RAFFLES INSTITUTION
2011 PRELIMINARY EXAMINATIONS
H2 CHEMISTRY – PAPER 2
(Suggested Solutions)

1 **(a)** $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

(b) Insoluble barium carbonate and barium sulfite may **co-precipitate with barium sulfate**. Concentrated hydrochloric acid reacts with any barium carbonate and barium sulfite present to form **soluble barium chloride**, and hence, this ensures that only barium sulfate is precipitated during the experiment.

(May accept full equations **with state symbols** involving acid with CO_3^{2-} and SO_3^{2-}.)

(c) Assumption: MCl_2 is soluble in water.

① **Weigh accurately about 0.50 g** of the impure solid metal sulfate in a **clean and dry weighing bottle**. (Accept: 0.50 – 1.00 g.)

② Using a **measuring cylinder**, add 50 cm^3 of deionised water to **dissolve the sulfate completely in a 500 cm^3 beaker**. Stir and add more deionised water to dissolve, if necessary. Using a measuring cylinder, **add 2 cm^3 of concentrated hydrochloric acid**. Stir and warm the mixture (to remove the impurities carbonate and sulfite).

③ Using a 100 cm^3 **measuring cylinder**, measure 10 cm^3 of the aqueous barium chloride and pour it into the sulfate solution. Stir the resulting mixture with a glass rod.

④ **Continue adding aqueous barium chloride dropwise, while stirring**, **until no more white precipitate forms** from the further addition of aqueous barium chloride.

⑤ **Filter the mixture** using a filter funnel which has been lined with filter paper which was **pre-weighed**. **Record** the mass of the filter paper.

⑥ **Using a dropper**, **add aqueous barium chloride to the filtrate**. If no precipitate forms, discard the filtrate. If more precipitate forms, repeat steps ④ to ⑥.

⑦ **Rinse** the white residue with some deionised water and **dry the precipitate using an infra-red lamp** until a **constant mass** is obtained.

⑧ **Weigh the dried precipitate with the filter paper** and **subtract the pre-weighed mass** in Step ⑤ from it to find the mass of the dried $BaSO_4$.

(d) $MSO_4 + BaCl_2 \longrightarrow MCl_2 + BaSO_4$

amt of MSO_4 in 0.892 g = amt of $BaSO_4$ obtained

$$= \frac{1.049}{137 + 32.1 + 4 \times 16.0}$$

$$= 0.004500 \text{ mol}$$

molar mass of M $= \frac{0.804 \times 0.892}{0.004500} - 32.1 - 4(16.0)$

$= 63.5 \text{ g mol}^{-1}$

The metal is copper.
Therefore, the metal sulfate is **$CuSO_4$**.

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2 **(a)** **(i)** To **quench** the reaction at the specified times by **rapidly lowering the temperature** of the reaction mixture.

(ii) Br_2 may undergo **disproportionation** in the presence of NaOH(aq) and it would **not be possible to determine the [Br_2] accurately**.

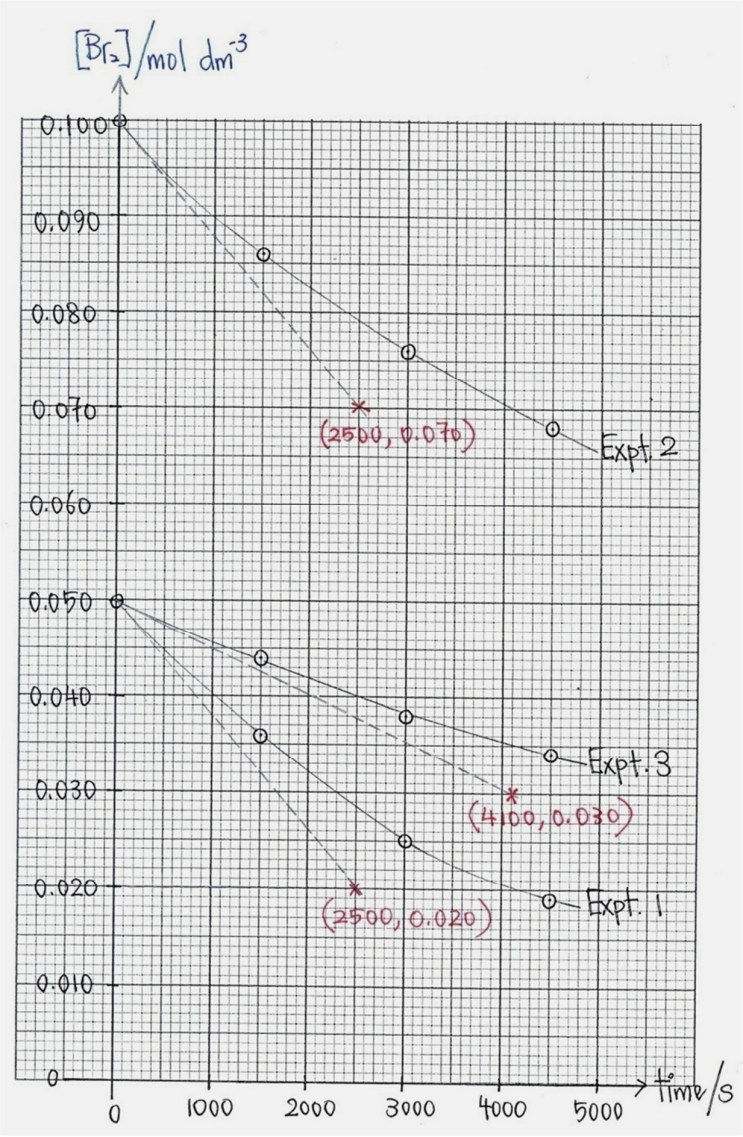
(iii) $2I^- + Br_2 \longrightarrow 2Br^- + I_2$

(iv) At the end point, the **yellow solution of I_2 decolourises**.
Hence there is no need for any indicator.

(b) By measuring the **change** in the **colour intensity** of the **orange Br_2(aq)**.
(The *change in colour intensity over time* gives the *rate* of reaction.)

May also accept changes in **electrical conductivity** / **pH of solution**.

(c) **(i)** y–axis: [Br_2(aq)] / mol dm^{-3} & x–axis: time / s
Properly plotted **curves** for Expts 1, 2 and 3.
(See next page.)



(ii) From Expt 1,

initial rate = $-[(0.020 - 0.050) / (2500 - 0)]$

= 1.20×10^{-5} mol dm^{-3} s^{-1}

From Expt 2,

initial rate = $-[(0.070 - 0.100) / (2500 - 0)]$

= 1.20×10^{-6} mol dm^{-3} s^{-1}

Compare Expt 1 and Expt 2.

When $[Br_2]$ is **doubled**, there is **no change** in the initial rate

$\Rightarrow$ reaction is zero order w.r.t. Br_2.

$\Rightarrow$ $a = 0$

From Expt 3,

initial rate = $-[(0.030 - 0.050) / (4100 - 0)]$

= 4.88×10^{-6} mol dm^{-3} s^{-1}

Compare Expt 1 and Expt 3.
When $[CH_3COCH_2Br]$ is increased 2.5 times,
the initial rate increases $1.20 \times 10^{-5} / 4.88 \times 10^{-6} = 2.5$ times.
$\Rightarrow$ reaction is zero order w.r.t. Br_2.
$\Rightarrow$ $b = 1$

OR

Compare Expt 1 and Expt 3.

$$\text{From} \quad \text{rate} = k[Br_2]^a [CH_3COCH_2Br]^b [H^+]$$

$$\frac{1.20 \times 10^{-5}}{4.88 \times 10^{-6}} = \frac{(0.050)^b}{(0.020)^b}$$

$$\Rightarrow \quad b = 1$$

(iii) $mol^{-1}\ dm^3\ s^{-1}$

(d) (i) $CH_3COCH_2Br + OH^- \longrightarrow CH_3COCHBr^- + H_2O$

(ii) Comparing $CH_3COCH_2^-$ and $CH_3COCHBr^-$, the presence of the **electron-withdrawing –Br group helps to disperse the negative charge and stabilises $CH_3COCHBr^-$**, hence successive brominations take place more readily in basic solution.

Also accepted:
The **electron-withdrawing –Br group** causes the H on the C bearing the Br in **CH_3COCH_2Br** to be **more acidic**.

(e) (i) *Homogeneous* equilibrium refers to an equilibrium in which **all the substances involved are in the *same phase***.

(ii) ① The rate of bromination will **increase** since increasing the total pressure **increases the concentration of the gaseous reactants** CH_3COCH_3 and Br_2 and the reactant molecules are closer together. The frequency of collisions between reactant molecules increases. The **frequency of effective collisions** also **increases**. Hence bromination rate increases.

② The position of equilibrium will be **unaffected** since an **equal number of gaseous molecules** is formed in both the forward and backward reactions.

3 (a) (i) Lattice energy is the amount of energy released when **one mole of a pure solid ionic compound** is formed from its **constituent gaseous ions**.

(ii) Lattice energy depends directly on the product of the charges of the ions and **inversely proportional to the inter-ionic distance**. Down Group II, only the **cationic size increases** and hence, the magnitude of the lattice energy decreases.

(b) (i) $2Sr(NO_3)_2(s) \longrightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$

(ii) Down the group, ionic radius increases,
charge density decreases, polarising power decreases,
thus decreasing distortion of the electron cloud of the NO_3^- anion.
N–O bond in $M(NO_3)_2$ is less weakened and less easily broken.
Thermal stability increases down the group.

(c) (i) $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$
$$= (1.5 \times 10^{-4})(2 \times 1.5 \times 10^{-4})^2$$
$$= 1.35 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

(ii) Let the solubility of $Mg(OH)_2$ in NaOH be s mol dm^{-3}.

$[OH^-]$ from NaOH = $(10 / 1000 \times 1.00) / 1.010 = 0.00990$ mol dm^{-3}
Hence, $K_{sp} = s(2s + 0.00990)^2$

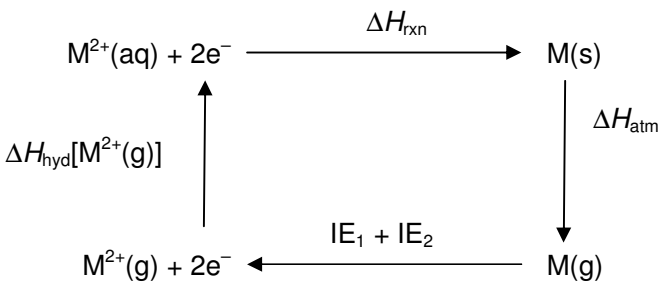
Since NaOH is a strong base, the contribution to $[OH^-]$ from $Mg(OH)_2$, a weak base, is negligible.

$s = [Mg^{2+}] = 1.37 \times 10^{-7}$ mol dm^{-3}

amt of Mg in the ppt
$= (1.5 \times 10^{-4} - 1.37 \times 10^{-7}) \times 1.01$
$= 1.499 \times 10^{-4}$ mol

mass of $Mg(OH)_2$ precipitated $= (1.499 \times 10^{-4})\ [24.3 + 2(17.0)]$
$= 8.74 \times 10^{-3}$ g

(d) (i)



(ii) Hence, $E^{\ominus} \propto \Delta H_{atm} + IE_1 + IE_2 + \Delta H_{hyd}$
All 3 magnitudes of the enthalpy changes decrease down the group.
ΔH_{atm} + IE_1 + IE_2 is endothermic while ΔH_{hyd} is exothermic.
Hence, adding up these results in insignificant changes to $E^{\ominus}$ down the group.

(e) Since Ca^{2+} has a smaller ionic radius than Sr^{2+}, it has a **higher charge density** and is **more extensively hydrated** by water molecules. This produces more drag and hence its ionic speed is lower than expected (in this case, it is identical with that of Sr^{2+}).

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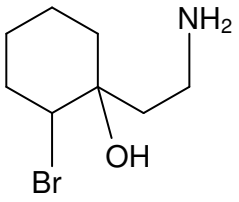
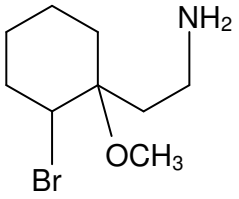
4 **(a)** P has a lower vapour pressure due to **intermolecular hydrogen bonding** (in addition to its van der Waals' forces) but there are only van der Waals' forces between the molecules of Q. There is **stronger attraction** between P molecules.

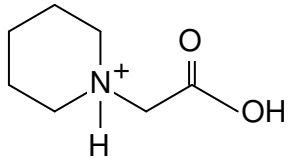
(b) **(i)**



(ii)



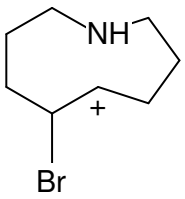
(c) Purple $KMnO_4$ **decolourises.**
Effervescence of **colourless gas** / **gas evolved** that gives a white **ppt with $Ca(OH)_2$(aq).**



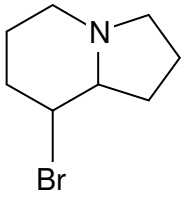
(d) Compound P does not exhibit geometric isomerism because the *trans*-isomer is too unstable to exist due to **ring strain**.

Compound Q does not exhibit geometric isomerism because the terminal carbon is bonded to **two identical** atoms (i.e. hydrogen).
OR Compound Q is a **terminal alkene.**

(e) **(i)**



(ii)

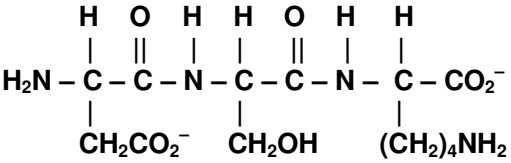


(f) **Partial double bond character** in the C–Br bond in C_6H_5Br causes the bond to be **stronger** than the C–Br bond in **S**. Hence S undergoes alkaline hydrolysis more readily.

May also accept:

- electron-rich benzene ring repels the OH^- nucleophile OR
- C bearing Br is less electron-deficient in bromobenzene and hence less susceptible to nucleophilic attack OR
- electronegative N intensifies the partial positive charge on C bearing Br in **S**, hence making it more susceptible towards nucleophilic attack by OH^-

5 **(a)**



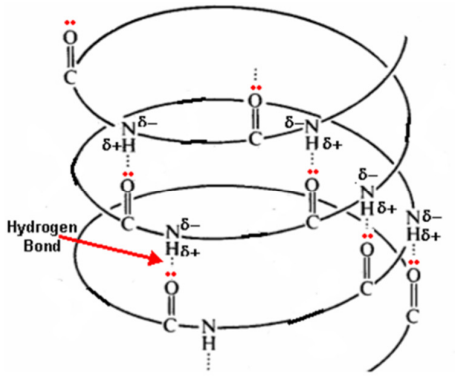
(b) Any 2 of the following:

- Ionic bond between charged $–CH_2COO^-$ and $–(CH_2)_4NH_3^+$ groups.
- Hydrogen bond between –OH of $–CH_2OH$ and $–CH_2OH$ groups.
- Disulfide bond between $–CH_2SH$ group of cysteine residues.
- Van der waals' forces between non-polar $–CH_3$ groups.

(c) Add **acidified $KMnO_4$ (OR acidified $K_2Cr_2O_7$)** to each solution and **heat**. **Serine will decolorise** the purple MnO_4^- (OR turns orange $Cr_2O_7^{2-}$ green) but **aspartic acid will not show any colour change**.

[Note: Na and PCl_5 are NOT accepted as aqueous solutions are used.]

(d) The α–helix has a regular coiled spiral polypeptide chain held in place by **intra-chain hydrogen bonds between peptide C=O group of n^{th} amino acid residue and peptide N–H group of $(n+4)^{th}$ amino acid residue** in the covalently bonded sequence. The **–R groups (side chains) point outside of the helix** and are perpendicular to the main axis of the helix.



(e) **Polar groups** such as
$-CH_2OH$, $-CH_2COOH$, $-CH_2SH$ and $-(CH_2)_4NH_2$ are hydrophilic, and will be located on the **surface** of the globular protein.

Non-polar, hydrophobic $-CH_3$ groups will be located inside the protein away from the aqueous surroundings.

(f) $H_3N^+-CH(CH_3)-COOH$; $H_3N^+-CH(CH_2SH)-COOH$

(g) The primary structure of the pentapeptide is **cys–ala–cys–ala–cys**.

Cysteine is before alanine since enzyme X cleaved the cys–ala peptide bond to give cys and two ala–cys.
Alanine is also before cysteine since enzyme Y cleaved the ala–cys peptide bond to give two cys–ala and cys.