# Determination of the Rate Law: Method of the initial rates

**Objective:** To calculate the rate constant and the order of the following chemical reaction:

$$2I^-(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2\,SO_4^{2-}(aq)$$

**The rate** of the reaction (its speed) follows the general equation:

| | |
|---|---|
| $\text{Rate} = k\,[I^-]^a[S_2O_8^{2-}]^b$ | – The constants "a" and "b" are called the order of the reaction with respect to each reactant.<br>– The sum of both constant "a" and "b" is the overall order of the chemical reaction.<br>– The constant k is called the rate constant of the reaction. Its units depends on the reaction order. |

The constants k, a and b can be obtained by measuring the change of the reaction rate with the change of the concentrations of either $I^-$ or $S_2O_8^{2-}$. A minimum of three different concentrations are required to access the three unknowns (simple math: 3 unknown = 3 equations). This subject will be covered in class. It is called: "Method of initial rates" (Zumdahl section 12.3, example table 12.4).

**Reaction rate calculation**:

The rate of the reaction is calculated with a secondary reaction called a "clock" reaction.

$$2\,S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow 2\,I^-(aq) + S_4O_6^{2-}(aq).$$

- This reaction is running together with the main reaction and they interact with one another.
- The speed of the clock reaction (or rate of "consumption" of $S_2O_3^{2-}$) is determined by the rate of production of $I_2$ from the main reaction.
- The speed of the clock reaction is fast; however it requires $I_2$ from the main reaction to proceed. Consequently, the clock reaction has to "wait" for the main reaction to progress and therefore, it has to run at the same speed.
- When all the $S_2O_3^{2-}$ of the clock reaction is consumed, the solution changes color ($I_2$ + starch).
- Knowing the initial concentration of $S_2O_3^{2-}$, and the time it takes for its complete consumption (color change of the solution), the rate of the main reaction can be calculated:

$$\text{Rate} = -\frac{\Delta[S_2O_3^{2-}]}{\Delta 2t}$$

Since all the $S_2O_3^{2-}$ is consumed and the initial time of the timer was zero, then the equation that should be used to calculate the rate, is this one:

$$\text{Rate} = \frac{[S_2O_3^{2-}]_{t=0}}{2t}$$

**Procedure:**

1– Mix all the chemical together quickly and start the stop clock simultaneously

2– Swirl the solutions gently until the solution turns to a dark colour. Record the time.

Name: ______________________________ Date ______________

## LABORATORY DATA SHEET: Determination of the Rate Law
## (method of initial rate)

Reaction: $2\ I^{-} + S_2O_8^{2-} \longrightarrow I_2 + 2\ SO_4^{2-}$ note: $S_2O_8^{2-} = (NH_4)_2S_2O_8$

TABLE 1: Reagent concentrations and temperature

[ $Na_2S_2O_3$ ] : ______________ M

[ KI ] : ______________ M

[ $(NH_4)_2S_2O_8$ ] : ______________ M

T : ______________ °C

TABLE 2: Solution composition and time observed for the "clock" reaction (Laboratory data sheet)

| | FLASK 1 | | | FLASK 2 | | | Time (s) | |
|---|---|---|---|---|---|---|---|---|
| Exp. | KI | KCl | $Na_2S_2O_3$ | $(NH_4)_2S_2O_8$ | $(NH_4)_2SO_4$ | starch | run 1 | run 2 |
| 1 | 30.0 mL | 0.0 mL | 15.0 mL | 30.0 mL | 0.0 mL | 5 drops | | |
| 2 | 15.0 mL | 15.0 mL | 15.0 mL | 30.0 mL | 0.0 mL | 5 drops | | |
| 3 | 30.0 mL | 0.0 mL | 15.0 mL | 10.0 mL | 20.0 mL | 5 drops | | |

Useful equations:

$$[\ S_2O_3^{2-}\ ]_o = \frac{([Na_2S_2O_3]\ \text{reagent}) \times (\text{volume}\ Na_2S_2O_3)}{\text{total volume}}$$

$$\text{Rate} = \frac{[S_2O_3^{2-}]_{t=0}}{2t}$$

$$[S_2O_8^{2-}]_o = \frac{([(NH_4)_2S_2O_8]\ \text{reagent}) \times (\text{volume}\ (NH_4)_2S_2O_8)}{\text{total volume}}$$

$$[I^{-}]_o = \frac{([KI]\ \text{reagent}) \times (\text{volume KI})}{\text{total volume}}$$

*The total volume for each run is 75.0 mL*

TABLE 3: Solution composition and time

| Exp. | average time, s | Rate, $M.s^{-1}$ | [ $S_2O_8^{2-}$ ]$_o$, M | [ $I^{-}$ ]$_o$, M |
|---|---|---|---|---|
| 1 | | | | |
| 2 | | | | |
| 3 | | | | |

## Sample calculations

| | |
|---|---|
| $[S_2O_3^{2-}]_o$ (exp 1) | Rate = $\frac{[S_2O_3^{2-}]_{t=0}}{2t}$ (exp 1) |
| $[S_2O_8^{2-}]_o$ (exp 1) | $[I^-]_o$ (exp 1) |

$S_2O_8^{2-}$ order determination $\frac{\text{exp}\,1}{\text{exp}\,3}$

$I^-$ order determination $\frac{\text{exp}\,1}{\text{exp}\,2}$

Determination of the rate constant k (exp 1)

Complete rate law (with units)

## Sample calculations

The concentration of $S_2O_3{}^{2-}$ is constant and is the same for everyone.

$[S_2O_3{}^{2-}]$:

$$[S_2O_3^{2-}]_o \quad = \quad \frac{(0.0036\,M)(15.0\,mL)}{(75.0\,mL)} \quad = 7.2 \times 10^{-4}\ M$$

The same calculations apply to the concentrations of $[I^-]_o$ and $[S_2O_8^{2-}]_o$

note: For all the solutions, 75.0 mL is always the total volume.

Rate of the reaction:

It took 30 s for the solution to change color. In this case the rate of the reaction is:

$$\text{Rate} = \frac{[S_2O_3^{2-}]_o}{2\,t} \quad = \quad \frac{7.4\times10^{-4}M}{2\times30\,s} \quad = 1.23 \times 10^{-5}\ M.s^{-1}.$$

(Teacher's sample calculations. Some numbers are fictitious; use you own experimental data)

| Exp. | average time, s | Rate, $M.s^{-1}$ | $[\ I^-\ ]_o$, M | $[\ S_2O_8^{2-}\ ]_o$, M |
|---|---|---|---|---|
| 1 | 15.0 s | $2.46 \times 10^{-5}\ M.s^{-1}$ | 0.144 M | 0.072 M |
| 2 | 30.0 s | $1.23 \times 10^{-5}\ M.s^{-1}$ | 0.072 M | 0.072 M |
| 3 | 90.0 s | $3.07 \times 10^{-6}\ M.s^{-1}$ | 0.072 M | 0.048 M |

$I^-$ order determination

$$\frac{\exp 1}{\exp 2} : \frac{\text{Rate1} = k\,[I^-]^a\,[S_2O_8^{2-}]^b}{\text{Rate2} = k\,[I^-]^a\,[S_2O_8^{2-}]^b} = \frac{2.46\times10^{-5} = k\,(0.144)^a(0.072)^b}{1.23\times10^{-5} = k\,(0.072)^a(0.072)^b}$$

consequently $\frac{\exp 1}{\exp 2}$ : $2 = 1 \times (2)^a \times (1)^b$ therefore a = 1, whatever the value of b.

*(note: the order is always an integer. Ex: if a = 0.97 it should be rounded to the closest integer or 1)*

$S_2O_8^{2-}$ order determination

$$\frac{\exp 2}{\exp 3} : \frac{\text{Rate2} = k\,[I^-]^1[S_2O_8^{2-}]^b}{\text{Rate3} = k\,[I^-]^1[S_2O_8^{2-}]^b} = \frac{1.23\times10^{-5} = k\,(0.072)^1(0.072)^b}{3.07\times10^{-6} = k\,(0.072)^1(0.048)^b}$$

the result is $\frac{\exp 3}{\exp 4}$ : $4.0 = 1 \times (1)^1 \times (2)^b$ therefore b = 2

k: Rate constant determination. Any experiment can be used to solve for k. Here, the exp 2 is taken.

$$\text{Rate} = k\,[I^-]^1\,[S_2O_8{}^{2-}]^2 \quad \rightarrow \quad k = \frac{\text{Rate}}{[I^-]^1[S_2O_8^{2-}]^2} \quad \rightarrow \quad k = \frac{1.23\times10^{-5}M.s^{-1}}{(0.072\ M)^1\,(0.072\ M)^2} \ = 0.033\ M^{-2}s^{-1}.$$

Finally, the complete rate law is:

**Rate = 0.033 $M^{-2}s^{-1}$ $[I^-]^1$ $[S_2O_8{}^{2-}]^2$ the overall order of this reaction is 3**

(Your *k* value and order could be different than the one from this sample calculation)