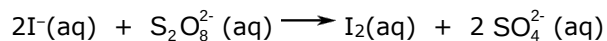


## Determination of the Rate Law: Method of the initial rates

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



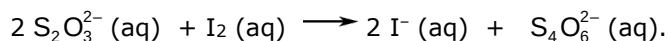
**The rate** of the reaction (its speed) follows the general equation:

$\text{Rate} = k [\text{I}^{-}]^a [\text{S}_2\text{O}_8^{2-}]^b$	<ul style="list-style-type: none"><li>– The constants “a” and “b” are called the order of the reaction with respect to each reactant.</li><li>– The sum of both constant “a” and “b” is the overall order of the chemical reaction.</li><li>– The constant k is called the rate constant of the reaction. Its units depends on the reaction order.</li></ul>
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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  $\text{I}^{-}$  or  $\text{S}_2\text{O}_8^{2-}$ . 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.



- 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  $\text{S}_2\text{O}_3^{2-}$ ) is determined by the rate of production of  $\text{I}_2$  from the main reaction.
- The speed of the clock reaction is fast; however it requires  $\text{I}_2$  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  $\text{S}_2\text{O}_3^{2-}$  of the clock reaction is consumed, the solution changes color ( $\text{I}_2$  + starch).
- Knowing the initial concentration of  $\text{S}_2\text{O}_3^{2-}$ , and the time it takes for its complete consumption (color change of the solution), the rate of the main reaction can be calculated:

$$\text{Rate} = - \frac{\Delta[\text{S}_2\text{O}_3^{2-}]}{\Delta t}$$

Since all the  $\text{S}_2\text{O}_3^{2-}$  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:

$$\text{Rate} = \frac{[\text{S}_2\text{O}_3^{2-}]_{t=0}}{2t}$$

### 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)**

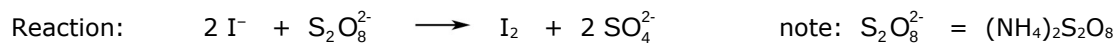


TABLE 1: Reagent concentrations and temperature

[  $\text{Na}_2\text{S}_2\text{O}_3$  ] : \_\_\_\_\_ M      [ KI ] : \_\_\_\_\_ M

[  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  ] : \_\_\_\_\_ M      T : \_\_\_\_\_ °C

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

Exp.	FLASK 1			FLASK 2			Time (s)	
	KI	KCl	$\text{Na}_2\text{S}_2\text{O}_3$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	$(\text{NH}_4)_2\text{SO}_4$	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:

$$[\text{S}_2\text{O}_3^{2-}]_0 = \frac{([\text{Na}_2\text{S}_2\text{O}_3] \text{ reagent}) \times (\text{volume } \text{Na}_2\text{S}_2\text{O}_3)}{\text{total volume}}$$

$$\text{Rate} = \frac{[\text{S}_2\text{O}_3^{2-}]_{t=0}}{2t}$$

$$[\text{S}_2\text{O}_8^{2-}]_0 = \frac{([\text{(NH}_4)_2\text{S}_2\text{O}_8] \text{ reagent}) \times (\text{volume } (\text{NH}_4)_2\text{S}_2\text{O}_8)}{\text{total volume}}$$

$$[\text{I}^-]_0 = \frac{([\text{KI}] \text{ reagent}) \times (\text{volume KI})}{\text{total volume}}$$

*The total volume for each run is 75.0 mL*

TABLE 3: Solution composition and time

Exp.	average time, s	Rate, $\text{M}\cdot\text{s}^{-1}$	[ $\text{S}_2\text{O}_8^{2-}$ ], M	[ $\text{I}^-$ ], M
1				
2				
3				

### Sample calculations

$[\text{S}_2\text{O}_8^{2-}]_0$ (exp 1)	$\text{Rate} = \frac{[\text{S}_2\text{O}_3^{2-}]_{t=0}}{2t}$ (exp 1)
$[\text{S}_2\text{O}_8^{2-}]_0$ (exp 1)	$[\text{I}^-]_0$ (exp 1)
$\text{S}_2\text{O}_8^{2-}$ order determination $\frac{\text{exp 1}}{\text{exp 3}}$	
$\text{I}^-$ 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  $\text{S}_2\text{O}_3^{2-}$  is constant and is the same for everyone.

$[\text{S}_2\text{O}_3^{2-}]$ :

$$[\text{S}_2\text{O}_3^{2-}]_0 = \frac{(0.0036\text{ M})(15.0\text{ mL})}{(75.0\text{ mL})} = 7.2 \times 10^{-4} \text{ M}$$

The same calculations apply to the concentrations of  $[\text{I}^-]_0$  and  $[\text{S}_2\text{O}_8^{2-}]_0$

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:

$$\text{Rate} = \frac{[\text{S}_2\text{O}_3^{2-}]_0}{2t} = \frac{7.2 \times 10^{-4} \text{ M}}{2 \times 30 \text{ s}} = 1.2 \times 10^{-5} \text{ M.s}^{-1}$$

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

Exp.	average time, s	Rate, $\text{M.s}^{-1}$	$[\text{I}^-]_0$ , M	$[\text{S}_2\text{O}_8^{2-}]_0$ , M
1	15.0 s	$2.46 \times 10^{-5} \text{ M.s}^{-1}$	0.144 M	0.072 M
2	30.0 s	$1.23 \times 10^{-5} \text{ M.s}^{-1}$	0.072 M	0.072 M
3	90.0 s	$3.07 \times 10^{-6} \text{ M.s}^{-1}$	0.072 M	0.048 M

$\text{I}^-$  order determination

$$\frac{\text{exp 1}}{\text{exp 2}} : \frac{\text{Rate 1} = k [\text{I}^-]^a [\text{S}_2\text{O}_8^{2-}]^b}{\text{Rate 2} = k [\text{I}^-]^a [\text{S}_2\text{O}_8^{2-}]^b} = \frac{2.46 \times 10^{-5} = k (0.144)^a (0.072)^b}{1.23 \times 10^{-5} = k (0.072)^a (0.072)^b}$$

consequently  $\frac{\text{exp 1}}{\text{exp 2}} : 2 = 1 \times (2)^a \times (1)^b$  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)

$\text{S}_2\text{O}_8^{2-}$  order determination

$$\frac{\text{exp 2}}{\text{exp 3}} : \frac{\text{Rate 2} = k [\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^b}{\text{Rate 3} = k [\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^b} = \frac{1.23 \times 10^{-5} = k (0.072)^1 (0.072)^b}{3.07 \times 10^{-6} = k (0.072)^1 (0.048)^b}$$

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

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

$$\text{Rate} = k [\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^2 \rightarrow k = \frac{\text{Rate}}{[\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^2} \rightarrow k = \frac{1.23 \times 10^{-5} \text{ M.s}^{-1}}{(0.072 \text{ M})^1 (0.072 \text{ M})^2} = 0.033 \text{ M}^{-2} \text{ s}^{-1}$$

Finally, the complete rate law is:

**Rate =  $0.033 \text{ M}^{-2} \text{ s}^{-1} [\text{I}^-]^1 [\text{S}_2\text{O}_8^{2-}]^2$  the overall order of this reaction is 3**

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