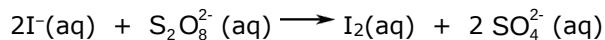


Determination of the Rate Law: Method of the initial rates

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



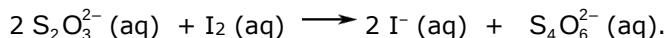
The rate of the reaction (its speed) follows the general equation:

Rate = $k [I^-]^a [S_2O_8^{2-}]^b$	<ul style="list-style-type: none">– The constants "a" and "b" are called the order of the reaction with respect to each reactant.– The sum of both constant "a" and "b" is the overall order of the chemical reaction.– The constant k is called the rate constant of the reaction. Its units depends on the reaction order.
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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 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.



- 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:

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

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)

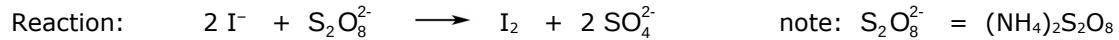


TABLE 1: Reagent concentrations and temperature

[$Na_2S_2O_3$] : _____ 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)

Exp.	FLASK 1			FLASK 2			Time (s)	
	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:

$$[S_2O_3^{2-}]_0 = \frac{([Na_2S_2O_3] \text{ reagent}) \times (\text{volume } Na_2S_2O_3)}{\text{total volume}} \quad \text{Rate} = \frac{[S_2O_3^{2-}]_{t=0}}{2t}$$

$$[S_2O_8^{2-}]_0 = \frac{([(NH_4)_2S_2O_8] \text{ reagent}) \times (\text{volume } (NH_4)_2S_2O_8)}{\text{total volume}} \quad [I^-]_0 = \frac{([KI] \text{ reagent}) \times (\text{volume } KI)}{\text{total volume}}$$

The total volume for each run is 75.0 mL

TABLE 3: Solution composition and time

Exp.	average time, s	Rate, $M \cdot s^{-1}$	[$S_2O_3^{2-}$] ₀ , M	[I^-] ₀ , M
1				
2				
3				

Sample calculations

$[S_2O_3^{2-}]_0$ (exp 1)	$Rate = \frac{[S_2O_3^{2-}]_{t=0}}{2t}$ (exp 1)
$[S_2O_8^{2-}]_0$ (exp 1)	$[I^-]_0$ (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.

$[S_2O_3^{2-}]$:

$$[S_2O_3^{2-}]_0 = \frac{(0.0036\text{ M})(15.0\text{ mL})}{(75.0\text{ mL})} = 7.2 \times 10^{-4} \text{ M}$$

The same calculations apply to the concentrations of $[I^-]_0$ and $[S_2O_8^{2-}]_0$

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:

$$\text{Rate} = \frac{[S_2O_3^{2-}]_0}{2t} = \frac{7.2 \times 10^{-4} \text{ M}}{2 \times 30 \text{ s}} = 1.23 \times 10^{-5} \text{ M.s}^{-1}.$$

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

Exp.	average time, s	Rate, M.s^{-1}	$[I^-]_0, \text{ M}$	$[S_2O_8^{2-}]_0, \text{ M}$
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

I^- order determination

$$\frac{\text{exp 1}}{\text{exp 2}} : \frac{\text{Rate1} = k [I^-]^a [S_2O_8^{2-}]^b}{\text{Rate2} = k [I^-]^a [S_2O_8^{2-}]^b} = \frac{2.46 \times 10^{-5} = k(0.144)^a(0.072)^b}{1.23 \times 10^{-5} = k(0.072)^a(0.072)^b}$$

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)

$S_2O_8^{2-}$ order determination

$$\frac{\text{exp 2}}{\text{exp 3}} : \frac{\text{Rate2} = k [I^-]^1 [S_2O_8^{2-}]^b}{\text{Rate3} = k [I^-]^1 [S_2O_8^{2-}]^b} = \frac{1.23 \times 10^{-5} = k(0.072)^1(0.072)^b}{3.07 \times 10^{-6} = k(0.072)^1(0.048)^b}$$

the result is

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

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

$$\text{Rate} = k [I^-]^1 [S_2O_8^{2-}]^2 \rightarrow k = \frac{\text{Rate}}{[I^-]^1 [S_2O_8^{2-}]^2} \rightarrow k = \frac{1.23 \times 10^{-5} \text{ M.s}^{-1}}{(0.072 \text{ M})^1 (0.072 \text{ M})^2} = 0.033 \text{ M}^{-2} \text{s}^{-1}.$$

Finally, the complete rate law is:

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

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