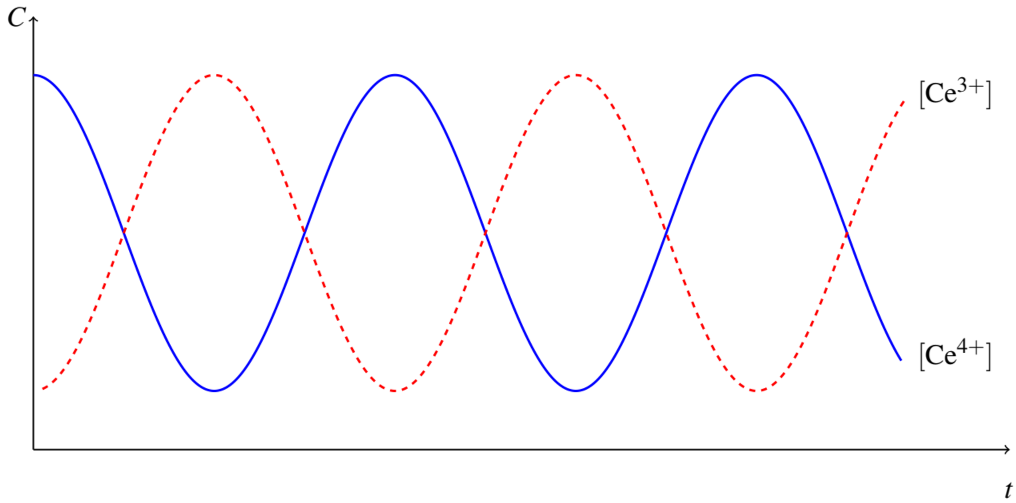
T2. Kinetics of the Belousov-Zhabotinsky reaction

6%							
2.1	2.2	2.3	2.4	2.5	2.6	2.7	$\sum$
2	11	4	2	9	4	3	35

When the chemicals $\mathrm{KBrO_3}$, $\mathrm{CH_2(COOH)_2}$ (malonic acid, – MA), $\mathrm{Ce(SO_4)_2}$, and $\mathrm{H_2SO_4}$ are mixed, the concentration, C, of Ce species and the colour of the solution oscillates between yellow (due to $\mathrm{Ce^{4+}}$) and colourless (due to $\mathrm{Ce^{3+}}$). A schematic picture is given below:



2.1	**Write** the overall balanced reaction equation of the Belousov-Zhabotinsky reaction (BZ reaction). Note: in this reaction, MA is oxidised to $\mathrm{CO_2}$, $\mathrm{BrO_3^-}$ is reduced to $\mathrm{Br^-}$, and Ce(IV) is a catalyst.	2.0 pt

The mechanism of the BZ reaction is shown below (BMA – $\mathrm{CHBr(COOH)_2}$):

Process A	$\begin{cases} (1)\ \mathrm{HBrO_2 + BrO_3^- + H^+ \xrightarrow{k_1} 2BrO_2^{\cdot} + H_2O} \\ (2)\ \mathrm{BrO_2^{\cdot} + Ce^{3+} + H^+ \xrightarrow{k_2} HBrO_2 + Ce^{4+}} \\ (3)\ \mathrm{2HBrO_2 \xrightarrow{k_3} BrO_3^- + HBrO + H^+} \end{cases}$	$k_1 = 1.0 \times 10^4\ \mathrm{M^{-2}\ s^{-1}}$ $k_2 = 6.2 \times 10^4\ \mathrm{M^{-2}\ s^{-1}}$ $k_3 = 4.0 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$
Process B	$\begin{cases} (4)\ \mathrm{HBrO_2 + Br^- + H^+ \xrightarrow{k_4} 2HBrO} \\ (5)\ \mathrm{BrO_3^- + Br^- + 2H^+ \xrightarrow{k_5} HBrO + HBrO_2} \\ (6)\ \mathrm{HBrO + MA \xrightarrow{k_6} BMA + H_2O} \end{cases}$	$k_4 = 2.0 \times 10^9\ \mathrm{M^{-2}\ s^{-1}}$ $k_5 = 2.1\ \mathrm{M^{-3}\ s^{-1}}$ $k_6 = 8.2\ \mathrm{M^{-1}\ s^{-1}}$
Process C	$\{ (7)\ \mathrm{Ce^{4+} + BMA \xrightarrow{k_7} Ce^{3+} + Br^-}$ + other products	$k_7 = 1.0 \times 10^2\ \mathrm{M^{-1}\ s^{-1}}$

In the BZ reaction, **Process C** occurs continuously, while **Processes A** and **B** alternate with each other. Assume that:

- when **Process A** occurs the solution is yellow and **Process B** practically does not occur;

- when **Process B** occurs the solution is colourless and **Process A** practically does not occur;

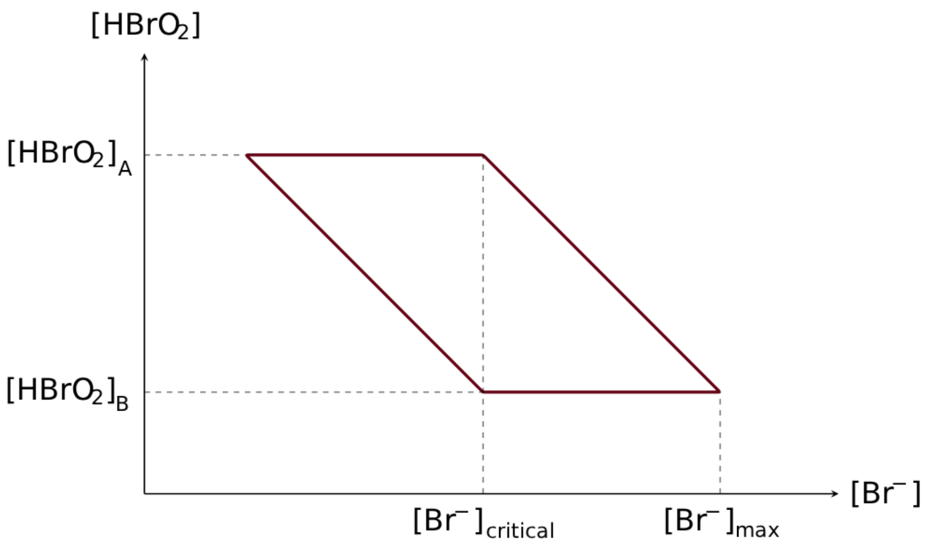
- $[\mathrm{BrO_3^-}]_0 = 0.06$ M, $[\mathrm{MA}]_0 = 0.1$ M, $[\mathrm{H^+}]_0 = 0.8$ M, $[\mathrm{Ce^{4+}}]_0 = 0.001$ M;

- the concentrations of the reactants (except $\mathrm{Ce^{4+}}$) and pH are maintained constant throughout the BZ reaction.

2.2	Using the steady-state approximation, **calculate** the stationary molar concentrations of $\mathrm{HBrO_2}$ in **Processes A** and **B**, $[\mathrm{HBrO_2}]_\mathrm{A}$ and $[\mathrm{HBrO_2}]_\mathrm{B}$.	11.0 pt

If you could not calculate $[\mathrm{HBrO_2}]_\mathrm{A}$ and $[\mathrm{HBrO_2}]_\mathrm{B}$, you can use the values $[\mathrm{HBrO_2}]_\mathrm{A} = 1 \times 10^{-5}$ M and $[\mathrm{HBrO_2}]_\mathrm{B} = 1 \times 10^{-10}$ M for the following calculations.

During the BZ reaction, the concentrations of $HBrO_2$ and Br^- oscillate strictly in relation to each other, and this is sketched in the phase portrait of $[HBrO_2]$ vs $[Br^-]$:



Here $[Br^-]_{max}$ is the maximum concentration and $[Br^-]_{critical}$ is the critical concentration of Br^- at which there is a switch over in processes from **A** to **B** or from **B** to **A**. To switch **Process A** to **Process B**, the reaction rate of the elementary step (4) must exceed that of the elementary step (1) and vice versa.

2.3	**Calculate** $[Br^-]_{critical}$.	4.0 pt

If you could not calculate $[Br^-]_{critical}$, use $[Br^-]_{critical} = 1 \times 10^{-7}$ M for the following calculations.

2.4	In **which direction** in the phase portrait of $[HBrO_2]$ vs $[Br^-]$ will the concentrations of $[HBrO_2]$ and $[Br^-]$ change over time? **Tick** the correct box.	2.0 pt

The system does not traverse the phase portrait of $[HBrO_2]$ vs $[Br^-]$ at a constant velocity, that is the concentration of $[Br^-]$ slowly decreases from $[Br^-]_{max} = 7.0 \times 10^{-4}$ M to $[Br^-]_{critical}$, and then almost immediately reaches $[Br^-]_{max}$ again.

2.5	**Calculate** based on the data the period of oscillations, τ, of the BZ reaction, in seconds.	9.0 pt

2.6 What will be the effect if the following actions **(1-4)** are performed on an open system where a BZ reaction is taking place? **Tick** only one box **(a-e)** for each case. 4.0 pt

1. Adding of small amount of Ce^{4+} during **Process A**. 2. Adding of a small amount of Ag^{+} during **Process B**. 3. Adding of a small amount of Br^{-} during **Process B**. 4. Continuous addition of Br^{-}.	[a] prolongs **Process A** [b] prolongs **Process B** [c] **Process A** switches to **Process B** [d] **Process B** switches to **Process A** [e] oscillations stop

2.7 Which graph qualitatively illustrates the rate of change of Gibbs energy ($\frac{dG}{dt}$) of a **closed** system in which an oscillatory reaction occurs? **Tick** the correct box. 3.0 pt