

# Unit Exam: Kinetics

On the following pages are problems covering material in kinetics. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer a question, then move on to another question; working on a new question may suggest an approach to a question that is more troublesome. If a question requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation and that work is relevant to the question.

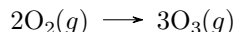
Problem	Points	Maximum	Problem	Points	Maximum
1	33.3	40	3	15.3	20
2	16.5	20	4	13.6	20
			Total	78.5	100

high score	scores 100–90	scores 89–80	scores $\leq 79$
98	3	6	11

A few constants are given here; other information is included within individual problems.

- density ( $d$ ) of water is 1.00 g/mL
- specific heat ( $S$ ) of water is 4.184 J/g  $\cdot$   $^{\circ}$ C
- the gas constant ( $R$ ) is 8.314 J/mol<sub>rxn</sub>  $\cdot$  K
- Faraday's constant ( $F$ ) is 96,485 J/V  $\cdot$  mol e<sup>-</sup>
- water's dissociation constant ( $K_w$ ) is  $1.00 \times 10^{-14}$

**Problem 1.** Ozone,  $O_3$ , is a powerful oxidizing agent that finds many uses including as a disinfectant for drinking water where it kills bacteria and viruses. Ozone is inherently unstable, decomposing to  $O_2$ .



The rate law for its decomposition follows the general rate law  $R = k[O_3]^\alpha$ . The rate of the reaction is easy to study because  $O_3$ , but not  $O_2$ , absorbs light at a wavelength of 254 nm. The set of plots on the next page show three views of the result of a single experiment in which the absorbance of  $O_3$  was followed as a function of time; the data is from Manning, et. al. *Chem. Educator* **2002**, 7, 278–283.

Based on these plots, report values for  $\alpha$  and for  $k$  (with units). Be sure it is clear how you arrived at your results.

**Answer.** *Note: Recall that from Beer's law absorbance is a linear function of concentration; thus, we can use absorbance as a proxy for concentration here and elsewhere in this problem.* Of the three plots, the one that is linear is  $\ln[\text{absorbance}]$  as a function of time, which is the linear integrated form of the rate law for a first-order reaction; thus, we know that  $\alpha$  is 1. The slope of this line—which you can determine by drawing the best straight line through the data, selecting two points on the line and calculating the change in  $y$  for a change in  $x$ —is  $-0.022$ , which gives  $k$  as  $0.022 \text{ min}^{-1}$

What is the half-life for the reaction? Be sure it is clear how you arrived at your value.

**Answer.** There are two ways to find the half-life. First, you can use the plot that shows the absorbance of as a function of time and find the time to decrease any initial absorbance by 50%. Second, you can solve for the half-life using your value for  $k$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.022 \text{ min}^{-1}} = 31.5 \text{ min}$$

How long will it take for the concentration of  $O_3$  to decrease to just 1.0% of its original value? Be sure it is clear how you arrived at your answer.

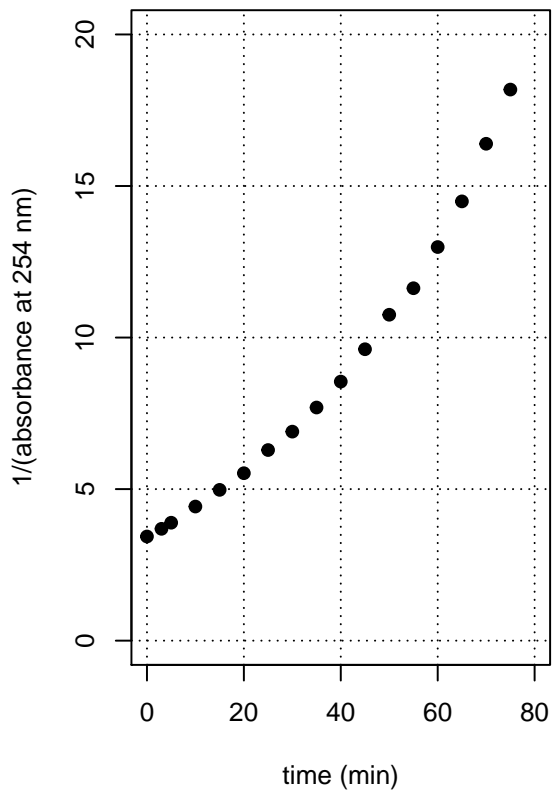
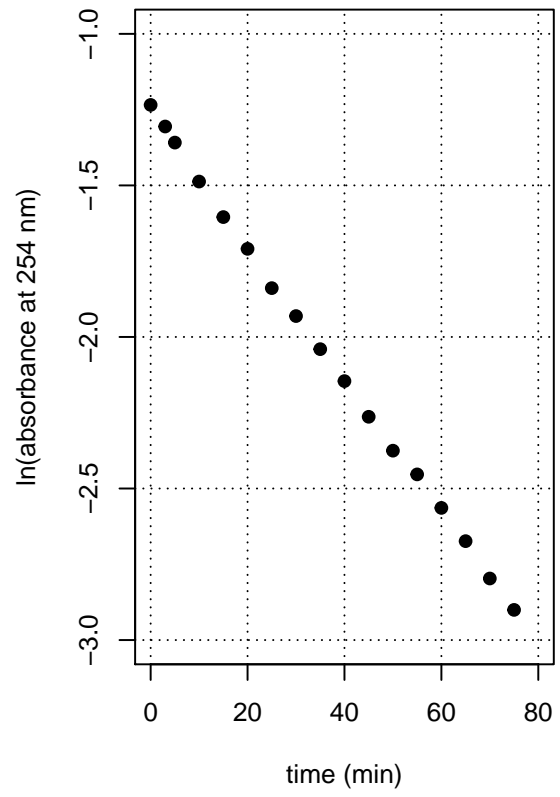
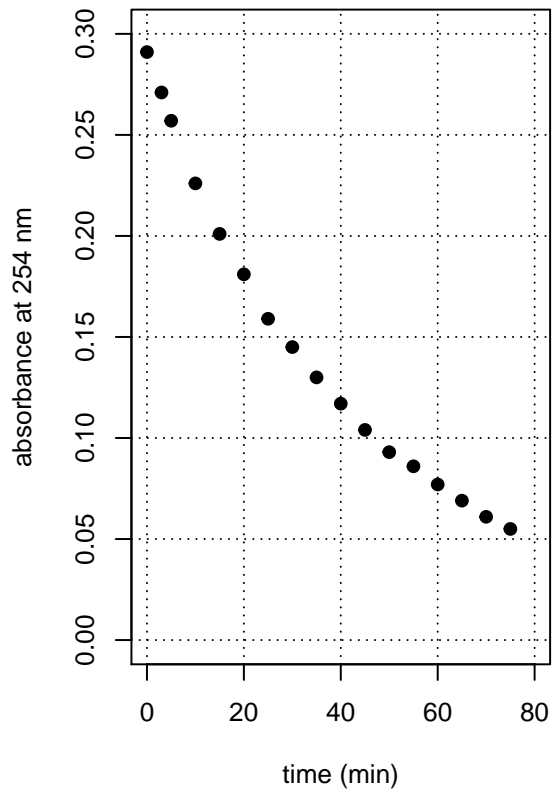
**Answer.** For a first-order reaction, we know that  $\ln[\text{absorbance}]_t = \ln[\text{absorbance}]_o - kt$ . If we begin with an absorbance of 1, then we have

$$\ln(0.01) = \ln(1) - (0.022 \text{ min}^{-1}) \times t$$

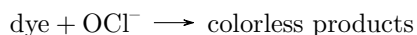
which gives  $t$  as 210 min.

Based on your rate law, is it possible for the reaction to take place in a single step? Explain your reasoning in 1–3 sentences.

**Answer.** No. If the reaction occurs in just a single step, then from collision theory we know that the rate law must be second-order in  $O_3$ . As it is first-order in  $O_3$ , the reaction must have more than one step.



**Problem 2.** This semester we did not have the opportunity to complete the lab entitled “Kinetics of the Bleaching of a Dye.” In this experiment we study how household bleach, which is a solution of NaOCl, breaks down a commercial food coloring, which serves as the dye. The reaction is



The rate law for the reaction follows the rate law  $R = k[\text{dye}]^\alpha[\text{OCl}^-]^\beta$ .

The kinetics of this reaction are studied by monitoring the absorbance of the dye as a function of time under pseudo-order conditions in which the rate law reduces to  $R = k_{\text{obs}}[\text{dye}]^\alpha$ . In one such experiment, the concentration of dye is 10.1  $\mu\text{M}$  and the concentration of bleach is 0.0518 M. An analysis of the data shows that the reaction is *first-order in dye* with an observed rate constant of 0.00236  $\text{s}^{-1}$ . Three additional experiments using the same concentration of dye, but varying concentrations of bleach, yield the following results (all results are from Kalmatsky *J. Chem. Educ.* **2013**, *90*, 1708–1709):

[NaOCl] (M)	$k_{\text{obs}}$ ( $\text{s}^{-1}$ )
0.103	0.00466
0.207	0.00959
0.311	0.01350

Using this data, report values for the reaction order for bleach,  $\beta$ , and for the reaction’s rate constant,  $k$ . Be sure it is clear how you arrived at your values.

**Answer.** To determine the reaction order for bleach, we compare the concentrations of bleach and the observed rate constant for any pair of experiments. For example, using the first two values in the table, we see that doubling the concentration of NaOCl results in a doubling of the observed rate constant; thus, we know that  $\beta = 1$  and that the reaction is first-order in NaOCl.

To find the rate constant,  $k$ , we note that  $k = k_{\text{obs}} \times [\text{NaOCl}]$ . Substituting in the observed rate constant and concentration of bleach for any experiment gives  $k$  as 0.045  $\text{M}^{-1} \text{s}^{-1}$ .

In 2–5 sentences, explain why it was necessary to study this reaction using pseudo-order conditions in which the concentration of dye always is significantly smaller than the concentration of bleach.

**Answer.** The key to this experiment is that we follow the reaction’s progress by monitoring the dye’s absorbance. If we run experiments where the  $[\text{dye}]$  is significantly greater than the  $[\text{NaOCl}]$ , then the dye’s concentration will not change; as a result, the absorbance of the reaction mixture will not change, which means we have no kinetic data available to us.

**Problem 3.** The decomposition of  $\text{H}_2\text{O}_2$ , as we know from our work in lab, is an exothermic reaction with a  $\Delta H$  of approximately  $-96 \text{ kJ/mol}_{\text{rxn}}$  for the reaction  $\text{H}_2\text{O}_2(aq) \rightarrow \text{H}_2\text{O}(l) + \frac{1}{2} \text{O}_2(g)$ . We also know that the reaction is very slow in the absence of a catalyst, but quite rapid when a catalyst is present. To determine a reaction's activation energy it is necessary to measure the reaction's rate at two or more temperatures, a task that can require a great deal of time and access to equipment to maintain a constant temperature.

Interestingly, it is possible to estimate the activation energy using data from a single calorimetry experiment—such as that you completed in lab—because the reaction's rate changes as heat is released and the solution warms up. The two plots on the following page, for example, show the original calorimetry data on the top and a transformation of that data into an Arrhenius plot. The equation of the best fit line through the Arrhenius plot data gives a slope of  $-6882$  and a  $y$ -intercept of  $19.90$ . The data shown are from Sweeney, et. al. *J. Chem. Educ.* **2014**, *91*, 1216–1219 and uses  $\Gamma^-$  as a catalyst.

Report values for the reaction's activation energy,  $E_a$ , and for the Arrhenius factor,  $A$ . Be sure it is clear how you arrived at your results.

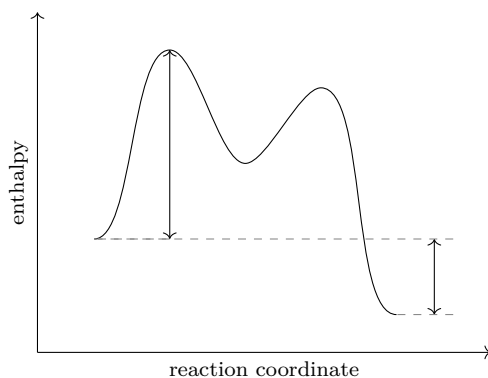
**Answer.** The Arrhenius equation is  $k = Ae^{-E_a/RT}$ , which we can rewrite in logarithmic form as

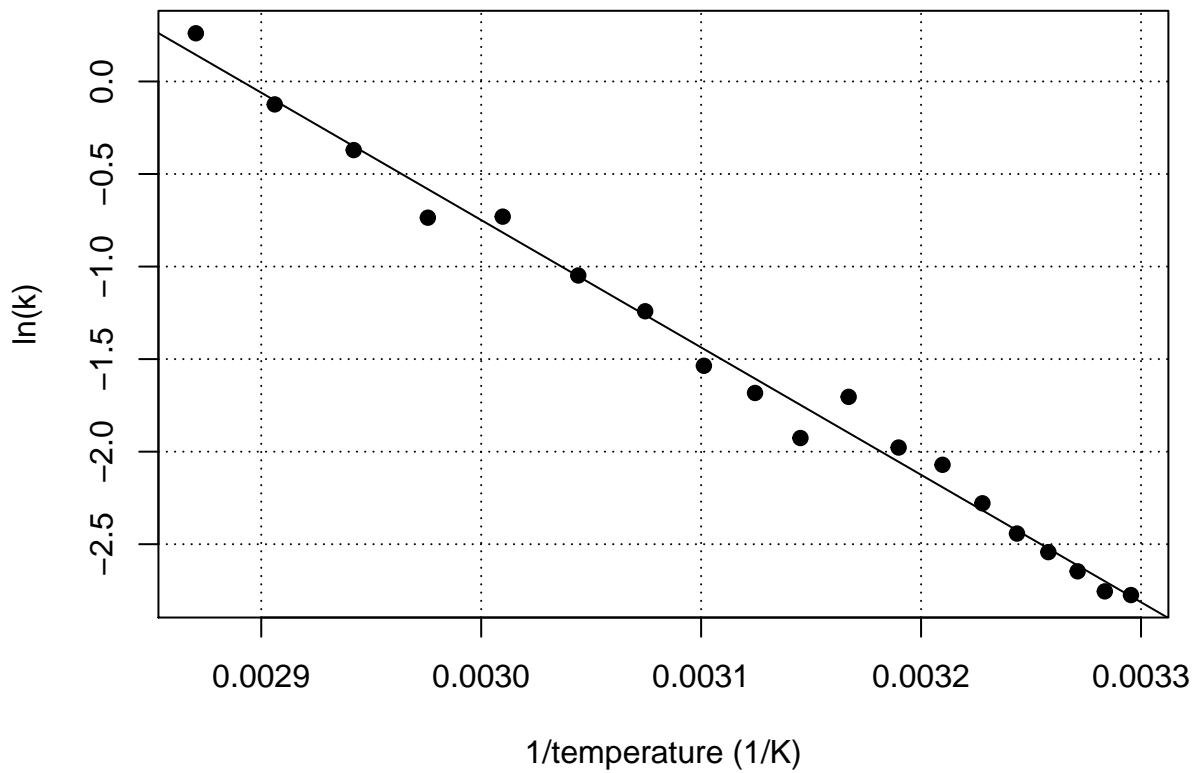
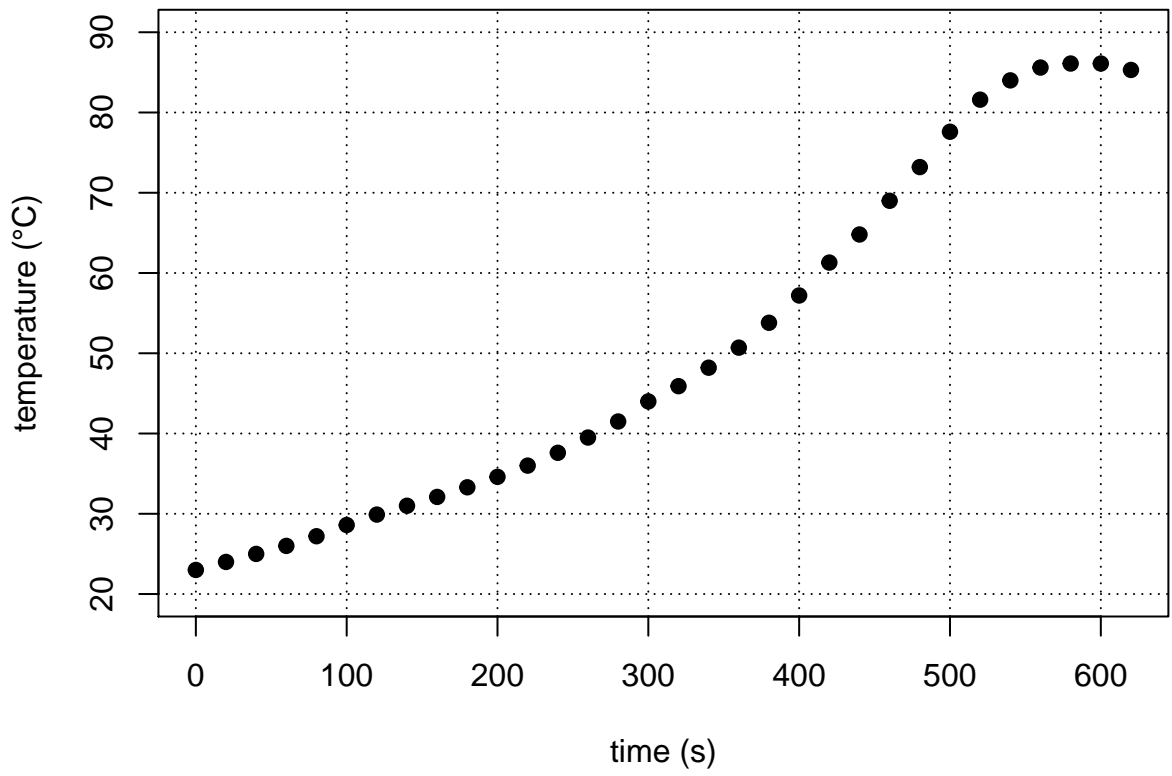
$$\ln(k) = \ln A - (E_a/R) \times (1/T)$$

This equation is in the form of a straight-line with slope that is equal to  $-E_a/R$  and a  $y$ -intercept that is equal to  $\ln(A)$ . Substituting in the experimental slope of  $-6882$  and solving gives the activation energy as  $57,200 \text{ J/mol}$ , or  $57.2 \text{ kJ/mol}$ . Substituting in the experimental  $y$ -intercept of  $19.90$  and solving gives  $A$  as  $4.4 \times 10^8 \text{ s}^{-1}$ . Note that the activation energy must be positive.

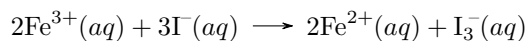
As we discussed in class, the mechanism for this reaction is believed to consist of two steps, the first of which is the rate-determining step in which  $\text{HOI}^-$  is an intermediate. Draw a reaction energy diagram for this reaction that shows enthalpy on the  $y$ -axis. For the  $x$ -axis, place the reactants on the left, the products on the right, and the intermediate in the middle. Label your graph to show  $\Delta H$  and  $E_a$ . Note that the activation energy here is a form of enthalpy.

**Answer.** The energy diagram is shown below. There are three essential features that your diagram must show: (a) there must be two activation energy barriers, one for each step; (b) the first activation energy barrier must be larger than the second because the first step is the rate-determining step; and (c) the enthalpy of the products must be lower than the enthalpy of the reactants because the reaction is exothermic. The arrow on the left shows the reaction's activation energy and the arrow on the right shows the reaction's change in enthalpy.

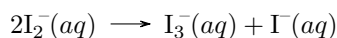
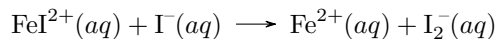
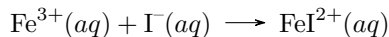




**Problem 4.** The oxidation of  $\text{I}^-$  by  $\text{Fe}^{3+}$  has an overall stoichiometry of



Bauer, et. al. (*J. Chem. Educ.* **2008**, *85*, 1123–1125) propose that the mechanism for the reaction involves three distinct steps, the third of which occurs just once for every two times that the first two reactions occur.



The third step is known to be much faster than either the first step or the second step. Explain how you can use a kinetic study to determine if it is the first step or the second step that is rate-determining. You may assume that any step that precedes the rate-determining step is at equilibrium.

**Answer.** First, we need to predict the rate law for the two possible scenarios: that the first step is the rate-determining step or that the second step is the rate-determining step. If the first step is the RDS, then the rate law simply is

$$R = k_1[\text{Fe}^{3+}][\text{I}^-]$$

where  $k_1$  is the rate constant for the mechanism's first step. If the second step is the RDS, then rate law is

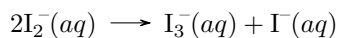
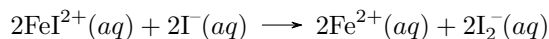
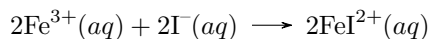
$$R = k_2[\text{FeI}^{2+}][\text{I}^-] = k_2K_1[\text{Fe}^{3+}][\text{I}^-]^2$$

where  $k_2$  is the rate constant for the mechanism's second step and  $K_1$  is the equilibrium constant for the mechanism's first step, which we assume is at equilibrium. Note that the reaction is first-order in  $\text{Fe}^{3+}$  in both cases, but that it is first-order in  $\text{I}^-$  if the first step is the RDS and second-order if the second step is the RDS.

A simple way to determine the reaction's experimental rate law with respect to iodide is to use the initial rate method to determine the reaction order for iodide.

A mechanism must explain the reaction's overall stoichiometry. Show that this is true for this proposed mechanism.

**Answer.** One of the requirements for collision theory is that the mechanisms steps must add together to yield the reaction's overall stoichiometry. We are told that the third step happens once for every two times that the first reaction occurs; thus



Adding these together and simplifying yields the overall reaction of

