NANYANG JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME: Teachers' Mark Scheme

CLASS: _____ TUTOR'S NAME: _____

CHEMISTRY 9729/02

Paper 2 Structured

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

For Examiner's Use

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^-.

$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$ [1] .....[1]

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

mass of AgCl precipitate in expt 1 = 0.737 – 0.620 = 0.117 g
mass of Cl^- present in 50 cm^3 portion
$= \frac{35.5}{35.5+107.9} \times 0.117 = 0.02896\ g \approx 0.0290\ g$ [1]

[1]

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

mass of AgCl precipitate in expt 2 = 0.799 – 0.651 = 0.148 g
mass of Cl^- present in 50 cm^3 portion = $\frac{35.5}{35.5+107.9} \times 0.148 = 0.03663\ g$ [1]
mass of Cl^- from ClO_3^- in 50 cm^3 = 0.03663 – 0.02896
= 0.007674 g ≈ 0.00767 g [1]

[2]

[Turn Over

For Examiner's Use

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

Since $n(ClO_3^-)$: $n(Cl^-)$ is 1 : 1,
mass of ClO_3^- present in 50 cm^3 = $0.007674 \times \frac{35.5+3(16)}{35.5}$ = 0.01805 g [1]
mass of ClO_3^- present in 250 cm^3 = $0.01805 \times \frac{250}{50}$ = 0.1805 g [1]
% ClO_3^- present in unknown compound = $\frac{0.1805}{68.962-67.620}$ x 100%
= 13.45% ≈ 13.5% [1]

[3]

(v) The $E^\ominus$ (ClO_3^-/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.

$E^\ominus$ (H^+/H_2) = 0.00 V
H_2 gas is an appropriate reducing agent. [1]
(also accept $E^\ominus$ (NO_3^-/NO_2) or $E^\ominus$ (SO_4^{2-}/SO_2) as their $E^\ominus$ < +1.47V)

E_{cell} = (+1.47) – (0.oo) = +1.47 V > 0

Since, E_{cell} > 0, the reaction is feasible. [1]

.....

..... [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.

mass of HCl in 1 cm^3 = $\frac{30}{100}$ x 1.15 = 0.3450 g [1]
[HCl] = $\frac{0.3450}{1.0+35.5}$ x 1000 = 9.45 mol dm^{-3} [1]

[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.

volume of HCl required = $\frac{5 \times 0.20}{9.452}$ = 0.106 dm^{-3} = 106 cm^3 [1]

[1]

For Examiner's Use

(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, $(NH_4)_2S_2O_3$, 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.

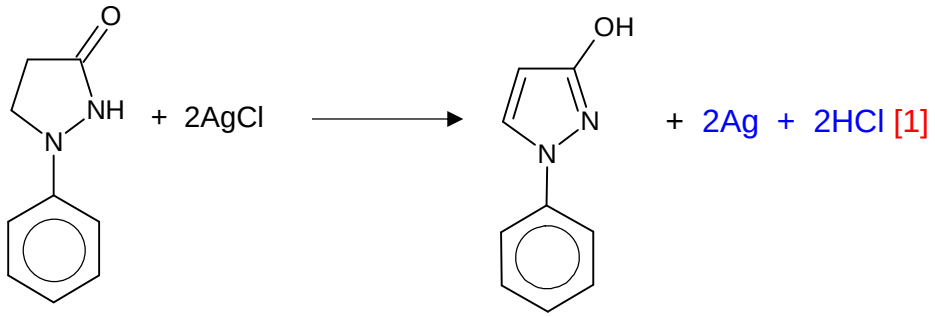
$2AgCl \xrightarrow{light} 2Ag + Cl_2$ [1]

..... [1]

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

Red. (Also accept orange or yellow) [1]..... [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 reducing agent [1]..... [2]

For Examiner's Use

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

Acetic acid / Citric acid / Any plausible acids. e.g. HCl, HNO_3, H_2SO_4 [1]

When acid is added, the pH will be lowered. Hence, the reaction will not proceed at lower pH. [1]

..... [2]

(v) When the non-exposed silver chloride crystals react with the fixer, $(NH_4)_2S_2O_3$, 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**: $(NH_4)_3[Ag(S_2O_3)_2]$ [1]..... compound **N**: NH_4Cl [1] .....[2]

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

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

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

compound **M** $[Ar]3d^{10}4s^{2}4p^{6}4d^{10}$ [1].....

Since the 4d orbitals are fully occupied, d–d transition cannot occur. [1]

Hence, compound **M** is colourless. [1]

.....

..... [2]

(viii) Explain why the fixer, $(NH_4)_2S_2O_3$, is able to make the image permanent and light resistant on the film.

The fixer is able to remove any remaining unexposed AgCl. Hence, there is no AgCl remaining on the film to undergo decomposition through the exposure of light to change the image on the film. [1]

.....

.....

..... [1]

[Total: 24]

For Examiner's Use

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.

$$N_2O_4(g) \quad 2NO_2(g) \qquad \Delta H > 0$$

(i) When 4.60 g of N_2O_4 is placed in an evacuated 1.48 dm^3 flask at 27 °C, the equilibrium pressure is 1 atm.

Calculate the value of K_p at 27 °C.

- Initial no of moles of N_2O_4 = 4.60 / (14.0 × 2 + 16.0 × 4) = 0.0500 mol

ICE table/eqm amounts:

N_2O_4 (g) ⇌ $2NO_2$ (g)

Initial / mol	0.0500	0
Eqm / mol	0.0500 – x	+2x

- PV = nRT

$(101325)(1.48 \times 10^{-3}) = n\ (8.31)(300)$
n(gases at eqm) = 0.06015 = 0.0602 mol

- Solve for x and find eqm amts

0.0500 – x + 2x = 0.06015
x = 0.01015

N_2O_4 (g) ⇌ $2NO_2$ (g)

Eqm / mol	0.03985	0.0203

- $K_p = \dfrac{(P_{NO_2})^2}{P_{N_2O_4}} = \dfrac{(\frac{0.02030}{0.06015} \times 1)^2}{\frac{0.03985}{0.06015} \times 1}$ = 0.172 atm

4 points 3 marks; 3 points: 2 marks; 2 points: 1 mark

Alternative solution in terms of partial pressure ICE table.

$P(N_2O_4\ \text{initial}) = \dfrac{0.05(8.314)(300)}{1.48 \times 10^{-3}} = 84220Pa = 0.08312atm$

ICE table/eqm partial pressures:

N_2O_4 (g) ⇌ $2NO_2$ (g)

Initial / atm	0.08312	0
Eqm / atm	0.08312 – x	+2x

0.08312 – x + 2x = 1
x = 0.1687 atm

$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(0.1687 \times 2)^2}{0.8312 - 0.1687}$ =0.172 atm

[3]

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

Temperature of system increases and by Le Chatelier's Principle, the forward endothermic reaction is favoured. Position of equlibrium shifts to the right to absorb added heat and more NO_2 is formed. Hence the reaction mixture becomes more brown. **[1]**

.....

..... [1]

For Examiner's Use

(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.

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

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.

$[H^+]$ in solution of $HNO_2 = 10^{-2.17} =$ 0.00676 $moldm^{-3}$
which is less than $[HNO_2] = 0.10$ $moldm^{-3}$.
Hence HNO_2 only dissociates partially and it is a weak acid. **[1]**

OR for the same concentration of acid, HNO_2 dissociates to produce a lower $[H^+]$ (as shown by the higher pH of the solution). Hence, it dissociates to a smaller extent and is a weak acid. ☒ higher pH so weaker acid.

(FYI. Not required in answer: $[H^+]$ in solution of $HNO_3 = 10^{-1.00} = 0.100$ mol dm^{-3} = $[HNO_3]$ hence Not required it is completely dissociated and HNO_3 is a strong acid.)

$K_a = \dfrac{[NO_2^-][H^+]}{[HNO_2]} = \dfrac{(0.00676)^2}{0.10 - 0.00676} = 4.90 \times 10^{-4}$ mol dm^{-3} **[1]**

[Note if students use $[H^+] = \sqrt{K_a . c}$ or $K_a = \dfrac{(0.00676)^2}{0.10} = 4.57 \times 10^{-4}$]

[2]

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

Nitric acid is a stronger acid as NO_3^- is a more stable conjugate base than NO_2^- as the negative charge is more effectively dispersed over a greater number of electronegative oxygen atoms (or vice versa). **[1]**

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.....

.....

..... [1]

For Examiner's Use

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.

Equivalence volume = 25.00 cm^3

At equivalence point, solution contains basic salt only.

$K_b = 10^{-14} / 4.90 \times 10^{-4} = 2.040 \times 10^{-11}$

[salt] = 25.0 x 0.1 / 50.0 = 0.05 $moldm^{-3}$

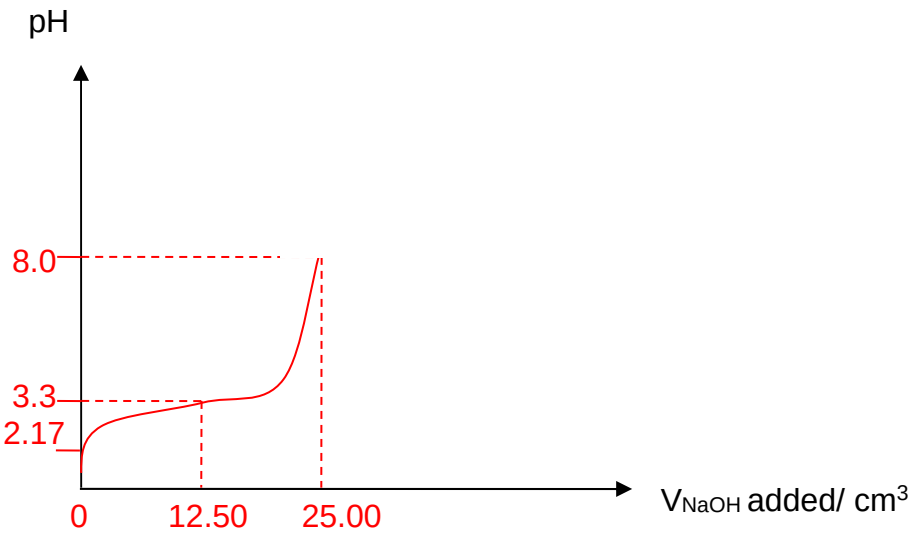
$[OH^-] = \sqrt{K_b.c} = \sqrt{2.040\times10^{-11}(0.05)} = 1.010\times10^{-6}$

pH = 14 – pOH = 14 – (–lg(1.010×10^{-6})) = 8.0

4 points [2], 2 points [1] ecf K_a value

[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.



Label following values

- Initial pH (given in question)
- Maximum buffering capacity occurs at 12.50 cm^3: pH = pK_a (–lg(4.90×10^{-4}) = 3.3)
- Equivalence point (calculated in iii)

Correct shape (relatively flat at buffer region)

*don't penalize if students sketch graph beyond 25.00 cm^3

4 points [2], 2-3 points [1]

[2]

[Total: 11]

For Examiner's Use

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

$$Br_2(aq) + HCOOH(aq) \rightarrow 2HBr(aq) + CO_2(g)$$

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.

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

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.

Expt	Vol. of 1.0 mol dm^{-3} Br_2 / cm^3	Vol. of 10.0 mol dm^{-3} HCOOH / cm^3	Vol. of water added / cm^3	Relative time for colour of bromine to disappear	Rate
1	10	10	0	1.4	10/1.4=7.14
2	40	20	20	2.8	
2a	40/4=10	20/4=5	20/4=5	2.8	10/2.8=3.57
3	5	10	5	1.4	5/1.4=3.57

Using expt 1 and 3,

When vol of Br_2 halved i.e. 10/5, the rate halved i.e. 7.14/3.57. Hence rate is directly proportional to Br_2, 1st order wrt Br_2.

Using expt 1 and 2a,

When vol of HCOOH halved i.e. 10/5, the rate halved i.e. 7.14/3.57. Hence rate is directly proportional to HCOOH, 1st order wrt HCOOH.

Since orders of reaction correspond to stoichiometric ratio of the overall equation, the reaction is elementary.

1 mark for finding order wrt Br_2

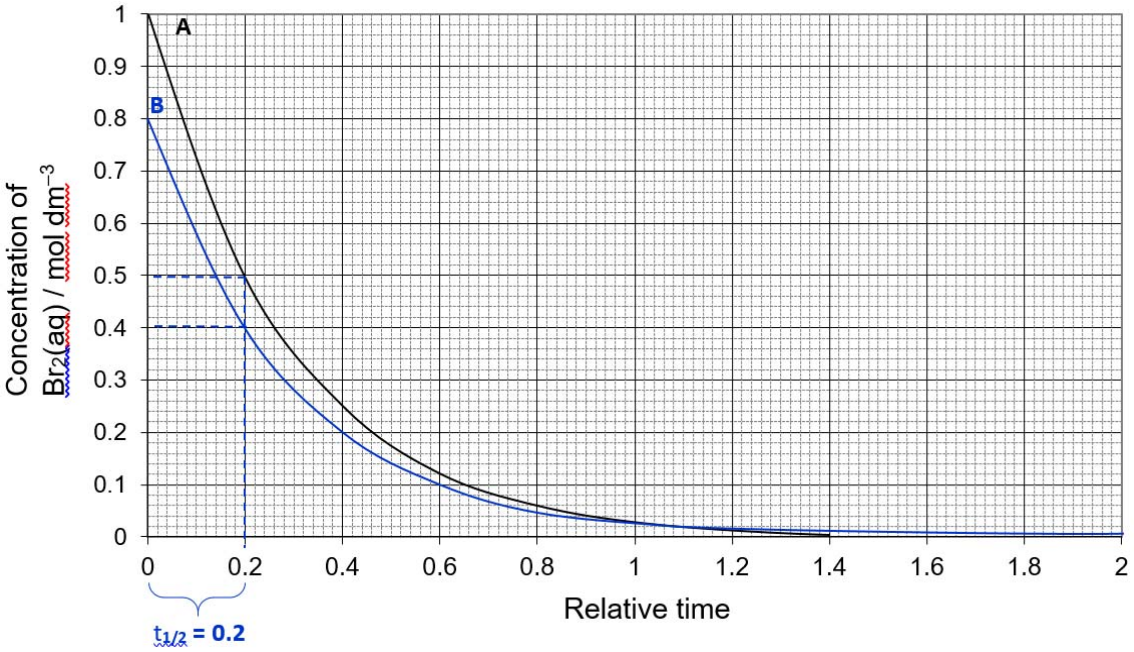
1 mark for finding order wrt HCOOH and deducing the hypothesis correctly

.....

..... [3]

For Examiner's Use

(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}.



(i) Define the term "half-life".

Time taken for concentration of reactant to reach half its original concentration.

..... [1]

(ii) The experiment was repeated using 0.8 mol dm^{-3} of Br_2(aq) and 10.0 mol dm^{-3} of HCOOH. On the axes above, draw the concentration-time graph of Br_2(aq) for the new experiment and label it 'Run **B'**.

On your graph, clearly state and label the half-life of Br_2(aq). [1]

Curve must show at least 2 constant half-lives. Only one half-life needs to be clearly labelled.

(iii) The experiment was repeated again using 1.0 mol dm^{-3} of Br_2(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.

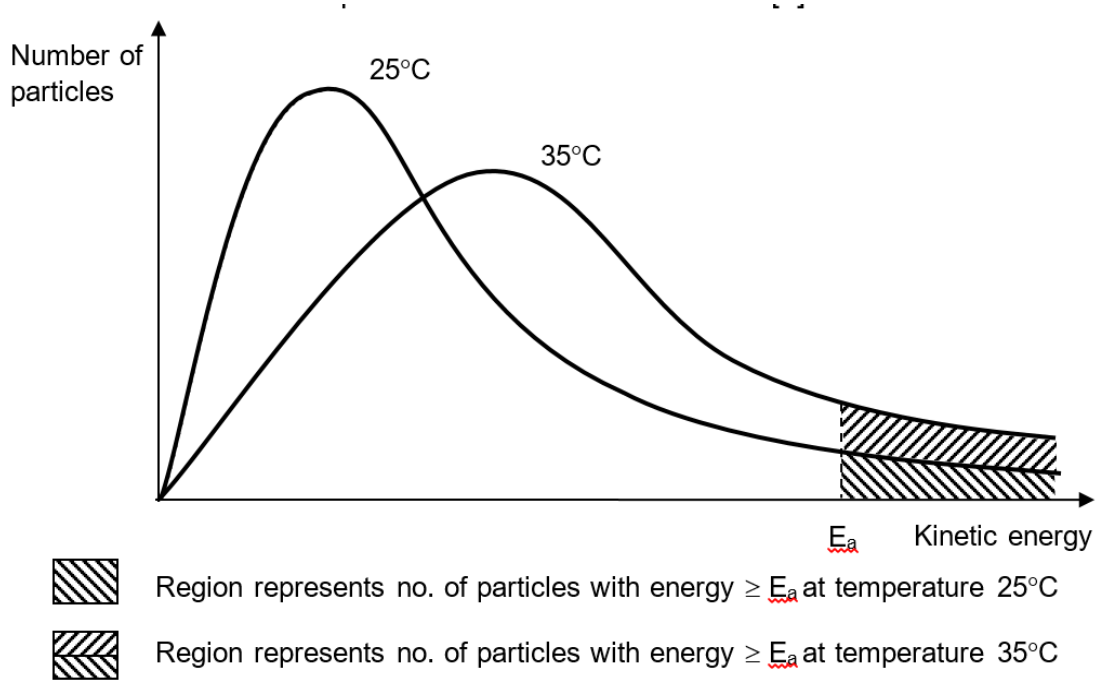
The reaction is a pseudo-first order reaction in which $\mathbf{t}_{1/2} = \dfrac{\ln 2}{k[HCOOH]}$

Hence if [HCOOH] halves, $t_{1/2}$ will double from 0.2 to 0.4.

..... [1]

For Examiner's Use

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



When the temperature increases by 10 °C,

⇒ the average kinetic energy of particles doubles

⇒ the shape of the Maxwell-Boltzmann curve flattens out such that double the number particles have energy ≥ E_a

⇒ the frequency of effective collisions doubles

⇒ Rate constant doubles, hence rate doubles

.....

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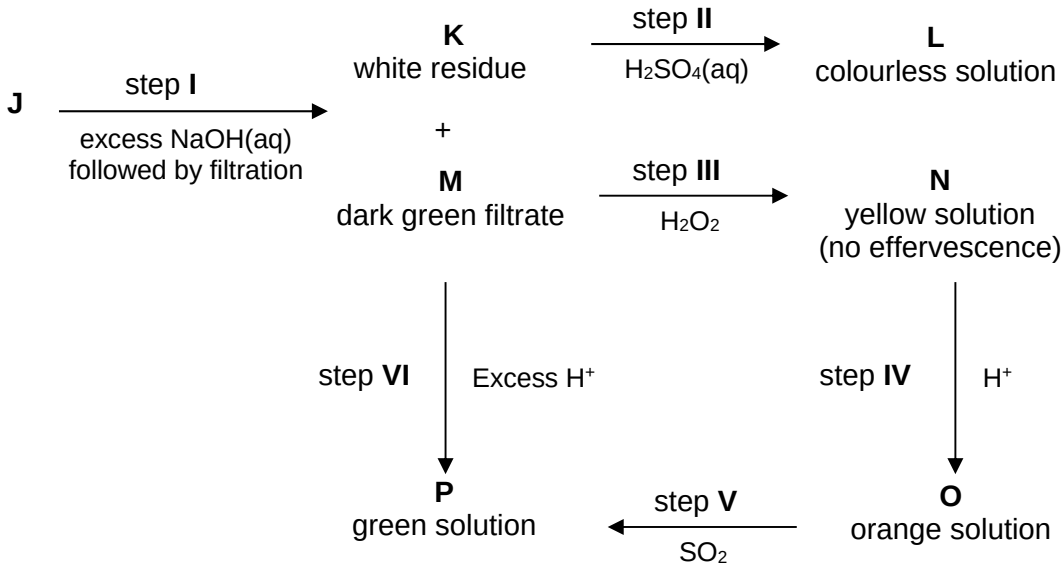
.....

..... [3]

[Total: 9]

For Examiner's Use

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 $Mg(OH)_2$ ..... **L** $MgSO_4$ or Mg^{2+} .....

M $[Cr(OH)_6]^{3-}$ ..... **N** CrO_4^{2-} .....

O $Cr_2O_7^{2-}$ ..... **P** Cr^{3+} or $[Cr(H_2O)_6]^{3+}$.....

[3]

6 correct [3]; 4, 5 correct [2]; 2, 3 correct [1] (Note: also accept Be for K & L)

[3]

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

H_2O_2 in step **III**: oxidising agent ..... .

SO_2 in step **V**: reducing agent ..... [1]

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

$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$ [1] ..... [1]

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

$Cr^{3+}(aq) + 3OH^-(aq)$ $Cr(OH)_3(s)$ (1)
or $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq)$ $Cr(H_2O)_3(OH)_3(s) + 3H_2O$
$Cr(OH)_3(s) + 3OH^-(aq)$ $Cr(OH)_6^{3-}(aq)$ (2)
When H^+ is added, it removes the excess $OH^-(aq)$ which was added. Position of equilibrium (2) will shift to the left to form grey-green ppt of $Cr(OH)_3$. [1]
When excess H^+ is added, it removes all the $OH^-(aq)$ in the solution. Position of equilibrium (1) will shift to the left forming green solution of Cr^{3+}. [1]

.....

..... [2]

For Examiner's Use

(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.

They have giant covalent structures with strong covalent bonds between atoms in a 3-dimensional network. [1] From carbon to germanium, the atomic radius increase and the bond length increase (C–C bond length < Si–Si bond length < Ge–Ge bond length), hence the covalent bond strength decrease from carbon to silicon to germanium. [1] Since the melting of these elements require breaking the covalent bonds between the respective atoms, the melting point decreases since less energy is required to break the weaker covalent bonds.

..... [2]

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

Down the group from carbon to germanium,

- the number of protons increases, nuclear charge increases.
- As the number of electron shells increases, shielding effect increases significantly.
- The outermost electron is further away from the nucleus, hence attraction between the nucleus and outermost electron decreases
- The first ionisation energy decreases down a group.

4 points – [2]; 2,3 points – 1

..... [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.

$SiCl_4 + H_2O \rightarrow SiO_2 + 4HCl$ [1] ..... [1]

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

Water molecules could not form co-ordinate/dative bonds with the central carbon atom of CCl_4 because carbon is in period 2 and does not have energetically accessible low lying orbitals to accommodate lone pair of electrons from O atom in H_2O. [1]

.....

..... [1]

[Total: 13]

For Examiner's Use

5 Azo dyes are made in large quantites 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 ^oC 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.

To avoid the temperature rising too much OR the reaction between sulfuric acid and water is exothermic as the sulfuric acid is diluted by the water in nitric acid

.....

..... [1]

(ii) Benzene is added slowly to the acid mixture, which is then warmed at 55 ^oC 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.

Prevents escape of benzene / volatile liquids [1]
reactants are immisicible/do not mix/form separate layers so they need to be stirred to make reaction rate acceptable or increase frequency of effective collisions or increase the surface area of contact between the two immiscible layers or to enable the reactant molecules to collide with the correct orientation [1]

.....

..... [2]

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

EITHER
benzene is toxic so use fume cupboard
OR
benzene/nitrobenzene is flammable so use heating mantle/water bath

.....

..... [1]

For Examiner's Use

(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.

sodium carbonate removes/neutralises (residual) acid [1]

..... [1]

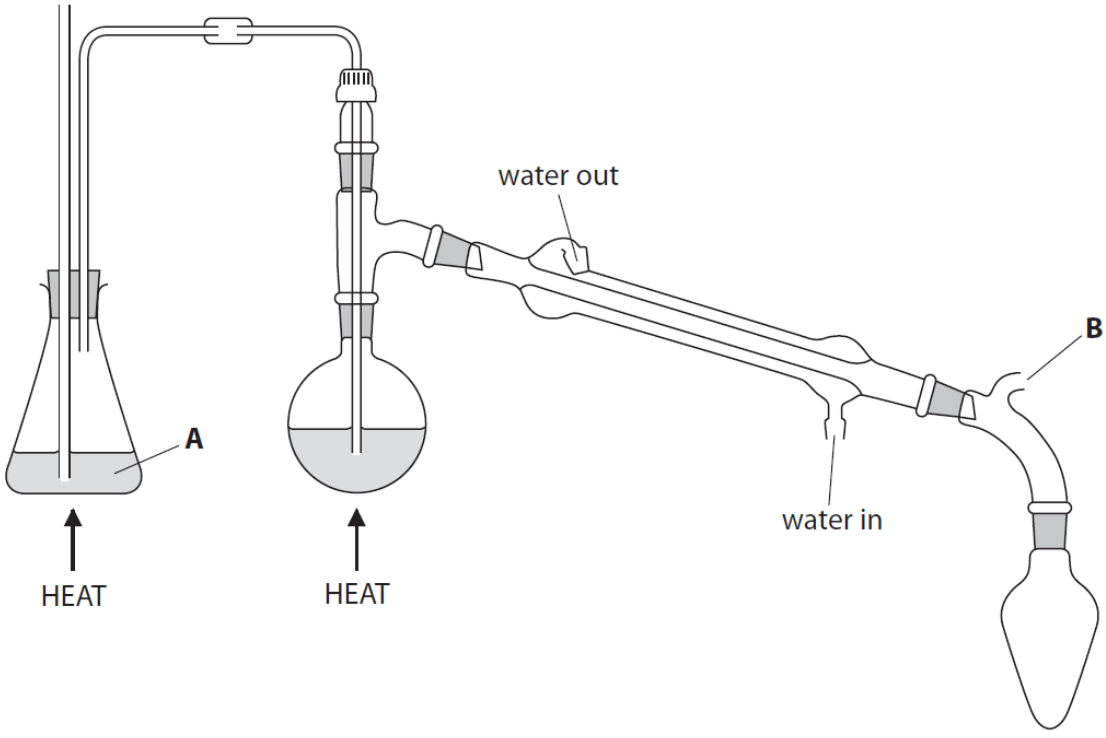
(v) The nitrobenzene layer is dried before being distilled to purify it. Identify a suitable drying agent.

(anhydrous) sodium sulfate / magnesium sulfate OR
(anhydrous) calcium chloride OR silica gel

..... [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**.

water (to produce steam) ..... [1]

For Examiner's Use

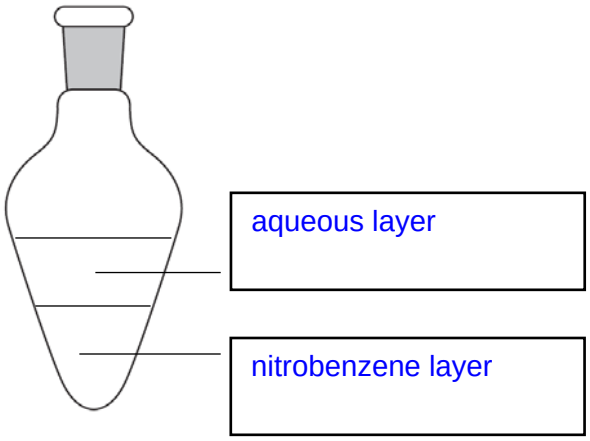
(ii) Explain the purpose of the part of the apparatus labelled **B**.

prevents pressure building up (by allowing gases/vapour to escape)
allow to prevent explosion

reject to allow gases/vapours to escape only
ignore the reference to 'air' for gases / vapours

..... [1]

(iii) On the diagram below, state the contents of the receiver at the end of the steam distillation.



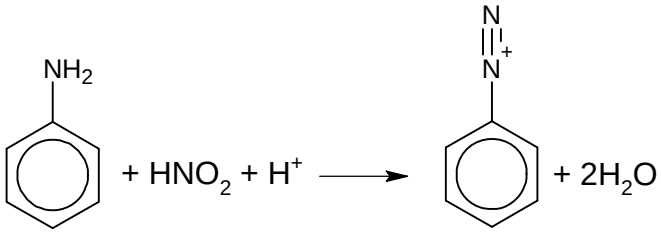
[1]

aqueous layer on top while nitrobenzene on bottom [1]

(c) The purified nitrobenzene is then reduced to phenylamine, $C_6H_5NH_2$.

The phenylamine is diazotised by reaction with nitrous acid at a temperature between 0 ^oC and 10 ^oC. 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.



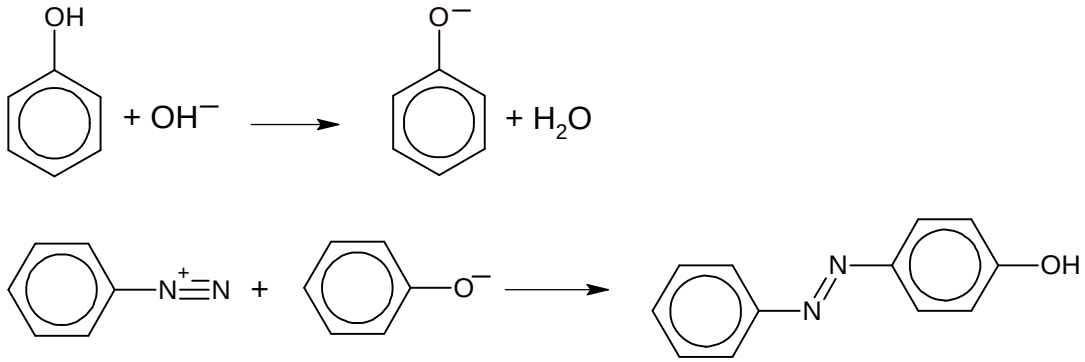
benzenediazonium ion

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, C_6H_5OH, 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.

For Examiner's Use



azo dye

(i) State the reagents and conditions needed to reduce nitrobenzene to phenylamine.

Sn, conc. HCl, under under reflux (followed by addition of NaOH(aq) [1]

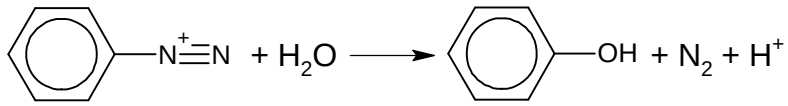
..... [1]

(ii) Explain why the temperature for diazotization to phenylamine must **not** be lower than 0 °C.

< 0 °C reaction is too slow [1]
allow mixture freezes

..... [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.

To prevent (much of the) azo dye remaining in solution on cooling
OR
Gives a saturated solution

.....

..... [1]

For Examiner's Use

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

To prevent crystallization (of the azo dye) [1]

..... [1]

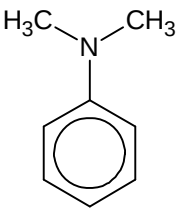
(iv) Suggest a reason why it is preferable to dry the solid in a desiccator rather than in an oven.

Decomposition could occur if the compound were to be heated
OR
Compound might melt

..... [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

There are 2 electron-donating $-CH_3$ groups [pt 1] attached to the N atom in N,N-dimethylphenylamine. Hence the electron density on the N atom in N,N-dimethylphenylamine is higher [pt 2] than that in phenylamine. The lone pair of electrons on the N atom in N,N-dimethylphenylamine is more available [pt 3] for dative bonding with a H^+.

.....

..... [1]

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

This group, $C_6H_5N{=}N-$ is an electron-withdrawing [pt 4] group which further disperses the negative charge on the O atom [pt 5] in the conjugate base of azo dye. The conjugate base formed by the azo dye is further stabilized [pt 6]. The azo dye donates proton more readily [pt 7].

.....

..... [2]

7 pts – 3 marks
5 – 6 pts – 2 marks
3 – 4 pts – 1 mark

[Total: 18]

[End of Paper]