Kinetics

Directions: This question is a long free-response question that requires about 23 minutes to answer and is worth 10 points. Show your work for each part in the space provided after that part. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.

In a chemistry class, students study the rates of three different chemical reactions. Answer questions about these three reactions, as shown below.

(a) A chemistry student studies the reaction of the peroxydisulfate ion with iodide ions, as shown in the balanced equation below. She carries out three different trials to measure the initial rate of formation of $I_3^-(aq)$, and the results are given in the table.

$$S_2O_8^{2-}(aq) + 3\,I^-(aq) \rightarrow 2\,SO_4^{2-}(aq) + I_3^-(aq)$$

Trial	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate of Formation of I_3^-
1	0.250 *M*	0.100 *M*	1.55×10^{-4} mol·L^{-1}·s^{-1}
2	0.500 *M*	0.100 *M*	3.10×10^{-4} mol·L^{-1}·s^{-1}
3	0.250 *M*	0.300 *M*	4.65×10^{-4} mol·L^{-1}·s^{-1}

(i) Write the rate law for the reaction.

Using Trials 1 and 2, $S_2O_8^{2-}$ doubles as rate doubles, so $S_2O_8^{2-}$ is 1st order.
Using Trials 1 and 3, I^- triples as rate triples, so I^- is 1st order.
Rate = $k[S_2O_8^{2-}][I^-]$
(1 point for determining or implying orders, 1 point for the correctly written rate law.)

(ii) Determine the rate constant of the reaction at this temperature, with appropriate units.

Rate = $k[S_2O_8^{2-}][I^-]$ Substitute data from any trial into the rate law (using Trial 1 here):
$(1.55 \times 10^{-4}\ \text{mol·L}^{-1}\text{·s}^{-1}) = k(0.250\ \text{mol·L}^{-1})(0.100\ \text{mol·L}^{-1})$
$k = \mathbf{6.20 \times 10^{-3}\ L·mol^{-1}·s^{-1}}$

(iii) Use the data above the calculate the initial rate of appearance of SO_4^{2-} in Trial 3.

Using the mole ratios from the balanced equation:
$\text{Rate}_{SO_4^{2-}} = 2 \times \text{Rate}_{I_3^-}$
$\text{Rate}_{SO_4^{2-}} = 2 \times (4.65 \times 10^{-4}\ \text{mol·L}^{-1}\text{·s}^{-1})$
$\text{Rate}_{SO_4^{2-}} = \mathbf{9.30 \times 10^{-4}\ mol·L^{-1}·s^{-1}}$

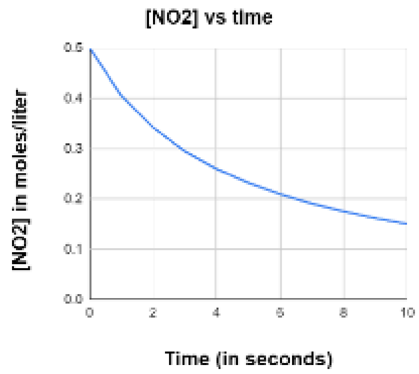
(iv) The student makes the claim that the reaction of peroxydisulfate with iodide ions take place in one step. Do you agree or disagree with the student's claim? Use information given in the balanced equation and/or the data table to defend your answer.

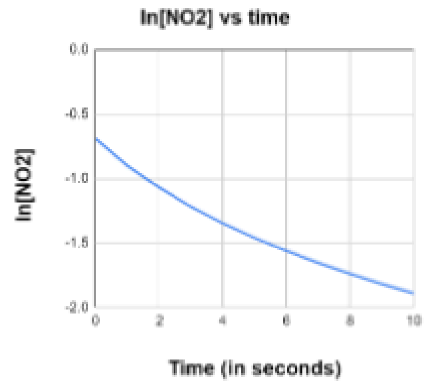
I disagree. If the reaction rate were to take place in one step, four molecules would be colliding simultaneously. Since that is very unlikely, the reaction is also unlikely to take place in one step. Also, the rate law indicates that the reaction is first order with regard to I^-. If the reaction took place in one step, the reaction would be third order with respect to I^-. The experimental rate law does not allow for the reaction to take place in just one step. (1 point for either or both of these reasons)

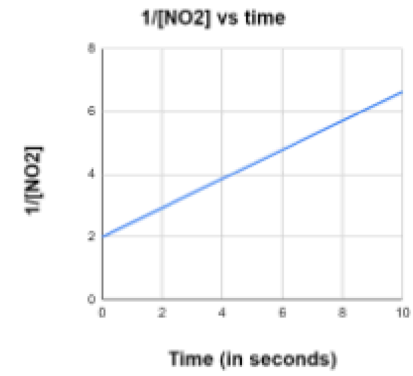
(b) Another student studies the rate of reaction for the decomposition of NO_2 gas, as represented by the following equation.

$$NO_2(g) \rightarrow NO(g) + O(g)$$

He makes three graphs, comparing the concentration of $[NO_2]$ versus time, the natural logarithm of $[NO_2]$ versus time, and $1/[NO_2]$ versus time, as shown below.







(i) Write the rate law for this reaction.

Rate = $k[NO_2]^2$

(ii) Without doing any calculations, state how the student could determine the rate constant for this reaction.

Calculate the slope of the graph of $\frac{1}{[NO2]}$ versus time. The slope of this graph is equal to the rate constant.

(c) A different student studies the two-step reaction mechanism shown below:

$$NO_2Cl \rightarrow NO_2 + Cl \qquad \text{(slow)}$$

$$\underline{NO_2Cl + Cl \rightarrow NO_2 + Cl_2} \qquad \text{(fast)}$$

$$2\,NO_2Cl \rightarrow 2\,NO_2 + Cl_2$$

(i) The student notes that Cl appears in the reaction mechanism, although it does not appear in the overall balanced equation. Explain the purpose of Cl in this mechanism.

Cl acts as a **reaction intermediate**, since it is produced in an early step and used up in a later step.

(ii) Write the rate law for this reaction.

Rate = $k[NO_2Cl]$

(iii) As the reaction proceeds, the concentration of NO_2Cl decreases. If the rate constant for this reaction at a certain temperature is equal to 3.6×10^{-2} min^{-1}, calculate the time required for the concentration of NO_2Cl to drop from 1.0×10^{-2} M to 9.4×10^{-4} M at this temperature.

$$\ln[A]_t - \ln[A]_0 = -k\,t$$

$$\ln(9.4 \times 10^{-4}) - \ln(1.0 \times 10^{-2}) = -(3.6 \times 10^{-2})(t)$$

$$-2.36 = -(3.6 \times 10^{-2})(t)$$

$$\mathbf{t = 66\ min}$$