RENDEZVOUS DISCUSSION CORNER
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CENTRE NUMBER	S					INDEX NUMBER					

CHEMISTRY 9729/02

Paper 2 Structured Questions

2 hours

Candidates answer on Question Paper

READ THESE INSTRUCTIONS FIRST

Answer **ALL** questions. The maximum marks awarded per question is indicated in the square brackets at the end of each question.

Do not turn over the booklet until you are told to do so.

This document consists of **26** printed pages, including this Cover Page, and **1** blank page.

FOR EXAMINER'S USE	
1	**/13**
2	**/8**
3	**/20**
4	**/10**
5	**/24**
TOTAL	**/75**

QUESTION 1

Squaric acid is a diprotic organic acid. Figure 1.1 shows the skeletal formula of squaric acid.

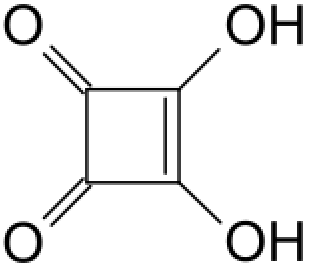

Figure 1.1

(a) (i) Suggest what the term 'diprotic organic acid' means.

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(ii) State the bond angle between two adjacent carbon atoms. Explain your answer.

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(b) (i) Squaric acid is not a perfect square because of the unequal bond lengths between any two adjacent carbon atoms. Explain why this occurs.

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(ii) Figure 1.2 shows the resonance stabilisation of the divalent squarate anion. Draw, on Fig 1.2, curly arrows and lone pairs to show how this resonance stabilisation is achieved, from left to right.

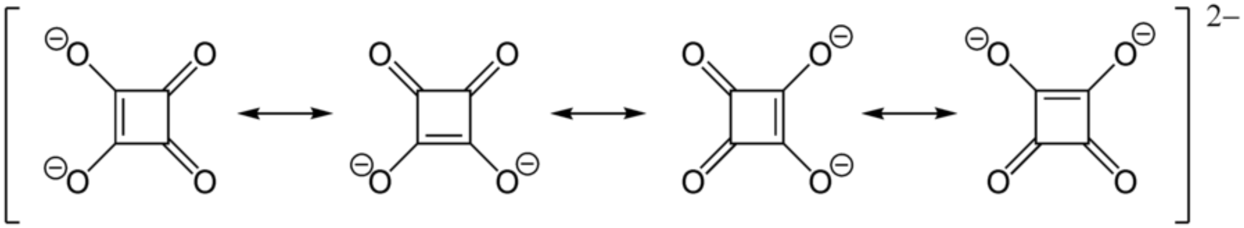

Figure 1.2

[1]

(iii) Hence, considering both (i) and (ii), explain why the divalent squarate anion is a perfect square.

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(c) Compare the pH of 1 mol of squaric acid 1 mol of ethanoic acid, of equal concentration. Explain **two** reasons.

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The divalent squarate anion is an example of the oxocarbon anion, which is a negative ion consisting solely of carbon and oxygen atoms, and therefore having the general formula $C_xO_y^{n-}$ for some integers x, y, and n.

(d) (i) Suggest structures for the following oxocarbon anions:

- dicarbonate ($C_2O_5^{2-}$)
- ethylenetetracarboxylate ($C_6O_8^{4-}$), and
- benzenehexolate ($C_6O_6^{6-}$).

[2]

Every oxocarbon anion can be matched in principle to the electrically neutral variant C_xO_y, known as the *neutralised species*.

(ii) By using one of the oxocarbon anions in (i), explain whether 'neutralising' an oxocarbon anion is an oxidation or reduction reaction. Hence, explain why as a rule, the neutralised species is more unstable than their corresponding oxocarbon anion.

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(iii) Each oxocarbon anion can also form a corresponding hydrogenated anion, $H_kC_xO_y^{m-}$. Find the average oxidation number of carbon in this ion, leaving your answer in terms of k, x, y, and m.

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[Total: 13]

QUESTION 2

Tautomers are constitutional isomers of a molecule that readily interconvert via a rapid equilibrium. An example is given in Figure 2.1.

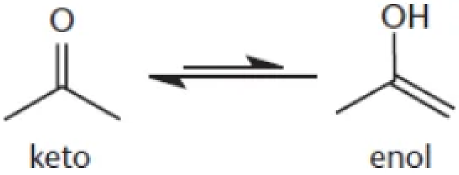

Figure 2.1

This process is known as tautomerisation, which is defined as the interconversion between constitutional isomers of a molecule, involving the the addition of a H-atom (proton) at one molecular site and its removal from another. It results in the switch between a single bond to a double bond in the main-bonding framework.

(a) (i) Define the term 'constitutional isomers' in context of Figure 2.1.

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....[1]

Figure 2.2 shows a natural amino acid, threonine .

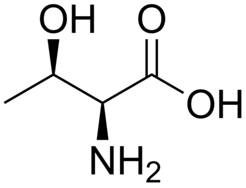

Figure 2.2

(ii) Draw the possible stereoisomers of threonine. You **must** use **R** to represent the R group of this amino acid.

[1]

(iii) Figure 2.3 shows a hypothetical compound that forms ionic bonds with threonine. Draw any 2 tautomers for that compound, **not** threonine.

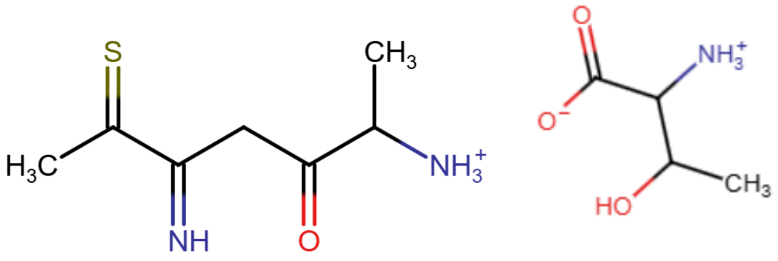

Figure 2.3

[1]

Figure 2.4 shows part of the reaction mechanism of tautomerism.

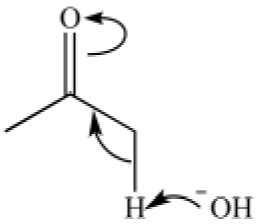

Figure 2.4

(iv) Considering figure 2.4, suggest why alkenes do not exhibit tautomerism.

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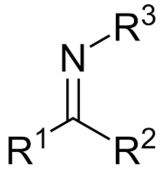
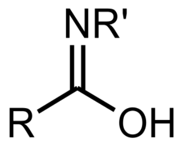
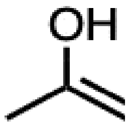
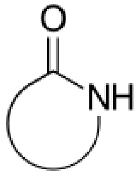
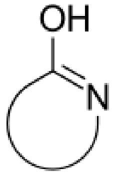
The following list shows some functional groups, with drawn structures for a selected few.

- Functional Groups without structures drawn:
    - Alcohol
    - Aldehyde
    - Ketone
    - Amine
    - Amide

Table 2.4 showing Functional Groups with Structures Drawn

Functional Group	**Imine**	**Imidic acid**	**Enol**	**Lactam**	**Lactim**
Structure					

(v) Using compounds **only** from that list and table, state possible tautomers between **different** functional groups. Express your answer in the form of “tautomer A-tautomer B”. For example, if you think alcohol and aldehydes are tautomers, write your answer as “alcohol-aldehyde”.

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(vi) Zwitterions are also considered tautomers of their respective amino acids. At different pH, different functional groups in amino acids are either protonated or deprotonated. State and briefly explain the order in which different deprotonated and protonated forms of threonine are formed, as pH increases from 1 to 14.

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[Total: 8]

QUESTION 3

Molar ionic strength is a function of the concentration of all ions present in that solution. It can be calculated using the following formula:

$$I = \frac{1}{2}\sum c_i z_i^2$$

where,

- $\sum$ is the sum of **all** ions in the solution,
- c_i is the **molar** concentration of ion *i* (in mol dm^{-3}),
- z_i is the charge number of that ion.

For example, the molar ionic strength of Na$^+$ solution can be calculated as follows:

$$Molar\ ionic\ strength\ = \frac{1}{2}(molar\ concentration\ of\ Na^+)(charge\ of\ \ Na^+)^2$$

If the solution were NaCl instead, the molar ionic strength is calculated as follows:

$$Molar\ ionic\ strength\ = \frac{1}{2}(molar\ concentration\ of\ Na^+)(charge\ of\ \ Na^+)^2$$
$$+ \frac{1}{2}(molar\ concentration\ of\ Cl^-)(charge\ of\ \ Cl^-)^2$$

(a) Using the above information, calculate the molar ionic strength when 20.0 cm^3 of 1.25 mol dm^{-3} of $MgCl_2$ is mixed with 20.0 cm^3 of solution containing 1.50 mol dm^{-3} of Mg^{2+} ions, stating its units.

[2]

The purpose of calculating ionic strength is to find the total electrolyte concentration in a solution, which will affect important properties such as the solubility of different salts.

Table 3.1 shows some salts with their solubility product value. Each salt is dissolved in separate solutions.

Salt	**Ksp value**
AgCN	1.2×10^{-16}
AgBr	3.3×10^{-13}
$PbCl_2$	1.7×10^{-5}
MgC_2O_4	8.6×10^{-5}

Table 3.1

(b) (i) By letting concentrations of ions be unknowns or otherwise, deduce which solution will have the highest molar ionic strength. You may use rough calculations, but should **not** perform specific calculations to solve for those unknowns to arrive at your answer.

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(ii) Explain one assumption that must be made for your answer to be valid.

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(iii) The Ksp value of Fe_2S_3 is 1.4×10^{-88}. Find the molar ionic strength of a fully saturated solution of Fe_2S_3.

[2]

(iv) Explain the following phenomenon:

- When solid NaCl is added to a solution with excess $PbCl_2$, the molar ionic strength increases.

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Salting in refers to the effect where increasing the low ionic strength of a solution increases the solubility of a solute, usually a protein. In contrast, *salting out* is a purification technique involving the reduced solubility of such proteins when a solution with already very high ionic strength is further increased.

During *salting in*, the binding of salt ions to the proteins ionisable groups decreases the interaction between oppositely charged groups on the protein molecules.

During *salting out,* when the salt concentration is increased, some of the water molecules are attracted by the salt ions, which decreases the number of water molecules available to interact with the charged part of the protein.

(c) (i) Sketch a graph of solubility of a protein **X** against salt concentration.

[1]

(ii) Explain the principles of *salting in* and s*alting out.* You may find it helpful to use a diagram.

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(d) Describe an experimental method involving titration to determine the Ksp value of a hydroxide salt. Though not necessary, you may find it useful to specify volumes and concentrations of chemicals. Briefly explain how the results may be processed.

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[Total: 20]

QUESTION 4

The island of stability is a predicted set of isotopes of superheavy elements that may have considerably longer half-lives than known isotopes of these elements.

The theoretical existence of these islands is attributed to stabilising effects of predicted "magic numbers" - the sum of protons and neutrons in the nucleus of an atom.

The seven most widely recognized magic numbers are 2, 8, 20, 28, 50, 82, and 126. They are found using this formula:

$$\frac{(k+1)(k+2)(k+3)}{3}$$

where k is an integer.

(a) (i) Scientists predict that atoms having the eighth magic number will also be stable, though they have yet to discover such elements. State the eighth magic number, and explain why it is so difficult to discover elements with that magic number.

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(ii) Sketch a graph showing the relationship between the number of protons in a nucleus and the number of neutrons in the same nucleus. Explain your answer.

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Nuclides with a magic number of each—such as Tin-132 (number of protons = 50, number of neutrons = 82), are referred to as "doubly magic" and are more stable than nearby nuclides as a result of greater binding energies.

(b) Use the information below and the *Data Booklet* to find elements **A** and **B** of the periodic table, both of which have a “doubly magic” nuclide.

- **A** is in the first three periods of the periodic table;
- **B** is in Group 14.

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(c) Roentgenium-282 (atomic number = 111) is the most stable isotope of Rg. It has a half life of 2.2 min and undergoes radioactive decay.

(i) Define the term *half-life* in the context of this question.

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(ii) Hence, suggest a reason for the presence of a dash (-) for the relative atomic mass of Rg in the periodic table in the *Data Booklet*.

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(iii) There are 1.30 mol of Rg in a sample. Calculate the amount of time it takes before 0.100 mol of Rg (or less) is left in a sample.

[1]

Discoveries of elements in the island of stability are very difficult, as they do not occur in nature. They have to be synthesised artificially in nuclear reactors.

(d) (i) Suggest **two** characteristics of nuclear reactors used for such synthesis.

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(ii) Much care must be taken when experimenting with such substances as they are highly reactive. Explain the reactivity of such superheavy elements.

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[Total: 10]

QUESTION 5

Reaction mechanisms can be represented as a reaction network, as shown in Figure 5.1.

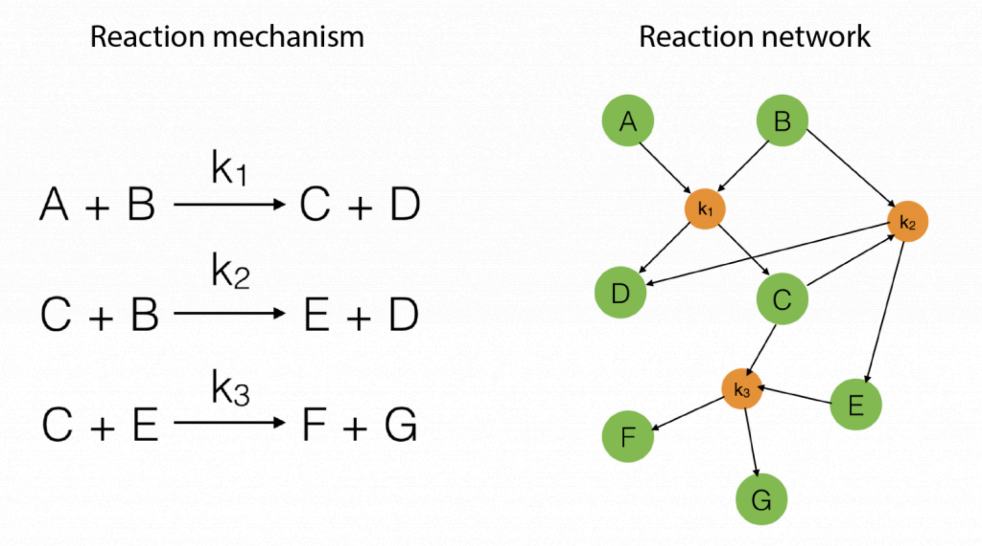

Figure 5.1

(a) (i) Assuming that all reactions are irreversible, draw reaction networks to show:

- the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide, and
- the catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction.

Use k’, k’’, k’’’, etc to label different rate constants.

[2]

(ii) Suggest a benefit of using such a model for representing reactions.

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(iii) Figure 5.2 shows a reaction network. **X** and **Y** are different ions of the same element.

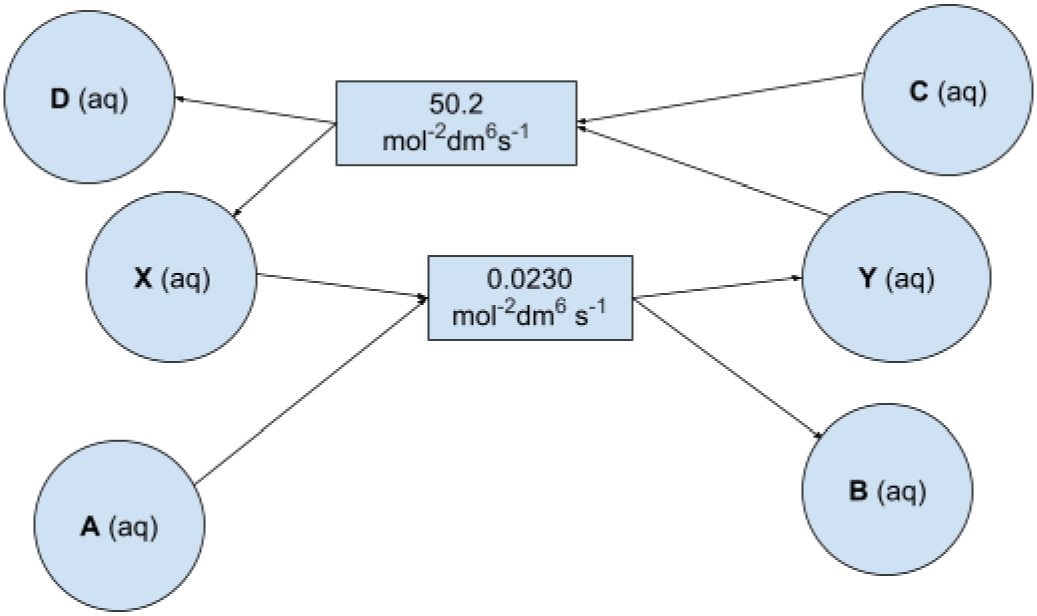

Figure 5.2

Explain the role of **X** and **Y** in a reaction to form **B**.

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It is given that the reaction in Figure 5.2 is between **X** and **A** to generate **Y** and **B**. The order of reaction with respect to **X** is 1. [**A**] can be monitored using a sensor. At intervals of time, a student takes a 15.0cm^3 aliquot and quenches it by adding 50.0cm^3 of ice water into the reaction mixture. A redox titration is then carried out. The titrant is 0.250 mol dm^{-3} $KMnO_4$. It is also given that the half equation in which **X** reacts with $KMnO_4$ is represented by the following reaction:

$$\mathbf{X}\text{ (aq)} \rightarrow \mathbf{Z}\text{ (aq)} + e^-$$

The following figure shows some of the results of the titration.

Time/ s	Final burette reading/ cm^3	Initial burette reading/ cm^3	Volume of $KMnO_4$/ cm^3	Concentration of **X** at specific time interval/ mol dm^{-3}	Concentration of **A**/ mol dm^{-3}
60	17.30	33.20			0.230

Table 5.3

(iv) By completing table 5.3, find the rate of reaction when time = 60s.

[3]

(v) A large amount of **C** (aq) contaminates the reaction mixture. Explain if it is still possible to find the initial rate of reaction, and the rate of reaction at t = 60s, between **X** and **A**, using the same experimental method.

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In complex reactions, stoichiometries are often represented in a more compact form called the stoichiometry matrix. The stoichiometry matrix is denoted by the symbol **N**. If a reaction network has n reactions and m participating molecular species, then the stoichiometry matrix will have correspondingly m rows and n columns. Figure 5.4 shows an example.

Reaction Network

R1: $2A + B \rightarrow C + 3D$

R2: $A + 3B \rightarrow C + E$

R3: $A \rightarrow 2B + D + E$

R4: $4B \rightarrow D + A$

R5: $D + 2B \rightarrow C + 2E$

R6: $C + 4E \rightarrow 3B + D$

Stoichiometric Matrix

$$\begin{array}{c|cccccc|}
 & R1 & R2 & R3 & R4 & R5 & R6 \\
\hline
A & -2 & -1 & -1 & 1 & 0 & 0 \\
B & -1 & -3 & 2 & -4 & -2 & 3 \\
C & 1 & 1 & 0 & 0 & 1 & -1 \\
D & 3 & 0 & 1 & 1 & -1 & 1 \\
E & 0 & 1 & 1 & 0 & 2 & -4 \\
\hline
\end{array}$$

Figure 5.4

Figure 5.5 shows a reaction mechanism.

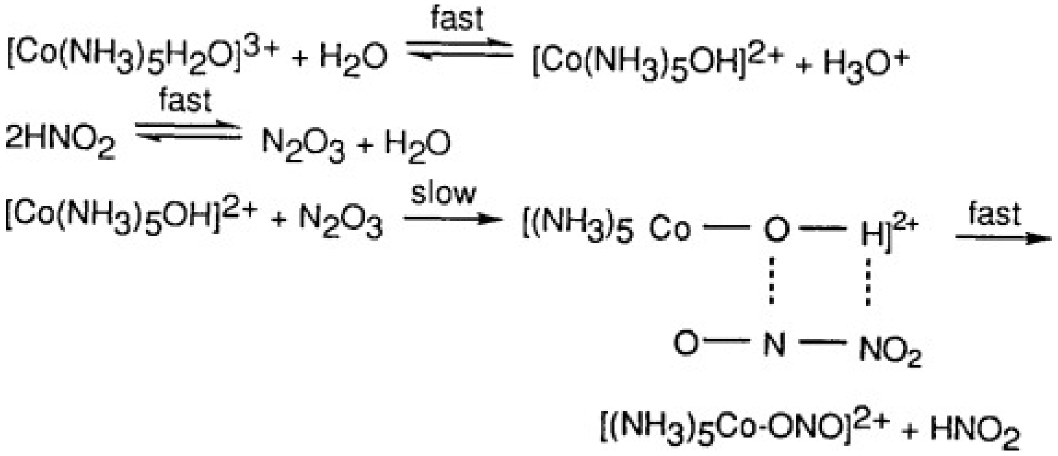

Figure 5.5

(b) (i) For the reaction shown in Figure 5.5,

- Construct a stoichiometric matrix, and
- Determine the rate equation.

[2]

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Question 5 continues on the next page

(ii) Explain the phenomenon in step 1 of the reaction in Figure 5.5.

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(c) A Belousov–Zhabotinsky reaction, or BZ reaction, is a reaction showing non-equilibrium thermodynamics. This means that the reaction mixture changes periodically from a colour to another, depending on the chemical species present in larger amounts.

When Belousov, the scientist who discovered this reaction, mixed excess $KBrO_3$, $Ce(SO_4)_2$, $CH_2(COOH)_2$, and $C_6H_8O_7$ (citric acid) in dilute sulfuric acid, the ratio of concentration of the Ce^{4+} and Ce^{3+} ions oscillated, causing the colour of the solution to oscillate between a yellow solution and a colourless solution respectively.

Zhabotinsky, another scientist who experimented with this reaction, further found the following:

- Oxidation of Ce^{3+} by $HBrO_3$ is an autocatalytic reaction
- Br^- ion is an inhibitor of the autocatalytic oxidation of Ce^{3+}.
- Ce^{4+} is reduced by bromomalonic acid (BMA), $BrCH(COOH)_2$.
- The Ce^{4+} reduction is accompanied by the production of Br^- from BMA

(i) Write a balanced equation for the following:

- Oxidation of Ce^{3+} by $HBrO_3$ to form products, including $HBrO_2$
- Reduction of Ce^{4+} by bromomalonic acid to form products, including CO_2

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(ii) Explain the observations of the BZ reaction, assuming that [Ce^{4+}] is extremely high when the experiment starts.

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(ii) A research article noted that the “BZ reaction makes it possible to observe the development of complex patterns in time and space by the naked eye”. Explain the chemical basis that allows for this to occur.

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(iii) Belousov noted that the frequency of oscillation increased with temperature. Use a diagram to explain why.

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[Total: 24]

END OF PAPER