

6/1/20



Rxn with RLS being studied

$$R = k[I^-]^a [S_2O_8^{2-}]^b$$

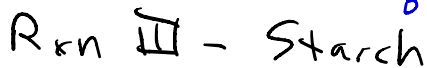
Part A -  $KI$  concentration is changed to determine order  $a$

Part B -  $(NH_4)_2S_2O_8$  concentration is changed to determine order  $b$



Rxn that controls the extent Rxn I occurs

Consumes  $I_3^-$  as it is formed



Rxn that causes the mixture to change colors, signaling the end of the rxn. Starch binds reversibly with  $I_3^-$  to change color.

Calculations

Rate =  $\frac{\Delta[I_3^-]}{\Delta t} = -1 \frac{\Delta[S_2O_3^{2-}]}{\Delta t}$  — Product of rxn with RLS controls "finish line"  
Due to stoichiometry

# original (stock) concentrations

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Reaction	Test Tube	0.2 % Starch	0.012 M	0.20 M	0.20 M
			Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	KI	KNO <sub>3</sub>
1	1A	0.10	0.20	0.80	0.00
2	2A	0.10	0.20	0.40	0.40
3	3A	0.10	0.20	0.20	0.60
4	4A	0.10	0.20	0.10	0.70

Reaction	Test Tube	0.20 M	0.20 M
		(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
1	1B	0.40	0.40
2	2B	0.40	0.40
3	3B	0.40	0.40
4	4B	0.40	0.40

Tables from part A  
Dilution

total volume = 1.9 mL

$$M_{\text{diluted}} = M_{\text{stock}} \cdot \frac{V_{\text{stock}}}{V_{\text{total}}}$$

$$[S_2O_3^{2-}] = 0.012M \cdot \frac{0.0002L}{0.0019L} = 0.00126$$

$$\text{Rate} = \frac{1}{2} \frac{\Delta[S_2O_3^{2-}]}{\Delta t} = \frac{1}{2} \cdot \frac{0.00126}{\Delta t} = 0.00063/\Delta t$$

Calculate order parameter a  
Part A - Reactions 1-4

Reaction	Test Tube	0.2 % Starch	0.012 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.20 M KI	0.20 M KNO <sub>3</sub>
1	1A	0.10	0.20	0.80	0.00
2	2A	0.10	0.20	0.40	0.40
3	3A	0.10	0.20	0.20	0.60
4	4A	0.10	0.20	0.10	0.70

rxn #	time (s)
1	36
2	75
3	133
4	290

In Part A, only [KI] changes in each trial.

Since changing [KI] changes rate (changes time), KI is involved in RLS,

$$\frac{R_1}{R_2} = \frac{k [\text{I}^-]_1^a [\text{S}_2\text{O}_8^{2-}]_1^b}{k [\text{I}^-]_2^a [\text{S}_2\text{O}_8^{2-}]_2^b} \quad [\text{S}_2\text{O}_8^{2-}]_1 = [\text{S}_2\text{O}_8^{2-}]_2 \quad (3)$$

All  $[\text{S}_2\text{O}_8^{2-}]$  same in part A

$$\frac{R_1}{R_2} = \frac{[\text{I}^-]_1^a}{[\text{I}^-]_2^a} = \left( \frac{[\text{I}^-]_1}{[\text{I}^-]_2} \right)^a = 2^a$$

In Part A,  $[\text{I}^-]_1 / [\text{I}^-]_2 = 2$

$$\frac{\text{rate rxn 1}}{\text{rate rxn 2}} = 2^a$$

$$a = \frac{\ln \left( \frac{\text{rate 1}}{\text{rate 2}} \right)}{\ln 2}$$

For part A, rxns 1+2, 2+3, and 3+4 are compared to determine the order parameter  $a$  from data

$$\text{rxn 1 rate} = 0.00063 / 36 = 1.75 \times 10^{-5}$$

$$\text{rxn 2 rate} = 0.00063 / 75 = 8.4 \times 10^{-6}$$

$$a = \frac{\ln \left( \frac{1.75 \times 10^{-5}}{8.4 \times 10^{-6}} \right)}{\ln (2)} = 1.05 \rightarrow 1$$

The rxn is first-order in  $\text{KI}$ .

In part B, reactions 5+6, 6+7, and 7+8 are compared to determine order parameter b.

→ Both reagents turn out to be first order,

$$\rightarrow R = k [I^-] [S_2O_8^{2-}]$$

Reactions 1-8 (Part A + Part B) are used to calculate k.

$$k = R / ([I^-] [S_2O_8^{2-}])$$

These are not the same as the stock concentrations.

$$\begin{aligned} [KI]_{\text{dilute}} &= [KI]_{\text{stock}} \cdot \frac{V_{\text{used}}}{V_{\text{total}}} \\ &= 0.20 \text{ M} \cdot \frac{0.0008 \text{ L}}{0.0019 \text{ L}} = 0.0842 \text{ M} \end{aligned}$$

Determining activation energy

$$k = A e^{-E_a/RT} \quad (\text{Arrhenius})$$

$$\ln k = \ln(A e^{-E_a/RT}) \quad (\text{expression})$$

$$\ln k = \ln A + \ln(e^{-E_a/RT})$$

$$\ln k = \ln A + (-E_a/RT)$$

$$\ln k = -E_a/RT + \ln A$$

$$\underbrace{\ln k}_Y = \underbrace{-\frac{E_a}{R}}_m \cdot \underbrace{\frac{1}{T}}_X + \underbrace{\ln A}_b$$

