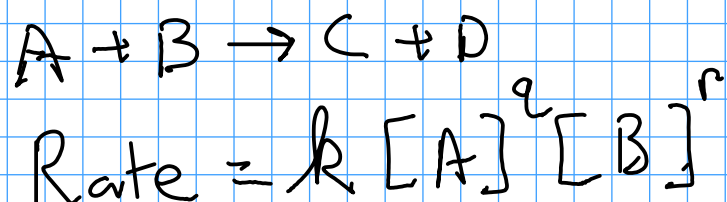


## Initial rates method:

- To determine the rate constant and reaction orders in a reaction, it's possible to monitor the rate of a reaction starting from time zero to a short time later where the concentrations of the reactants haven't changed much. In other words, we look at the INITIAL RATE.

- To determine the rate constant and orders, we need to perform several experiments - one for each order to determine and one baseline experiment to determine the rate constant.

Example:



... we want to find the rate constant 'k', and the orders 'q' and 'r'.

Trial	[A]	[B]	Rate $\frac{\Delta [A]}{s}$	
1	0.150	0.150		Baseline experiment
2	0.300	0.150		Double (A) to find 'q'
3	0.150	0.300		Double (B) to find 'r'

Trial	[A]	[B]	Rate $\frac{\Delta [A]}{s}$
1	0.150	0.150	0.0016875
2	0.300	0.150	0.0033750
3	0.150	0.300	0.0067500

The rate law is:

$$\text{Rate} = k [A]^q [B]^r$$

... so how do we use the data above to find out the values of 'k', 'q', and 'r'?

We observe that in the second trial ((A) doubled), the rate has doubled!

$$(2 \times [A])^q = 2 \times \text{Rate}; \quad q = 1$$

We observe that in the third trial ((B) doubled), the rate has quadrupled.

$$(2 \times [B])^r = 4 \times \text{Rate}; \quad r = 2$$

$$\text{Rate} = k [A] [B]^2$$

Trial	[A]	[B]	Rate $\frac{\Delta[A]}{s}$	Calculated 'k'
1	0.150	0.150	0.0016875	0.500
2	0.300	0.150	0.0033750	0.500
3	0.150	0.300	0.0067500	0.800

$$\text{Rate} = k[A][B]^2$$

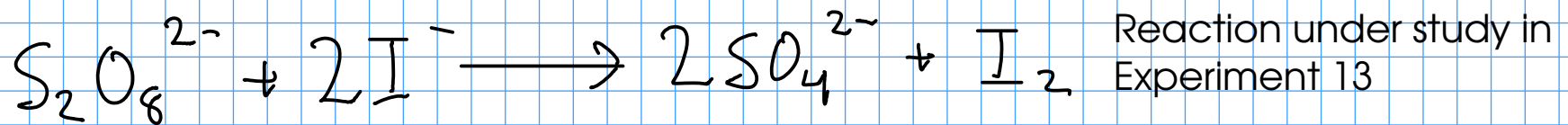
Now, we'd like to know the value of 'k'. Solve rate law for 'k'.

$$k = \frac{\text{Rate}}{[A][B]^2}$$

Plug in each set of data to this equation and calculate 'k'!

The average of these calculated 'k' values equals the rate constant.  
(For real data, expect some experimental error in these numbers!)

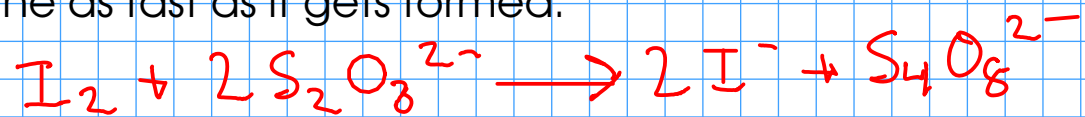
$$\text{Rate} = 0.500[A][B]^2$$



How do we monitor this? IODINE ( $\text{I}_2$ ) will form a complex with starch, forming an intense BLUE COLOR.

It would be nice to DELAY the formation of blue color (somehow) until a certain amount of iodine had been formed!

We can delay the formation of blue color by using a FAST side reaction to consume iodine as fast as it gets formed.



... so when all of the thiosulfate ion is consumed, the reaction vessel will contain iodine and turn blue. At that point,

$$\Delta[\text{S}_2\text{O}_8^{2-}] = \frac{1}{2} [\text{S}_2\text{O}_8^{2-}]_{\text{initial}}$$

$$\text{Rate} = \frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\text{time}}$$

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}]^a [\text{I}^-]^n$$