A LEVEL Cambridge Topical Past Papers

CHEMISTRY

PAPER 4 2017 — 2023

CHEMISTRY 9701

TOPICAL PAST PAPER WORKSHEETS

2017 - 2023 | Questions + Mark scheme

AVAILABLE PAPERS

P1	**P2**	**P4**
1473 Questions	299 Questions	365 Questions

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AN INTRODUCTION TO THE CHEMISTRY OF TRANSITION ELEMENTS	12	1	40
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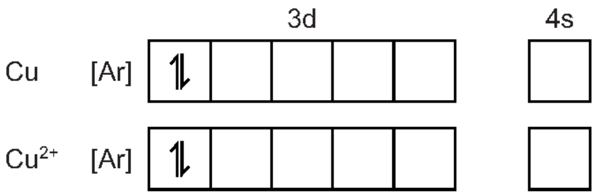
1 - (9701/42_Winter_2018_Q2) - *Atoms,molecules & Stoichiometry, An Introduction To The Chemistry Of Transition Elements*

(a) Complete the electronic configuration for Cu and Cu^{2+}.



[2]

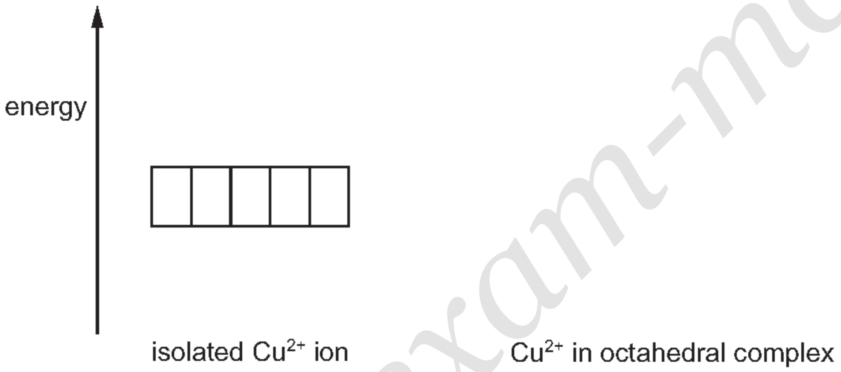
(b) **(i)** The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

Explain what is meant by the term *degenerate* in this context.

....

.... [1]

(ii) Complete the diagram to describe the splitting of the 3d orbital energy levels in an octahedral complex.



[1]

(c) **(i)** 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, *en*, is a bidentate ligand.

Explain what is meant by the term *bidentate*.

....

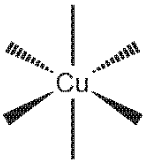
....

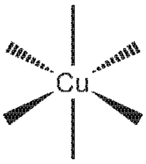
.... [1]

(ii) Cu^{2+} ions and *en* form the complex ion $[Cu(en)_3]^{2+}$.

Draw the two optical isomers of this complex ion.

You may use  to represent *en*.





[2]

2 - (9701/41_Winter_2018_Q4) - *Group 2, Atoms,molecules & Stoichiometry, Equilibria*

(a) The enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of the Group 2 sulfates becomes more endothermic down the group.

State and explain the trend in the solubility of the Group 2 sulfates down the group.

....

....

....

....

.... [3]

(b) **(i)** Write the expression for K_w, the ionic product of water.

K_w =

[1]

(ii) The numerical value of K_w increases with increasing temperature.

Place a tick (✓) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio $[H^+]:[OH^-]$.

effect of increasing temperature of water	decrease	stay the same	increase
pH			
ratio $[H^+]:[OH^-]$			

[2]

(c) An aqueous solution of sodium hydroxide has a pH of 13.25 at 298 K.

Calculate the concentration of this sodium hydroxide solution.

concentration = ... mol dm^{-3} [2]

(d) Buffer solutions are used to regulate the pH of a solution to keep its pH value within a narrow range.

Write **two** equations to describe how hydrogencarbonate ions, HCO_3^-, and carbonic acid, H_2CO_3, control the pH of blood.

....

.... [2]

(e) The K_a for ethanoic acid is $1.75 \times 10^{-5}\,mol\,dm^{-3}$ at 298 K.

(i) When ethanoic acid is dissolved in water, an equilibrium mixture containing two acid-base pairs is formed.

Write an equation for this equilibrium. In the boxes label each species acidic or basic to show its behaviour in this equilibrium.

CH_3CO_2H + ... $\rightleftharpoons$ .... + ...

☐ ☐ ☐ ☐

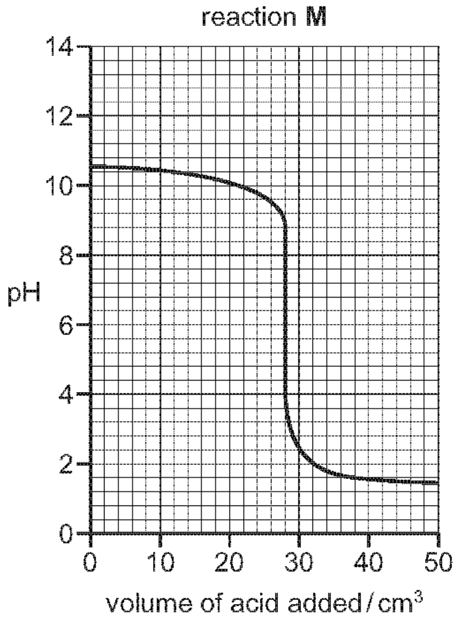
[2]

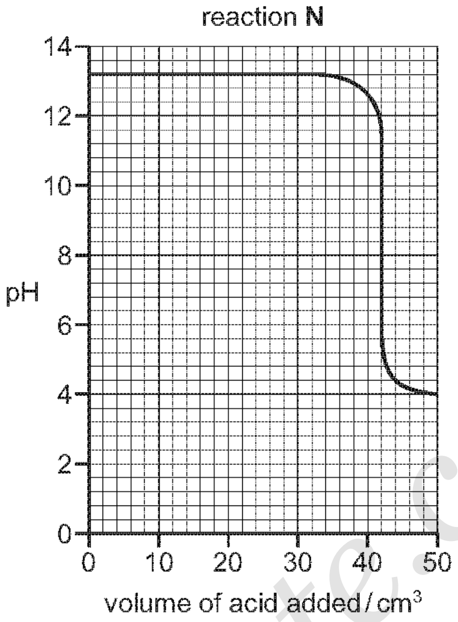
(ii) A buffer solution was prepared by adding $30.0\,cm^3$ of $0.25\,mol\,dm^{-3}$ ethanoic acid, an excess, to $20.0\,cm^3$ of $0.15\,mol\,dm^{-3}$ sodium hydroxide.

Calculate the pH of the buffer solution formed at 298 K. Give your answer to **one** decimal place.

pH = ... [4]

(f) Titration curves for two different acid-base reactions, **M** and **N**, are shown.





(i) Use the titration curve for reaction **M** to deduce the volume of acid added at the end-point for this titration.

volume of acid added at the end-point = ... cm^3 [1]

(ii) The table shows some acid-base indicators.

name of indicator	pH range of colour change
malachite green	0.2–1.8
bromocresol green	3.8–5.4
bromothymol blue	6.0–7.6
thymolphthalein	9.3–10.6

Name a suitable indicator for each of the acid-base titrations **M** and **N**. Explain your answers.

reaction **M** .... reaction **N** ....

explanation ....

....

[2]

3 - (9701/42_Winter_2018_Q5) - *Group 2, Atoms,molecules & Stoichiometry, Equilibria*

(a) Explain why the thermal stability of the Group 2 nitrates increases down the group.

....

....

.... [2]

(b) Sodium nitrite, $NaNO_2$, is a decomposition product from heating sodium nitrate, $NaNO_3$.

A student analysed a sample of sodium nitrite by titration with aqueous cerium(IV) ions, Ce^{4+}(aq). The equation for the titration reaction is shown.

$$NO_2^-(aq) + 2Ce^{4+}(aq) + H_2O(l) \rightarrow 2Ce^{3+}(aq) + NO_3^-(aq) + 2H^+(aq)$$

- 0.138 g of impure sodium nitrite was dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution required 21.80 cm^3 of 0.0400 $mol\,dm^{-3}$ Ce^{4+}(aq) to reach the end-point.

You should assume the impurity does not react with Ce^{4+}(aq).

Calculate the percentage purity of the sample of sodium nitrite.

.... % [3]

(c) Acidified manganate(VII) ions, MnO_4^-, can also be used to analyse solutions containing nitrite ions, NO_2^-, by titration. In acidic solution, NO_2^- ions exist as HNO_2.

(i) Use the *Data Booklet* to construct an ionic equation for this reaction.

....

....

.... [2]

(ii) Use $E^\ominus$ values to calculate the $E^\ominus_{cell}$ for this reaction.

$E^\ominus_{cell}$ = ... V [1]

(d) Nitrous acid, HNO_2, is a weak acid with a K_a of 6.9×10^{-4} mol dm^{-3} at 298 K.

(i) Explain the difference between a strong acid and a weak acid.

....

.... [1]

(ii) Write the expression for the acid dissociation constant, K_a, for HNO_2.

K_a =

[1]

(iii) Calculate the pH of 0.15 mol dm^{-3} HNO_2.

pH = ... [2]

(iv) Calculate the percentage of HNO_2 molecules that are ionised in 0.15 mol dm^{-3} HNO_2.

% ionisation = ... [1]

(e) Solutions containing a mixture of HNO_2 and $NaNO_2$ are buffer solutions.

(i) Define what is meant by the term *buffer solution*.

....

....

.... [2]

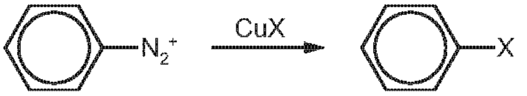
(ii) Write **two** equations to show how a solution containing a mixture of HNO_2 and $NaNO_2$ acts as a buffer.

....

.... [2]

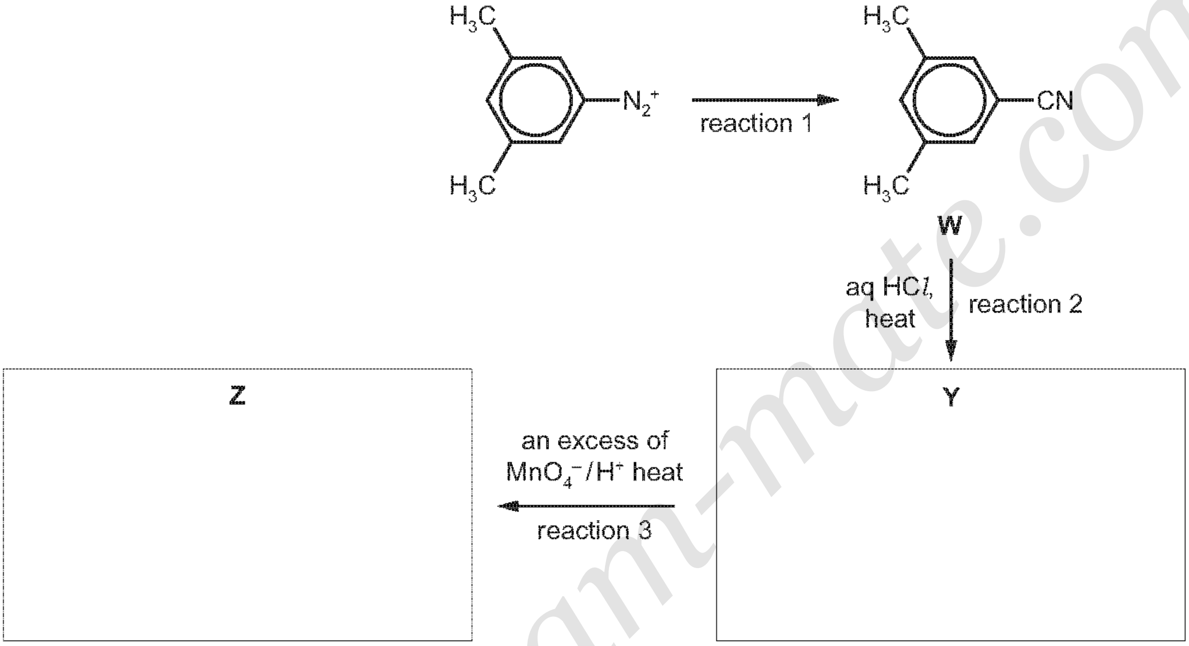
(f) Nitrous acid is used in the preparation of diazonium salts. The $-N_2^+$ group in the diazonium ion can be replaced with C*l*, Br or CN as shown.

The reagent used is a copper(I) salt, CuX.



diazonium ion where X = C*l*, Br or CN

This reaction can be used in the synthesis of compound **Z** as shown.



(i) Suggest the reagent used in reaction 1.

.... [1]

(ii) Suggest structures of compounds **Y** and **Z** and draw them in the boxes above. [2]

Compounds **W** and **Z** were analysed using carbon-13 NMR spectroscopy.

(g) Predict the number of peaks in the carbon-13 NMR spectra of **W** and **Z**.

	number of peaks
W	
Z	

[2]

4 - (9701/41_Summer_2019_Q1) - *Electrochemistry, Atoms,molecules & Stoichiometry*

(a) Aqueous solutions of copper(II) salts contain the blue-coloured $[Cu(H_2O)_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

  ionic equation ....

  type of reaction ....

  colour and state of the copper-containing product ....

- reaction with concentrated hydrochloric acid

  ionic equation ....

  type of reaction ....

  colour and state of the copper-containing product ....

[6]

(b) Chloride ions can be identified using aqueous silver nitrate, $AgNO_3(aq)$.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

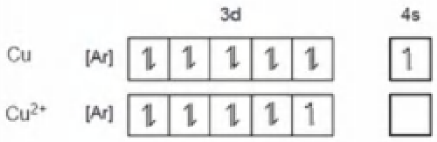
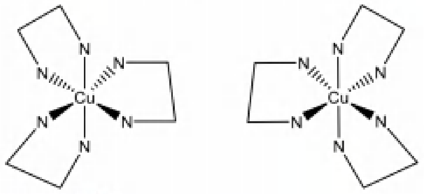
0.303 g of a chloride of sulfur is completely hydrolysed with water. All the chlorine atoms present in the chloride of sulfur are converted into chloride ions. The solution is diluted to 100.0 cm^3. A 25.00 cm^3 sample of this solution is titrated with 0.0500 mol dm^{-3} $AgNO_3(aq)$. The titration requires 22.40 cm^3 of 0.0500 mol dm^{-3} $AgNO_3(aq)$.

Calculate the empirical formula of the chloride of sulfur. Show all your working.

empirical formula of chloride of sulfur = ... [3]

ANSWERS

1 **-** (9701/42_Winter_2018_Q2) **-** *Atoms,molecules & Stoichiometry, An Introduction To The Chemistry Of Transition Elements*

(a)	 [1] × 2	2
(b)(i)	orbitals have the same energy	1
(b)(ii)	d-d splitting seen, leading to 2 upper and 3 lower orbitals	1
(c)	an ion / molecule that donates two pairs of electrons	1
(d)	 one correct [1] two correct and mirror images of each other [1]	2

2 **-** (9701/41_Winter_2018_Q4) **-** *Group 2, Atoms,molecules & Stoichiometry, Equilibria*

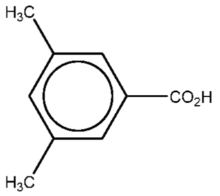
<table>
<tr><td>(a)</td><td>M1 solubility decreases (down the Group) [1]
M2 because lattice energy and hydration energy decreases
OR lattice energy and hydration energy become less exothermic / more endothermic [1]
M3 because hydration energy decreases to a greater extent (than does ΔH_{Latt}) [1]</td><td>3</td></tr>
<tr><td>(b)(i)</td><td>(K_w =) [H$^+$][OH$^-$]</td><td>1</td></tr>
<tr><td>(b)(ii)</td><td>[1] or each correct tick
<table>
<tr><td>effect of increasing temperature</td><td>decreases</td><td>stay the same</td><td>increase</td></tr>
<tr><td>pH</td><td>✓</td><td></td><td></td></tr>
<tr><td>ratio of [H$^+$]:[OH$^-$]</td><td></td><td>✓</td><td></td></tr>
</table></td><td>2</td></tr>
<tr><td>(c)</td><td>[H$^+$] = $10^{-13.25}$ = 5.62×10^{-14} [1]
[OH$^-$] = K_w/[H$^+$] = $1.0 \times 10^{-14}/5.62 \times 10^{-14}$
[OH$^-$] = 0.18 (0.178) (mol dm^{-3}) [1] ecf correct answer scores [2]</td><td>2</td></tr>
<tr><td>(d)</td><td>$HCO_3^- + H^+ \rightarrow H_2CO_3$ OR $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ [1]
$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$ [1]</td><td>2</td></tr>
<tr><td>(e)(i)</td><td>$\boldsymbol{CH_3COOH} + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ [1]
acid + base ⇌ base + acid [1]</td><td>2</td></tr>
<tr><td>(e)(ii)</td><td>M1 moles NaOH = 0.15 × 20/1000 = 0.0030 AND initial moles CH_3COOH = 0.25 × 30/1000 OR 0.0075 [1]
M2 equilibrium moles CH_3COOH = 0.0045 AND equilibrium moles CH_3COONa = 0.0030 [1]
M3 [CH_3COOH] = 0.0045/0.05 = 0.090 AND [CH_3COONa] = 0.003/0.05 = 0.060
[H$^+$] = K_a × [CH_3COOH]/[CH_3COONa] = 2.625 × 10^{-5} [1]
M4 pH = –log[H$^+$] = 4.6 [1] correct answer scores [4]</td><td>4</td></tr>
<tr><td>(f)(i)</td><td>end point = 28 cm^3</td><td>1</td></tr>
<tr><td>(f)(ii)</td><td>M1 reaction M bromothymol (blue) / bromocresol (green) AND reaction N bromothymol (blue) / thymolphthalein [1]
M2 (both indicators have) a pH range / colour change within / in end-point / vertical region / sharp fall of the graph [1]</td><td>2</td></tr>
</table>

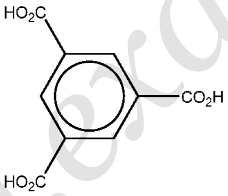
3 - (9701/42_Winter_2018_Q5) - *Group 2, Atoms,molecules & Stoichiometry, Equilibria*

<table>
<tr><td>(a)</td><td>ionic radius / ion size increases OR charge density decreases (down the group) [1]

less polarisation / distortion of anion / nitrate ion / NO_3^- / nitrate group
OR
N-O / N=O bond is less weakened / distorted / polarised
OR
more energy to break N-O / N=O bond [1]</td><td>2</td></tr>
<tr><td>(b)</td><td>• moles of Ce^{4+} = 0.0400 × 21.8 / 1000 = 8.72 × 10^{-4} (moles of Ce^{4+})
• moles of NO_2^- = 8.72 × 10^{-4} / 2 = 4.36 × 10^{-4} in 25 cm^3 (use of 2:1 ratio correctly)
• moles of NO_2^- = 4.36 × 10^{-4} × 4 = 1.74(4) × 10^{-3} in 100 cm^3 (use of 4:1 ratio correctly)
• mass $NaNO_2$ = 1.74(4) × 10^{-3} × (23.0 + 14.0 + 32.0) = 0.120 g (use of M_r correctly)
• % purity = 0.120 / 0.138 = 86.96% (use of 0.0138 correctly)

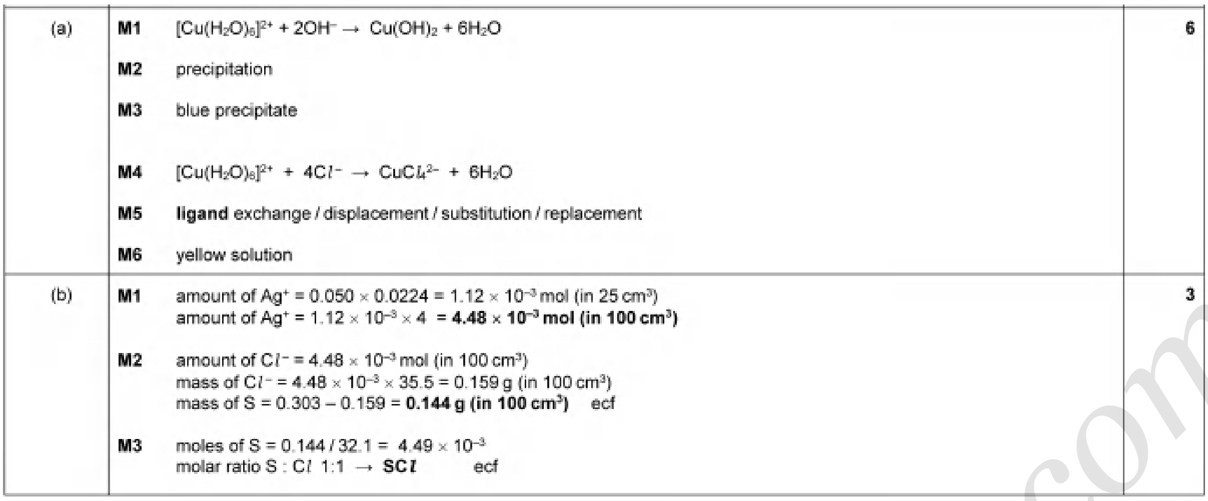
two points = [1]
four points = [2]
all five points = [3]</td><td>3</td></tr>
<tr><td>(c)(i)</td><td>$5NO_2^- + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
OR $5HNO_2 + 2MnO_4^- + H^+ \rightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

all species correct [1] balanced [1]</td><td>2</td></tr>
<tr><td>(c)(ii)</td><td>E°_{cell} = 1.52 – 0.94 = 0.58 (V)</td><td>1</td></tr>
<tr><td>(d)(i)</td><td>weak acid is partly ionised and strong acid is completely ionised</td><td>1</td></tr>
<tr><td>(d)(ii)</td><td>$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$</td><td>1</td></tr>
<tr><td>(d)(iii)</td><td>$K_a = [H^+]^2 / [HNO_2]$
$[H^+] = \sqrt{0.00069} \times 0.15 = 1.02 \times 10^{-2}$ [1]
pH = –log[H^+] = 2.0 (1.99) [1] minimum 2 sigificant figures</td><td>2</td></tr>
<tr><td>(d)(iv)</td><td>% ionisation = 100 × 1.02 × 10^{-2} / 0.15 = 6.7–6.8 %</td><td>1</td></tr>
<tr><td>(e)(i)</td><td>M1 A solution that resists changes in pH [1]
M2 when small amounts of acid or alkali are added to it [1]</td><td>2</td></tr>
<tr><td>(e)(ii)</td><td>M1 $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$ [1]
M2 $NO_2^- + H^+ \rightarrow HNO_2$ [1]</td><td>2</td></tr>
<tr><td>(f)(i)</td><td>CuCN / copper(I) cyanide</td><td>1</td></tr>
<tr><td>(f)(ii)</td><td>

Y


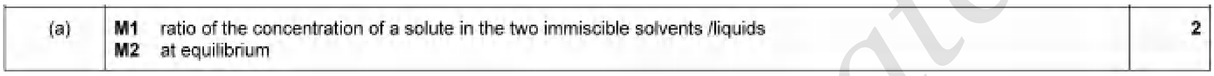
Z
[1] × 2</td><td>2</td></tr>
<tr><td>(g)</td><td><table><tr><td></td><td>number of peaks</td></tr><tr><td>W</td><td>6</td></tr><tr><td>Z</td><td>3</td></tr></table>[1] × 2</td><td>2</td></tr>
</table>

4 **-** (9701/41_Summer_2019_Q1) **-** *Electrochemistry, Atoms,molecules & Stoichiometry*

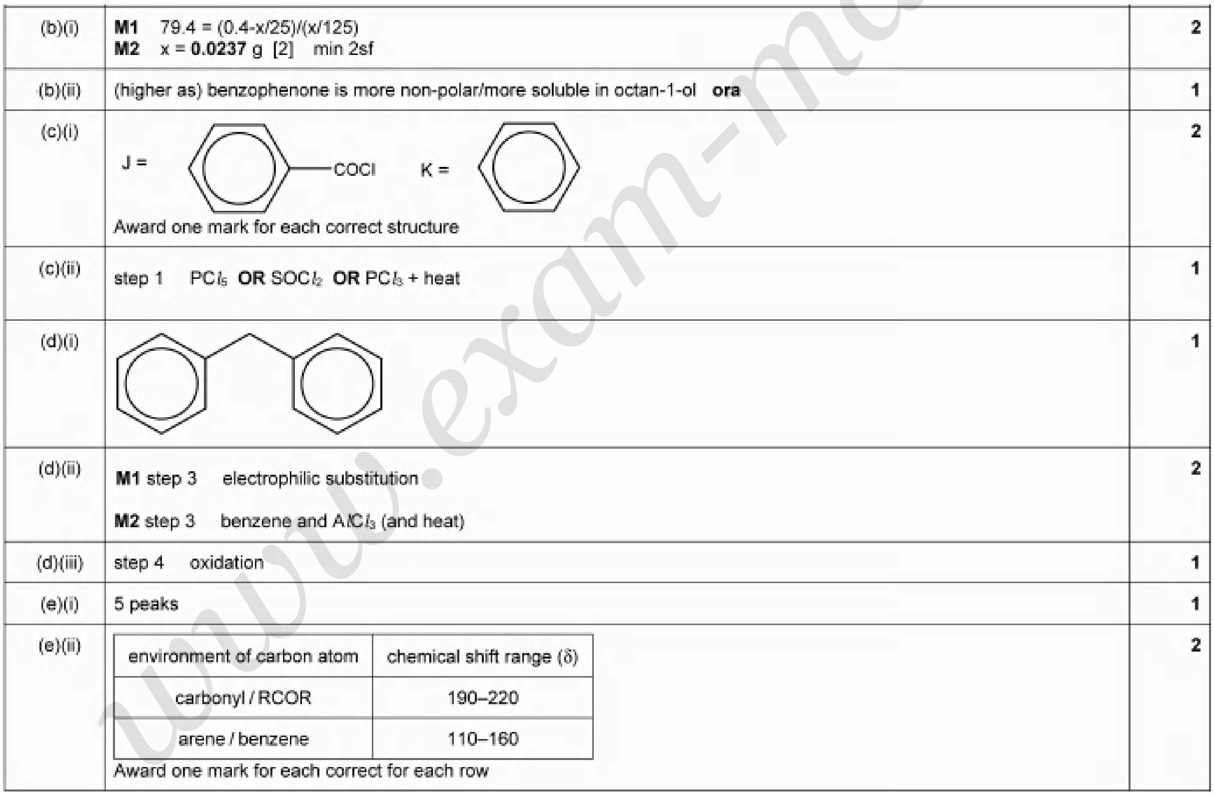


(a)	**M1** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ **M2** precipitation **M3** blue precipitate **M4** $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow CuCl_4^{2-} + 6H_2O$ **M5** **ligand** exchange / displacement / substitution / replacement **M6** yellow solution	**6**
(b)	**M1** amount of $Ag^+ = 0.050 \times 0.0224 = 1.12 \times 10^{-3}$ mol (in 25 cm^3) amount of $Ag^+ = 1.12 \times 10^{-3} \times 4$ = **4.48 × 10^{-3} mol (in 100 cm^3)** **M2** amount of $Cl^- = 4.48 \times 10^{-3}$ mol (in 100 cm^3) mass of $Cl^- = 4.48 \times 10^{-3} \times 35.5 = 0.159$ g (in 100 cm^3) mass of S = 0.303 – 0.159 = **0.144 g (in 100 cm^3)** ecf **M3** moles of S = 0.144 / 32.1 = 4.49×10^{-3} molar ratio S : Cl 1:1 → **SCl** ecf	**3**

5 **-** (9701/42_Summer_2020_Q5) **-** *Equilibria, Atoms,molecules & Stoichiometry, Group 2*



(a)	**M1** ratio of the concentration of a solute in the two immiscible solvents /liquids **M2** at equilibrium	**2**



(b)(i)	**M1** 79.4 = (0.4-x/25)/(x/125) **M2** x = **0.0237** g [2] min 2sf	**2**
(b)(ii)	(higher as) benzophenone is more non-polar/more soluble in octan-1-ol **ora**	**1**
(c)(i)	J = COCl K = Award one mark for each correct structure	**2**
(c)(ii)	step 1 PCl_5 **OR** $SOCl_2$ **OR** PCl_3 + heat	**1**
(d)(i)		**1**
(d)(ii)	**M1** step 3 electrophilic substitution **M2** step 3 benzene and $AlCl_3$ (and heat)	**2**
(d)(iii)	step 4 oxidation	**1**
(e)(i)	5 peaks	**1**
(e)(ii)	environment of carbon atom | chemical shift range (δ) carbonyl / RCOR | 190–220 arene / benzene | 110–160 Award one mark for each correct for each row	**2**