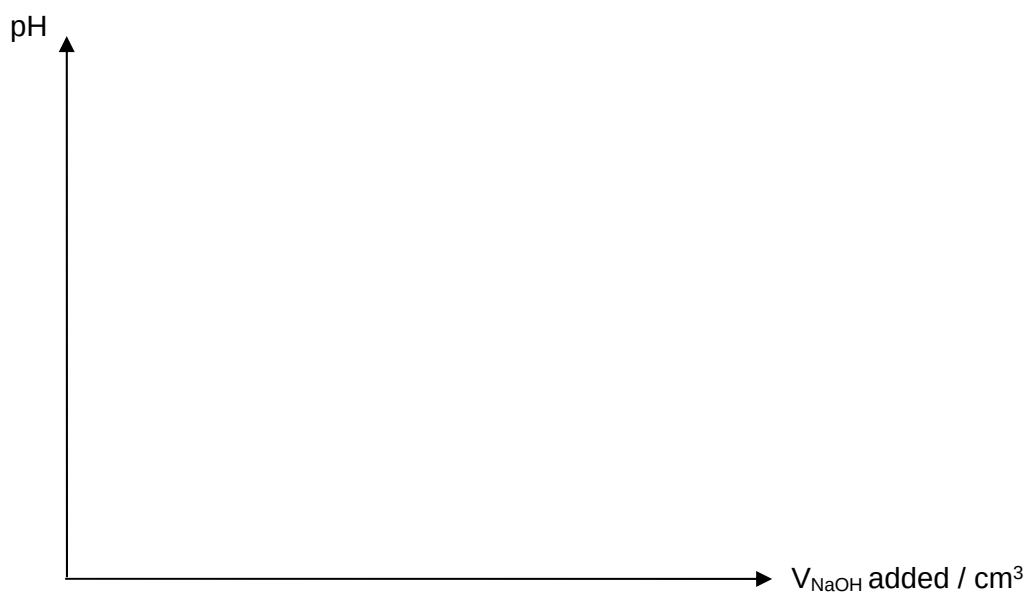
 [1]

25.0 cm^3 of the prepared 0.10 mol dm^{-3} nitrous acid was titrated with 0.10 mol dm^{-3} aqueous sodium hydroxide.

- (iii)** Using your value of K_a calculated in part **(i)**, calculate the pH when 25.00 cm^3 of aqueous sodium hydroxide has been added.

[2]

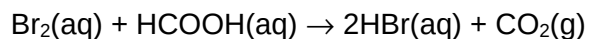
- (iv) On the given axes below, sketch the pH-volume added graph you would expect to obtain when the above titration was performed. Label the appropriate pH at various key points on the graph.



[2]

[Total: 11]

- 3 The equation for the reaction between bromine and methanoic acid is as follows:



It is hypothesised that the reaction is elementary. To prove this hypothesis, volumes of the two reactants were varied and the rate of the reaction is measured in terms of the rate at which the bromine concentration changes. When the total volume is kept constant, the following relationship is true.

$$\text{rate of reaction} \propto \frac{\text{volume of bromine used}}{\text{time for color of bromine to disappear}}$$

The temperature of the reaction mixture was maintained at 25 °C.

The following results were obtained in three repeated experiments:

Expt	Volume of 1.0 mol dm ⁻³ Br ₂ / cm ³	Volume of 10.0 mol dm ⁻³ HCOOH / cm ³	Volume of water added / cm ³	Relative time for colour of bromine to disappear
1	10	10	0	1.4
2	40	20	20	2.8
3	5	10	5	1.4

- (a) By comparing the rates of reactions, explain how the results of the three experiments support the hypothesis that the reaction is elementary.

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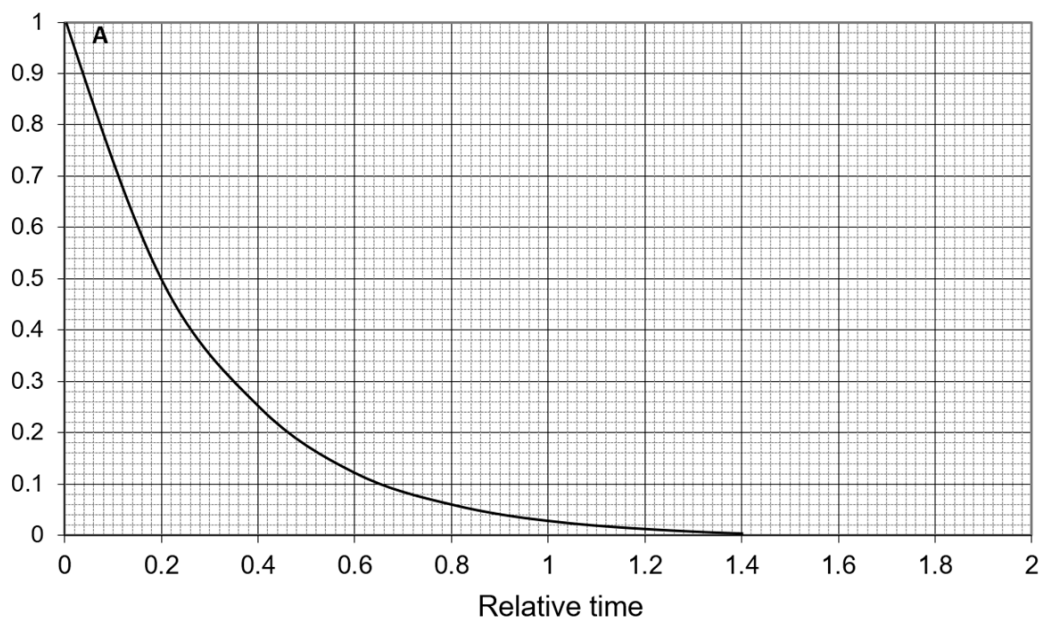
.....

.....

..... [3]

- (b) During another experiment, the concentration of Br_2 was monitored over time and the following graph (Run **A**) was obtained. The concentration of HCOOH used was 10.0 mol dm^{-3} .

Concentration of $\text{Br}_2(\text{aq})$
/ mol dm^{-3}



- (i) Define the term “half-life”.

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

- (ii) The experiment was repeated using 0.8 mol dm^{-3} of $\text{Br}_2(\text{aq})$ and 10.0 mol dm^{-3} of HCOOH . On the axes above, draw the concentration-time graph of $\text{Br}_2(\text{aq})$ for the new experiment and label it ‘Run **B**’.

On your graph, clearly state and label the half-life of $\text{Br}_2(\text{aq})$. [1]

- (iii) The experiment was repeated again using 1.0 mol dm^{-3} of $\text{Br}_2(\text{aq})$ and 5.0 mol dm^{-3} of HCOOH (Run **C**). In comparison to Run **A**, state how the half-life of the experiment will change.

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

- (c) By drawing a suitable illustration, estimate and explain the change in rate of reaction when temperature is increased to 35 °C.

.....

.....

.....

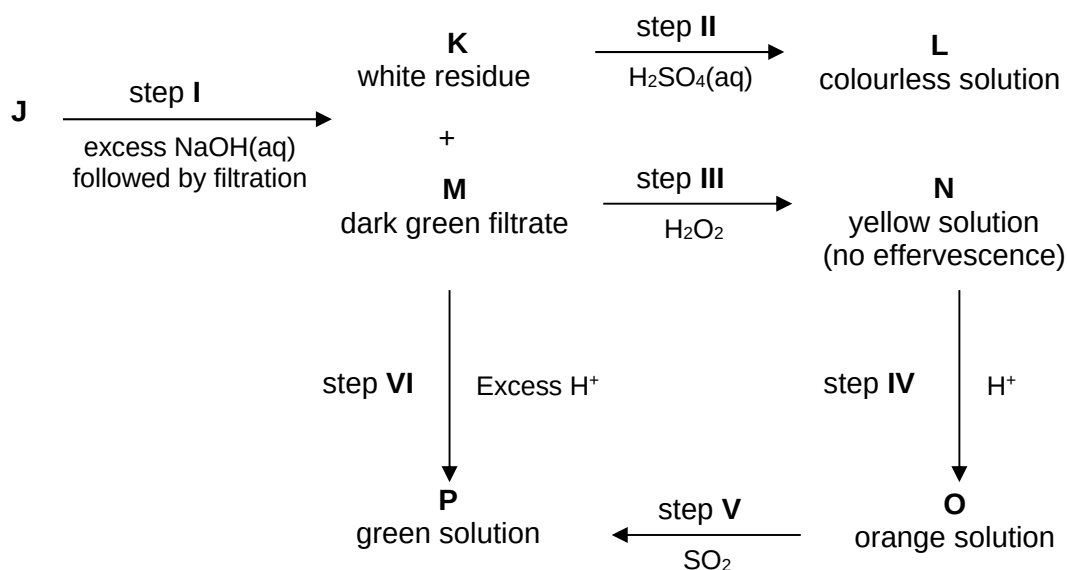
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.....

..... [3]

[Total: 9]

- 4(a) Solution **J** contains a Group 2 ion and a transition metal ion. The following reaction scheme shows how **J** reacts with some common reagents in the laboratory.



- (i) State the identities of **K**, **L**, **M**, **N**, **O** and **P**.

K..... **L**.....
M..... **N**.....
O..... **P**.....

[3]

- (ii) State the roles of H_2O_2 and SO_2 in steps **III** and **V** respectively.

H_2O_2 in step **III**:

SO_2 in step **V**: [1]

- (iii) Write an ionic equation to explain the formation of solution **P** in step **V**.

..... [1]

- (iv) Explain how solution **P** can be formed in step **VI**.

.....

 [2]

- (b) Among the elements of Group 14, those towards the top, carbon to germanium, have very different properties from those at the bottom, tin and lead.
For example, the melting points show a marked change after germanium.

element	C	Si	Ge	Sn	Pb
mp / °C	>3550	1410	937	232	327

Carbon, silicon and germanium each form a solid with the same type of structure.

- (i) Explain why the melting points of these elements decrease from carbon to germanium.

.....

 [2]

- (ii) Explain how first ionisation energy changes from carbon to germanium.

.....

 [2]

Carbon and silicon each form a tetrachloride. CCl_4 has no reaction with water; SiCl_4 reacts violently with water.

- (iii) Write a balanced equation for the reaction of SiCl_4 with water.

..... [1]

- (iv) Suggest an explanation for the inertness of CCl_4 to water.

.....

 [1]

[Total: 13]

5 Azo dyes are made in large quantities from benzene, C_6H_6 , via nitrobenzene, $C_6H_5NO_2$ (density = 1.20 g cm^{-3}), and phenylamine, $C_6H_5NH_2$.

(a) The preparation of nitrobenzene requires benzene to be warmed under reflux at about 55°C with a mixture of concentrated nitric and sulfuric acids. Some information about these substances is given below:

Benzene: immiscible with water; highly flammable; extremely toxic by ingestion or inhalation; known carcinogen.

Concentrated nitric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent. The acid contains about 30 % water by volume.

Concentrated sulfuric acid: miscible with water; causes severe burns to eyes and skin; strong oxidising agent; dilution with water is very exothermic and can be dangerous.

(i) Nitric acid is placed in a suitable flask and sulfuric acid is added slowly with cooling of the flask. Explain why cooling is necessary.

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

(ii) Benzene is added slowly to the acid mixture, which is then warmed at 55°C for 45 minutes under reflux with vigorous stirring of the reaction mixture.

Explain why the reflux condenser is necessary and also why the mixture is vigorously stirred.

.....
.....
..... [2]

(iii) State, with a reason, **one** other precaution (other than wearing protective wear) that would be necessary when carrying out the experiment.

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

(iv) The reaction mixture is then poured into a large excess of cold water, the liquid nitrobenzene layer is separated and *washed* with sodium carbonate solution. Explain why this washing is necessary.

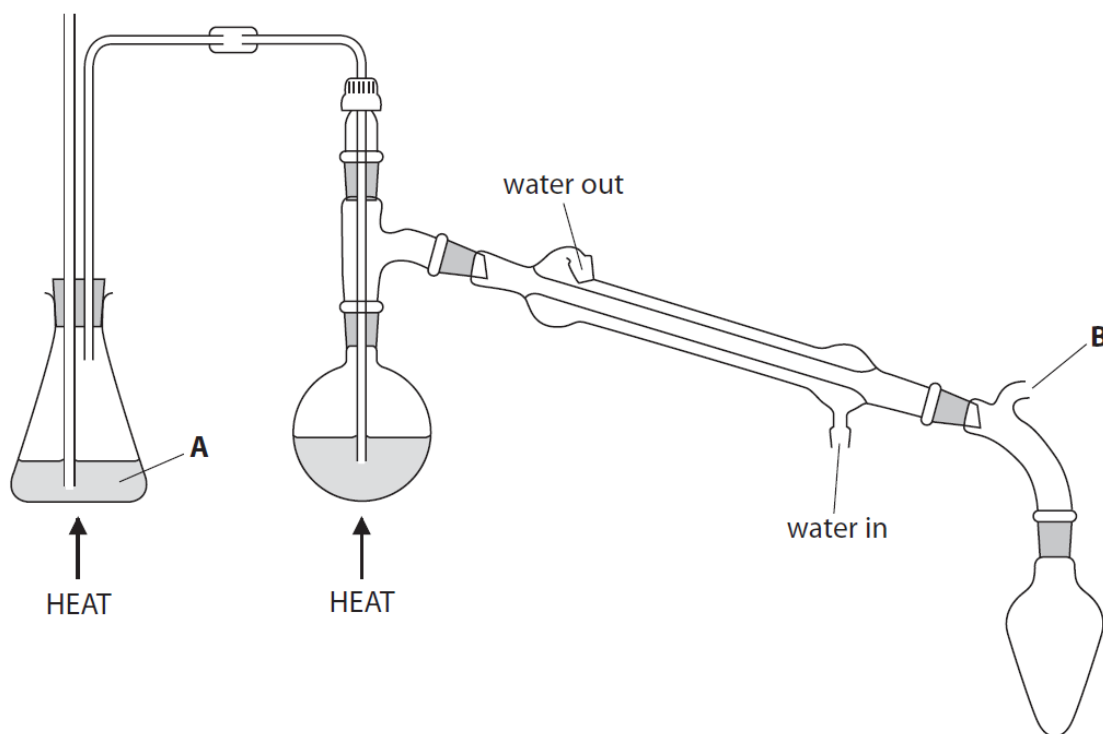
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..... [1]

(v) The nitrobenzene layer is dried before being distilled to purify it. Identify a suitable drying agent.

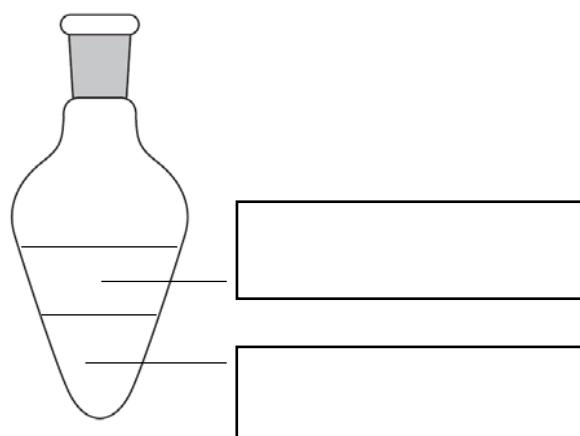
..... [1]

- (b) Steam distillation is a purification process to separate nitrobenzene from the reaction mixture. During the process of steam distillation, a current of steam is blown through a mixture containing the desired organic substance to be distilled. This caused the desired organic substance to vaporise. The vapour containing the desired organic substance can then be condensed and collected. This method is used predominantly to purify liquids that are not very volatile and are immiscible with water.

The diagram below shows a steam distillation apparatus used to extract nitrobenzene from the reaction mixture.



- (i) Identify substance A.
..... [1]
- (ii) Explain the purpose of the part of the apparatus labelled B.
..... [1]
- (iii) On the diagram below, state the contents of the receiver at the end of the steam distillation.

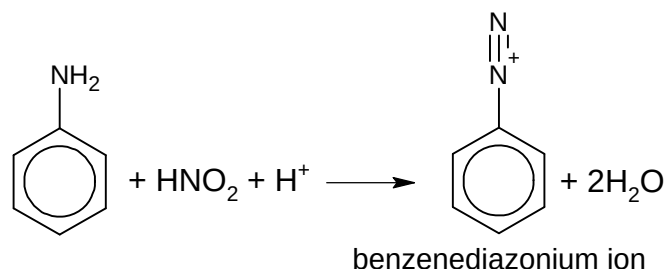


[1]

- (c) The purified nitrobenzene is then reduced to phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.

The phenylamine is diazotised by reaction with nitrous acid at a temperature between 0°C and 10°C . Nitrous acid is generated in the reaction mixture from sodium nitrite and hydrochloric acid.

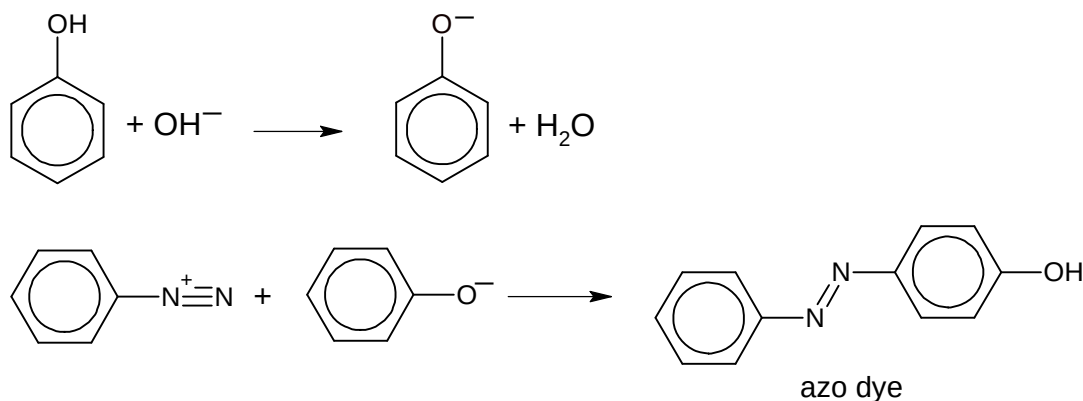
The ionic equation for the diazotisation of phenylamine to produce benzenediazonium ion is as shown below.



If the above reaction is warmed, benzenediazonium ion will undergo hydrolysis to give phenol. A gas will also be produced and the resulting mixture is acidic.

Reaction of the benzenediazonium compound with an alkaline solution of a phenol, $\text{C}_6\text{H}_5\text{OH}$, will produce a solid azo dye, which is purified by recrystallisation.

The equations for the reaction between benzenediazonium ion and phenol to produce the solid azo dye are shown below.



- (i) State the reagents and conditions needed to reduce nitrobenzene to phenylamine.
..... [1]
- (ii) Explain why the temperature for diazotization to phenylamine must **not** be lower than 0°C .
..... [1]
- (iii) Write an equation to show benzenediazonium ion undergoing hydrolysis upon warming.
..... [1]

- (d) Purification by recrystallisation requires the following steps:
1. The azo dye is dissolved in a minimum volume of hot solvent.
 2. The solution is filtered through a pre-heated funnel.
 3. The solution is cooled and filtered using a Buchner funnel.
 4. The solid is washed with a small amount of cold solvent.
 5. The solid is dried in a desiccator.

(i) Explain why a **minimum** volume of hot solvent is used in step 1.

..... [1]

(ii) Explain why the funnel must be pre-heated.

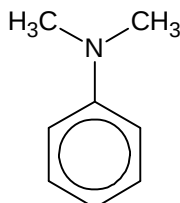
..... [1]

(iii) Suggest a reason why it is preferable to dry the solid in a desiccator rather than in an oven.

..... [1]

(e) This question compares the acidity and basicity of some organic compounds.

(i) Explain why an aqueous solution of N,N-dimethylphenylamine is more basic than an aqueous solution of phenylamine.



N,N-dimethylphenylamine

..... [1]

(ii) Explain why an aqueous solution of azo dye is more acidic than an aqueous solution of phenol.

..... [2]

[Total: 18]