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:

$$A + B \rightarrow C + D$$

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

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

Trial	[A]	[B]	Rate $\frac{\Delta[A]}{sec}$	
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 $\frac{\Delta[A]}{sec}$	
1	0.150	0.150	0.0016875	Baseline experiment
2	0.300	0.150	0.0033750	Double (A) to find 'q'
3	0.150	0.300	0.0067500	Double (B) to find 'r'

$$Rate = k[A]^q[B]^r$$

... 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!

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

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

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

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

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

$$Rate = k[A][B]^2$$

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

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

Trial	[A]	[B]	Rate $\frac{\Delta[A]}{sec}$	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	0.500

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

$$Rate = 0.500[A][B]^2$$

THE IODINE CLOCK REACTION

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

Reaction under study in Experiment 13

How do we monitor this? IODINE (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. Thiosulfate ion reacts with iodine quickly.

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_8^{2-}$$

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

$$\Delta[S_2O_8^{2-}] = \frac{1}{2}[S_2O_3^{2-}]_{initial}$$

$$Rate = \frac{\Delta[S_2O_8^{2-}]}{time}$$

$$Rate = k[S_2O_8^{2-}]^q[I^-]^r$$