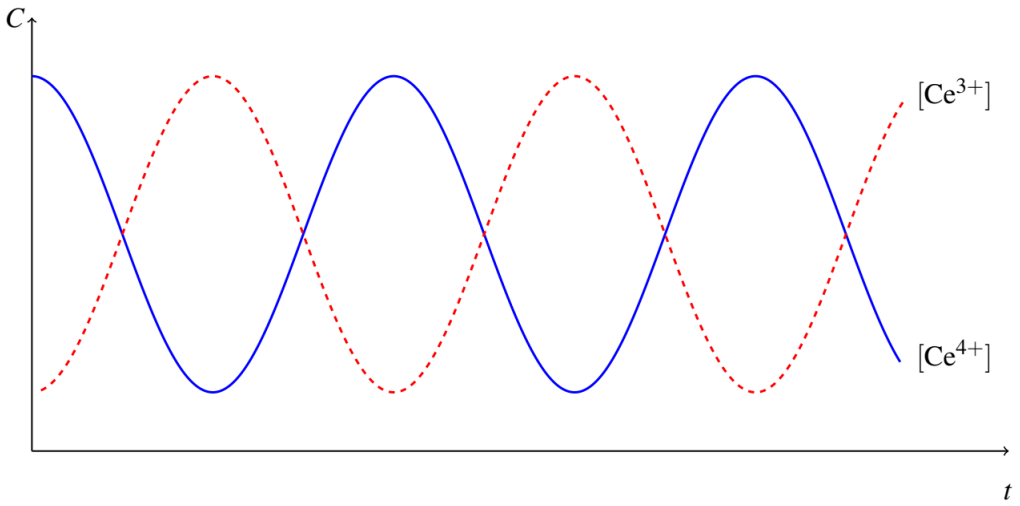
T2. Kinetics of the Belousov-Zhabotinsky reaction

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 $KBrO_3$, $CH_2(COOH)_2$ (malonic acid, – MA), $Ce(SO_4)_2$, and H_2SO_4 are mixed, the concentration, C, of Ce species and the colour of the solution oscillates between yellow (due to Ce^{4+}) and colourless (due to 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 CO_2, BrO_3^- is reduced to Br^-, and Ce(IV) is a catalyst. 2.0 pt

Solution:

$3CH_2(COOH)_2 + 4BrO_3^- \rightarrow 9CO_2 + 4Br^- + 6H_2O$

or

$3CH_2(COOH)_2 + 4KBrO_3 \rightarrow 9CO_2 + 4KBr + 6H_2O$

For fully correct reaction equation: 2 points.
If only coefficient of H_2O is wrong: 1 point.

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

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

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;

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

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

2.2 Using the steady-state approximation, **calculate** the stationary molar concentrations of $HBrO_2$ in **Processes A** and **B**, $[HBrO_2]_A$ and $[HBrO_2]_B$. 11.0 pt

SOLUTION:

$$\frac{d[BrO_2^{\cdot}]}{dt} = 2k_1[HBrO_2][BrO_3^-][H^+] - k_2[BrO_2^{\cdot}][Ce^{3+}][H^+] = 0 \quad (eq.2.1)$$

$$\frac{d[HBrO_2]}{dt} = -k_1[HBrO_2][BrO_3^-][H^+] + k_2[BrO_2^{\cdot}][Ce^{3+}][H^+] - 2k_3[HBrO_2]^2 = 0 \quad (eq.2.2)$$

When adding equations 2.1 and 2.2 we get the following:

$$k_1[HBrO_2][BrO_3^-][H^+] - 2k_3[HBrO_2]^2 = 0 \quad (eq.2.3)$$

$$[HBrO_2]_A = \frac{k_1}{2k_3}[BrO_3^-][H^+] \quad (eq.2.4)$$

$$[HBrO_2]_A = \frac{1.0\times10^4}{2\times4.0\times10^7} \times 0.06 \times 0.8 = 6.0 \times 10^{-6}\ \text{M}$$

The steady-state approximation for **Process B**:

$$\frac{d[HBrO_2]}{dt} = -k_4[HBrO_2][Br^-][H^+] + k_5[BrO_3^-][Br^-][H^+]^2 = 0 \quad (eq.2.5)$$

$$[HBrO_2]_B = \frac{k_5}{k_4}[BrO_3^-][H^+] \quad (eq.2.6)$$

$$[HBrO_2]_B = \frac{2.1}{2.0\times10^9} \times 0.06 \times 0.8 = 5.04 \times 10^{-11}\ \text{M}$$

$$[HBrO_2]_A = 6.0 \times 10^{-6}\ \text{M} \qquad [HBrO_2]_B = 5.04 \times 10^{-11}\ \text{M}$$

For fully correct equations 2.1, 2.2 and 2.5: 2 points each.

If only one incorrect coefficient in front of the rate constant in equations 2.1, 2.2 and 2.5: 1 point each.

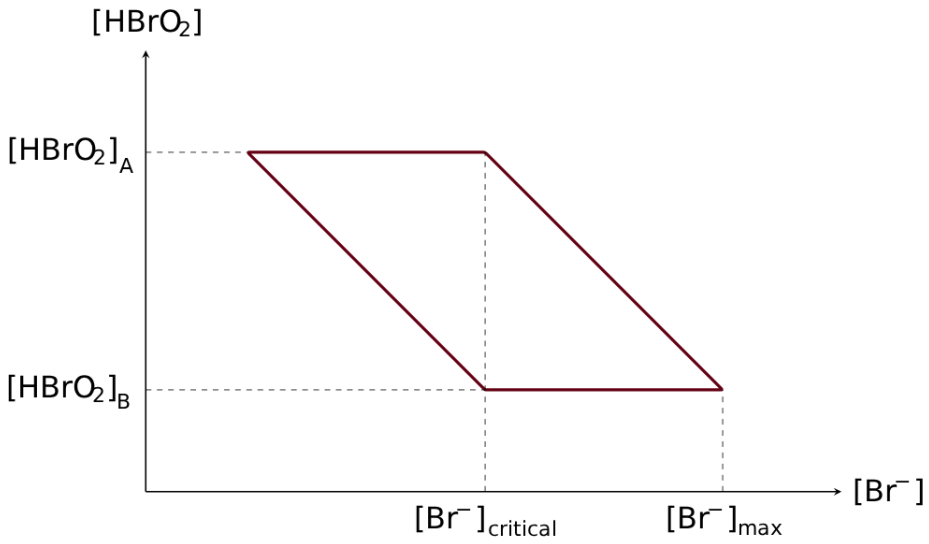
For corresponding equations 2.3, 2.4 and 2.6: 1 point each.

For calculated $[HBrO_2]_A$ and $[HBrO_2]_B$ values: 1 point each.

For correct calculation without formula derivation: full marks.

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

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



Here $[\mathrm{Br^-}]_{\mathrm{max}}$ is the maximum concentration and $[\mathrm{Br^-}]_{\mathrm{critical}}$ is the critical concentration of $\mathrm{Br^-}$ 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** $[\mathrm{Br^-}]_{\mathrm{critical}}$. 4.0 pt

SOLUTION:

During the switching process the following equality is observed:

$$k_1[\mathrm{HBrO_2}][\mathrm{BrO_3^-}][\mathrm{H^+}] = k_4[\mathrm{HBrO_2}][\mathrm{Br^-}][\mathrm{H^+}] \quad (\mathrm{eq.3.1})$$

$$[\mathrm{Br^-}]_{critical} = \frac{k_1}{k_4}[\mathrm{BrO_3^-}] \quad (\mathrm{eq.3.2})$$

$$[\mathrm{Br^-}]_{critical} = \frac{1.0\times10^4}{2.0\times10^9} \cdot 0.06 = 3.0 \times 10^{-7}\ \mathrm{M}$$

$$[\mathrm{Br^-}]_{critical} = 3.0 \times 10^{-7}\ \mathrm{M}$$

For fully correct equation 3.1: 1 point.
For fully correct equation 3.2: 2 points.
For calculated $[\mathrm{Br^-}]_{\mathrm{critical}}$ value: 1 point.
For correct calculation without formula derivation: full marks.

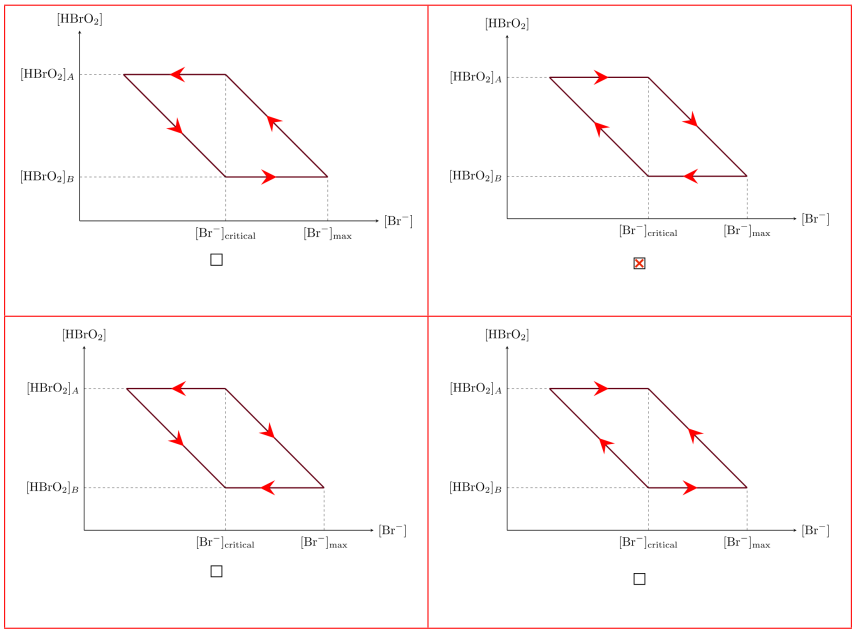
If you could not calculate $[\mathrm{Br^-}]_{\mathrm{critical}}$*, use* $[\mathrm{Br^-}]_{\mathrm{critical}} = 1 \times 10^{-7}$ M *for the following calculations.*

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

SOLUTION:

As the process should be cyclic and not converge in equilibrium points, options **c** and **d** do not fit this criterion.

If $r_1 > r_4$ (relatively low concentration of bromide) **Process B** switches to **Process A**, otherwise if $r_1 < r_4$ (relatively high concentration of bromide) **Process A** switches to **Process B**. During **process A** concentration of bromide increases (due to conjugate **process C**), while during **process B** it decreases. So the right option should account for the change in concentrations in such a way that fits this scenario. Therefore, the correct answer is a clockwise phase portrait.



Only for correct answer: 2 points.

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

SOLUTION:

From the conditions of the problem, it can be understood that the period of oscillations, τ (s), is equal to the time it takes for the concentration of bromide to decrease from the maximum to the critical value. The decrease in bromide concentration occurs during **Process B**.

Let's write a kinetic equation for the change of $[Br^-]$ considering $\left[Ce^{4+}\right] \approx 0 \rightarrow k_7 \left[Ce^{4+}\right] [BMA] \approx 0$ (eq.5.1) during **Process B**:

$$-\frac{d[Br^-]}{dt} = k_4[HBrO_2][Br^-][H^+] + k_5[BrO_3^-][Br^-][H^+]^2 \quad \text{(eq.5.2)}$$

$$-\frac{d[Br^-]}{dt} = \left(k_4[HBrO_2]_B[H^+] + k_5[BrO_3^-][H^+]^2\right)[Br^-] = k^*[Br^-]$$

where

$$k^* = k_4[HBrO_2]_B[H^+] + k_5[BrO_3^-][H^+]^2 \quad \text{(eq.5.3)}$$

Thus, we obtain a first order kinetic equation. For this equation:

$$k^* = 2.0 \times 10^9 \times 5.04 \times 10^{-11} \times 0.8 + 2.1 \times 0.06 \times 0.8^2 = 0.16128 \text{ s}^{-1}$$

$$[Br^-]_{critical} = [Br^-]_{max} \cdot e^{-k^*\tau}$$

$$\tau = \frac{\ln\left([Br^-]_{max}/[Br^-]_{critical}\right)}{k^*} \quad \text{(eq.5.4)}$$

$$\tau = \frac{\ln\left(7.0\times10^{-4}/(3.0\times10^{-7})\right)}{0.16128\ s^{-1}} = 48 \text{ s}$$

For values $[HBrO_2]_B = 1.0 \times 10^{-10}$ M and $[Br^-]_{critical} = 1.0 \times 10^{-7}$ M:

$$k^* = 2.0 \times 10^9 \times 1.0 \times 10^{-10} \times 0.8 + 2.1 \times 0.06 \times 0.8^2 = 0.24064 \text{ s}^{-1}$$

$$\tau = \frac{\ln\left(\frac{[Br^-]_{max}}{[Br^-]_{critical}}\right)}{k^*} = \frac{\ln\left(7.0\times10^{-4}/(1.0\times10^{-7})\right)}{0.24064 \text{ s}^{-1}} = 37 \text{ s}$$

For correct equations 5.1, 5.2 and 5.3: 2 points each.
For correct equation 5.4: 1 point.
For calculated k^* value: 1 point.
For calculated τ value: 1 point.
For correct calculation without formula derivation: full marks.

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

SOLUTION:

	[a]	[b]	[c]	[d]	[e]
1.			×		
2.				×	
3.		×			
4.					×

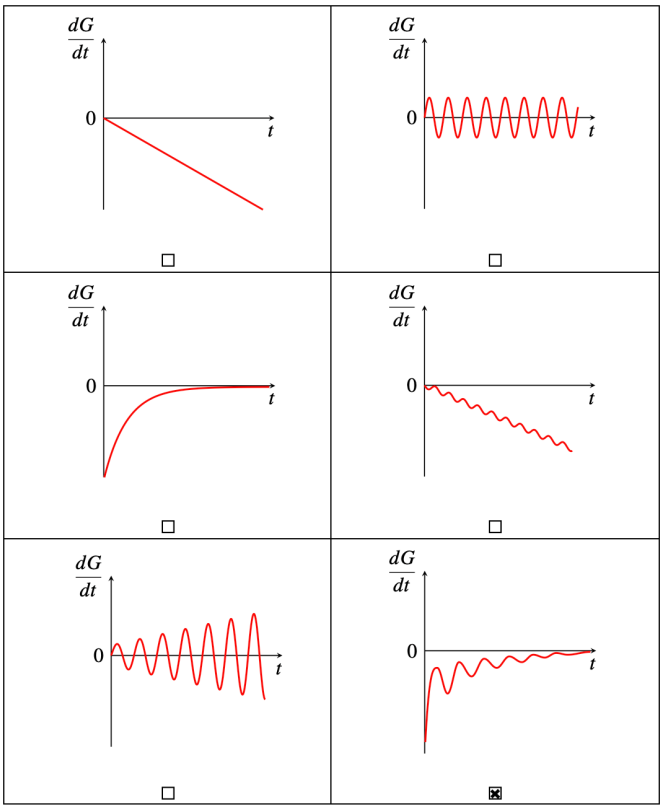
1. "Adding of small amount of Ce^{4+} during **Process A**" will lead to the formation of Br^{-} in **Process C**, there will be $r_1 < r_4$ and "[c] **Process A** switches to **Process B**".
2. "Adding of small amount of Ag^{+} during **Process B**" will lead to precipitation of AgBr, there will be $r_1 > r_4$ and "[d] **Process B** switches to **Process A**".
3. "Adding of small amount of Br^{-} during **Process B**" will lead to increase in $[Br^{-}]_{max}$ value, accordingly, the time required to reduce $[Br^{-}]_{max}$ to $[Br^{-}]_{critical}$ will be extended, so it will "[b] prolongs **Process B**".
4. "Continuously adding of Br^{-}" will lead to the concentration of Br^{-} always being above the $[Br^{-}]_{critical}$ value and **Process B** never switching to **Process A**, so it will "[e] stop oscillations".

For correct answers: 1 point each.

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

SOLUTION:

In the oscillatory reaction, the Gibbs energy exhibits oscillatory behavior over time, rather than decreasing monotonically as in most typical chemical reactions. In closed systems, the oscillations dampen over time → the system eventually reaches equilibrium ($\frac{dG}{dt} = 0$). dG must be less than 0 every time. So, correct answer is last one:



For correct answer: 3 points.

For ticking middle left box which describes $\frac{dG}{dt}$ of a non-oscillatory reaction in a closed system: 1 point.