Rxn I - $KI + (NH_4)_2S_2O_8 \longrightarrow I_3^-$

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 - $(NH_4)_2S_2O$ & concentration is changed to determine order b

Rxn II - $Na_2S_2O_3 + I_3^-$] controls stoichiometry

Rxn that controls the extent Rxn I occurs

Consumes I_3^- as it is formed

Rxn III - Starch

Rxn that causes the mixture to change colors, signaling the end of the rxn.

Starch binds reversibly with I_3^- to change color.

Calculations

Product of rxn with RLS

$$\text{Rate} = \frac{\Delta[I_3^-]}{\Delta t} = -\frac{1}{2}\frac{\Delta[S_2O_3^{-2}]}{\Delta t}$$

controls "finish line"

Due to stoichiometry

original (stock) concentrations

Reaction	Test Tube	0.2 % Starch	0.012 M $Na_2S_2O_3$	0.20 M KI	0.20 M KNO_3
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 $(NH_4)_2S_2O_8$	0.20 M $(NH_4)_2SO_4$
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

total volume = 1.9 mL

Dilution

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

$$[S_2O_3^{-2}] = 0.012M \cdot \frac{.0002L}{.0019L} = 0.00126$$

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

$$= 0.00063/\Delta t$$

Calculate order parameter q

Part A- Reactions 1-4

Reaction	Test Tube	0.2 % Starch	0.012 M $Na_2S_2O_3$	0.20 M KI	0.20 M KNO_3
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,

$$\frac{R_1}{R_2} = \frac{k[I^-]_1^a [S_2O_8^{-2}]_1^b}{k[I^-]_2^a [S_2O_8^{-2}]_2^b}$$

$[S_2O_8^{-2}]_1 = [S_2O_8^{-2}]_2$

All $[S_2O_8^{-2}]$ same in part A

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

In Part A, $[I^-]_1 / [I^-]_2 = 2$

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

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

For part A, rxns 1+2, 2+3, and 3+4 are compared to determine the order parameter (a)

from data

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

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 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,

→ $R = k[I^-][S_2O_8^{-2}]$

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.

$$[KI]_{dilute} = [KI]_{stock} \cdot \frac{V_{used}}{V_{total}}$$

$$= 0.20\,M \cdot \frac{0.0008\,L}{0.0019\,L} = 0.0842\,M$$

Determining activation energy

$$k = Ae^{-Ea/RT}$$ (Arrhenius expression)

$$\ln k = \ln\left(Ae^{-Ea/RT}\right)$$

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

$$\ln k = \ln A + \left(-Ea/RT\right)$$

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

$$\underbrace{\ln k}_{Y} = \underbrace{-\frac{Ea}{R}}_{m} \cdot \underbrace{\frac{1}{T}}_{X} + \underbrace{\ln A}_{b}$$