LECTURE DEMONSTRATION #1 (CLOCK REACTION)

The aqueous reaction between two anions, peroxydisulfate ($S_2O_8^{2-}$) and thiosulfate ($S_2O_3^{2-}$), to form sulfate (SO_4^{2-}) and dithionate ($S_4O_6^{2-}$) anions is accelerated by iodide (I^-). In the course of the reaction, iodide is converted to triiodide (I_3^-) temporarily, then I_3^- is returned to I^-. Consequently, I_3^- is an **intermediate** and iodide is a **catalyst**. The **net reaction** is, therefore,

$$\underset{\text{peroxydisulfate}}{S_2O_8^{2-}} \;+\; \underset{\text{thiosulfate}}{2\,S_2O_3^{2-}} \;\rightarrow\; \underset{\text{sulfate}}{2\,SO_4^{2-}} \;+\; \underset{\text{dithionate}}{S_4O_6^{2-}}$$

while the two reactions involving the consumption and re-generation of the catalyst are

$$S_2O_8^{2-} + 3\,I^- \rightarrow 2\,SO_4^{2-} + I_3^-$$
$$2\,S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3\,I^-$$

which, you'll note, add to the net reaction.

Our goal is to find the kinetic rate law, which we'll assume has the general form

$$Rate = -\frac{d\,[S_2O_8^{2-}]}{dt} = k\,[S_2O_8^{2-}]^m\,[I^-]^n$$

where *k* is the rate constant, and *m* and *n* are **reaction order exponents**. These are the quantities we seek, and here's how we'll do it. Triiodide (itself colorless) forms a colored complex with starch, but, since the step that destroys triiodide is faster than its reaction with starch, **no color can form as long as some of the thiosulfate reactant is present**. As soon as the thiosulfate is gone, the color rapidly appears (as long as some peroxydisulfate and iodide are present, which we'll ensure is the case). Thus, our primary data are initial concentrations and the time τ required for the color to appear after the solution is initially mixed.

If we make the initial amount of peroxydisulfate much larger than the initial amount of thiosulfate, we will be able to measure a very good approximation to the **initial rate**:

$$Rate \;=\; -\frac{d\,[S_2O_8^{2-}]}{dt} \;\cong\; -\frac{[S_2O_8^{2-}]_{t\,=\,\tau} - [S_2O_8^{2-}]_{t\,=\,0}}{\tau}$$

We'll measure **τ** for three different reaction mixtures:

Reagent	**Mixture A**	**Mixture B**	**Mixture C**
0.01 **M** $Na_2S_2O_3$	100 mL	100 mL	100 mL
0.2 **M** KI	250 mL	250 mL	125 mL
Starch Indicator	25 mL	25 mL	25 mL
0.2 **M** $Na_2S_2O_8$	250 mL	125 mL	250 mL
0.2 **M** Na_2SO_4	0 mL	125 mL	0 mL
0.2 **M** KNO_3	0 mL	0 L	125 mL

Note that the total volume of each solution is the same, 625 mL. The KNO_3 added in mixture C is chemically inert. It is there simply to keep the total ion concentration constant in all three mixtures. The table on the next page should be completed in advance so that experimental data can be added in class as they are collected.

Clock Reaction Data and Calculations

The table below should be completed in advance, except for the boxes with the thicker outline which rely on data we will measure in lecture.

	MIXTURE A	**MIXTURE B**	**MIXTURE C**
$[S_2O_3^{2-}]_{t=0}$			
$[S_2O_8^{2-}]_{t=0}$			
$[I^-]_{t=0}$			
$[S_2O_8^{2-}]_{t=\tau}$			
τ/s			
Rate/ (units?)			
k/ (units?)			

Once τ has been measured for each mixture, the *Rate* can be calculated from the expression on the previous page. Comparison between experiments with different initial concentrations allow us to find the reaction orders *m* and *n*. Once we know these orders, the rates, and the initial concentrations, we can find *k* and deduce its units. We end with the full rate expression. (You should fill in the boxes.)

$$Rate = -\frac{d\,[S_2O_8^{2-}]}{dt} = \boxed{}\,[S_2O_8^{2-}]^{\boxed{}}\,[I^-]^{\boxed{}}$$