

Clock Reaction Calculations, 2005

Here's how I found the value of k for the clock reaction, with calculations shown for **mixture B** (see the results on the last page of this document).

Try to solve the problem yourself first, and use this guide if necessary.

A note on concentrations. From the handout, you are given the volumes of reagents added, and their concentrations. By adding up the volumes, you can get the total volume. From the concentration and volume of a given reagent, such as $\text{S}_2\text{O}_3^{2-}$, you can find how many moles of it are present, and thus its concentration.

See step 2 below for advice on calculating the FINAL concentrations of the reagents, when the reaction is over.

1. First write down the rate law. From comparison of the rates for mixtures A, B, and C, the reaction is first order in $\text{S}_2\text{O}_8^{2-}$ and in I^- .

$$\text{Rate} = -d/dt [\text{S}_2\text{O}_8^{2-}] = -1/2 d/dt [\text{S}_2\text{O}_3^{2-}] = k [\text{S}_2\text{O}_8^{2-}] [\text{I}^-]$$

2. You can find the rate constant by looking at the rate of change of the concentrations of $[\text{S}_2\text{O}_8^{2-}]$ or $[\text{S}_2\text{O}_3^{2-}]$.

a. the $[\text{S}_2\text{O}_3^{2-}]$ goes from its initial concentration to zero, so the change in its concentration is always (final concentration – initial concentration) = $0 - 1.6 \times 10^{-3} \text{ M} = -1.6 \text{ mM}$.

b. From the stoichiometry, the change in concentration of $[\text{S}_2\text{O}_8^{2-}]$ must be half that of $[\text{S}_2\text{O}_3^{2-}]$, or -0.8 mM (you can confirm this from the data in the table).

3. The rate is given by the change in concentration over time, so divide by the time. Here I've done it both for $[\text{S}_2\text{O}_3^{2-}]$ and also for $[\text{S}_2\text{O}_8^{2-}]$.

$$\text{Rate} = -1/2 \, d/dt [\text{S}_2\text{O}_3]^{2-} = -1/2 [-1.6 \text{ mM}]/68 \text{ s} = 1.18 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{Rate} = -d/dt [\text{S}_2\text{O}_8]^{2-} = -[-0.8 \text{ mM}]/68 \text{ s} = 1.18 \times 10^{-5} \text{ Ms}^{-1}$$

[note that this rate equation is used on the last page (results)]

4. Plug this back into the rate law (part 1 above) along with the initial concentrations of $\text{S}_2\text{O}_8^{2-}$ and I^- to obtain

$$\text{Rate} = 1.18 \times 10^{-5} \text{ Ms}^{-1} = k [4 \times 10^{-2} \text{ M}] [8 \times 10^{-2} \text{ M}]$$

$$\mathbf{k = 3.69 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}}$$

[Note -- I used the initial concentrations of $\text{S}_2\text{O}_8^{2-}$ and of I^- in this calculation, on the assumption that they do not change significantly over the course of the reaction. You can check this assumption by using their final concentrations (for example, that of $\text{S}_2\text{O}_8^{2-}$ is $7.92 \times 10^{-2} \text{ M}$, see the table) and seeing if k changes significantly.]

5. Repeat for mixtures A and C (see next page to check your work). Do you get the same k (within experimental error)?

6. You can use the same procedure for the 2nd demo, the temperature dependence of this reaction.

Here's the procedure repeated for A and C

3. The rate is given by the change in concentration over time, so divide by the time. Here I've done it both for $[\text{S}_2\text{O}_3^{2-}]$ and also for $[\text{S}_2\text{O}_8^{2-}]$.

$$\text{A- Rate} = -1/2 \, d/dt [\text{S}_2\text{O}_3^{2-}] = -1/2 [-1.6 \text{ mM}]/35 \text{ s} = 2.29 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{A- Rate} = -d/dt [\text{S}_2\text{O}_8^{2-}] = -[-0.8 \text{ mM}]/35 \text{ s} = 2.29 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{C- Rate} = -1/2 \, d/dt [\text{S}_2\text{O}_3^{2-}] = -1/2 [-1.6 \text{ mM}]/66 \text{ s} = 1.21 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{C- Rate} = -d/dt [\text{S}_2\text{O}_8^{2-}] = -[-0.8 \text{ mM}]/66 \text{ s} = 1.21 \times 10^{-5} \text{ Ms}^{-1}$$

4. Plug this back into the rate law (part 1 above) along with the initial concentrations of $\text{S}_2\text{O}_8^{2-}$ and I^- to obtain

$$\text{A- Rate} = 2.29 \times 10^{-5} \text{ Ms}^{-1} = k [8 \times 10^{-2} \text{ M}] [8 \times 10^{-2} \text{ M}]$$

$$\text{A- } k = 3.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

$$\text{C- Rate} = 1.21 \times 10^{-5} \text{ Ms}^{-1} = k [8 \times 10^{-2} \text{ M}] [4 \times 10^{-2} \text{ M}]$$

$$\text{C- } k = 3.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$$

The rate constants from the 3 experiments should all match within experimental error. **They're pretty close:** 3.6, 3.7 and $3.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Ignoring any possible errors in preparing the solutions, other sources of error are the timing and the temperature.

2005 Clock Reaction Data and Calculations 21±1°C

	MIXTURE A	MIXTURE B	MIXTURE C
$[S_2O_3^{2-}]_{t=0}$	1.6 mM	1.6 mM	1.6 mM
$[S_2O_8^{2-}]_{t=0}$	80 mM	40 mM	80 mM
$[I^-]_{t=0}$	80 mM	80 mM	40 mM
$[S_2O_8^{2-}]_{t=\tau}$	79.2 mM	39.2 mM	79.2 mM
τ/s	35	68	66
Rate ^l (units?)	$2.29 \times 10^{-5} \text{ Ms}^{-1}$	$1.18 \times 10^{-5} \text{ Ms}^{-1}$	$1.21 \times 10^{-5} \text{ Ms}^{-1}$
k_I (units?)	$3.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	$3.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$	$3.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$

$$\text{Rate} = -\frac{d[S_2O_8^{2-}]}{dt} \cong -\frac{[S_2O_8^{2-}]_{t=\tau} - [S_2O_8^{2-}]_{t=0}}{\tau} = \frac{0.8 \text{ mM}}{\tau}$$

$$\text{Rate} = -\frac{d[S_2O_8^{2-}]}{dt} = \boxed{} [S_2O_8^{2-}]^{\boxed{}} [I^-]^{\boxed{}}$$

$$\text{Rate} \sim 3.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} [S_2O_8^{2-}] [I^-]$$