

Unit Exam: Kinetics

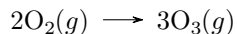
On the following pages are problems covering material in kinetics. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer a question, then move on to another question; working on a new question may suggest an approach 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		40	3		20
2		20	4		20
			Total		100

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_{rxn} \cdot K
- Faraday's constant (F) is 96,485 J/V \cdot mol e⁻
- water's dissociation constant (K_w) is 1.00×10^{-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 .



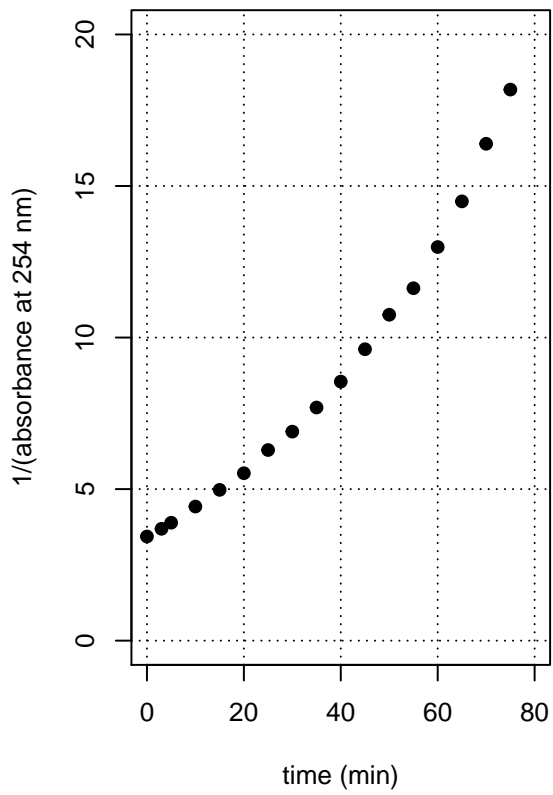
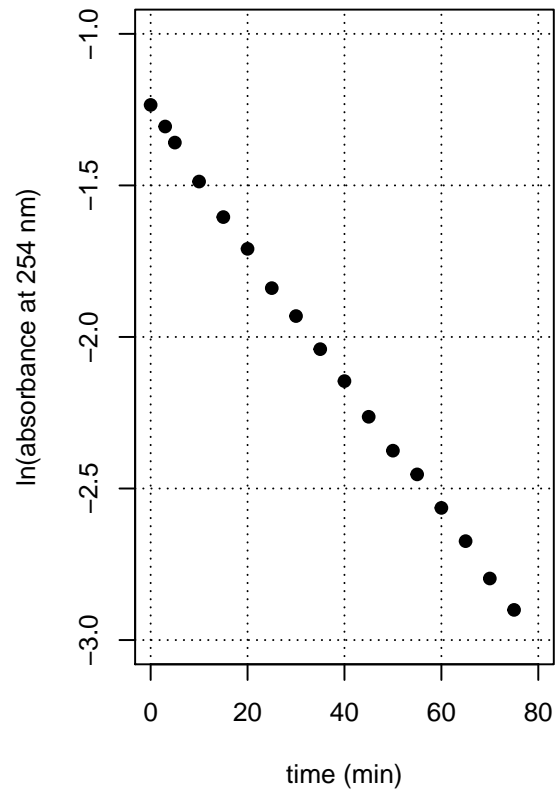
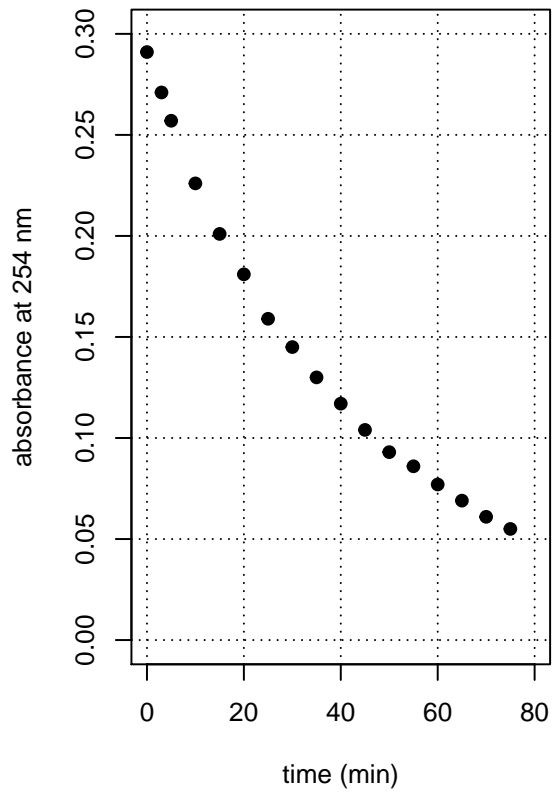
The rate law for its decomposition follows the general rate law $R = k[O_3]^\alpha$. The rate of the reaction is easy to study because O_3 , but not O_2 , absorbs light at a wavelength of 254 nm. The set of plots on the next page show three views of the result of a single experiment in which the absorbance 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 α and for k (with units). Be sure it is clear how you arrived at your results.

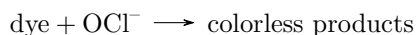
What is the half-life for the reaction? Be sure it is clear how you arrived at your value.

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.

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.



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 μM 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 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_{obs} (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, β , and for the reaction’s rate constant, k . Be sure it is clear how you arrived at your values.

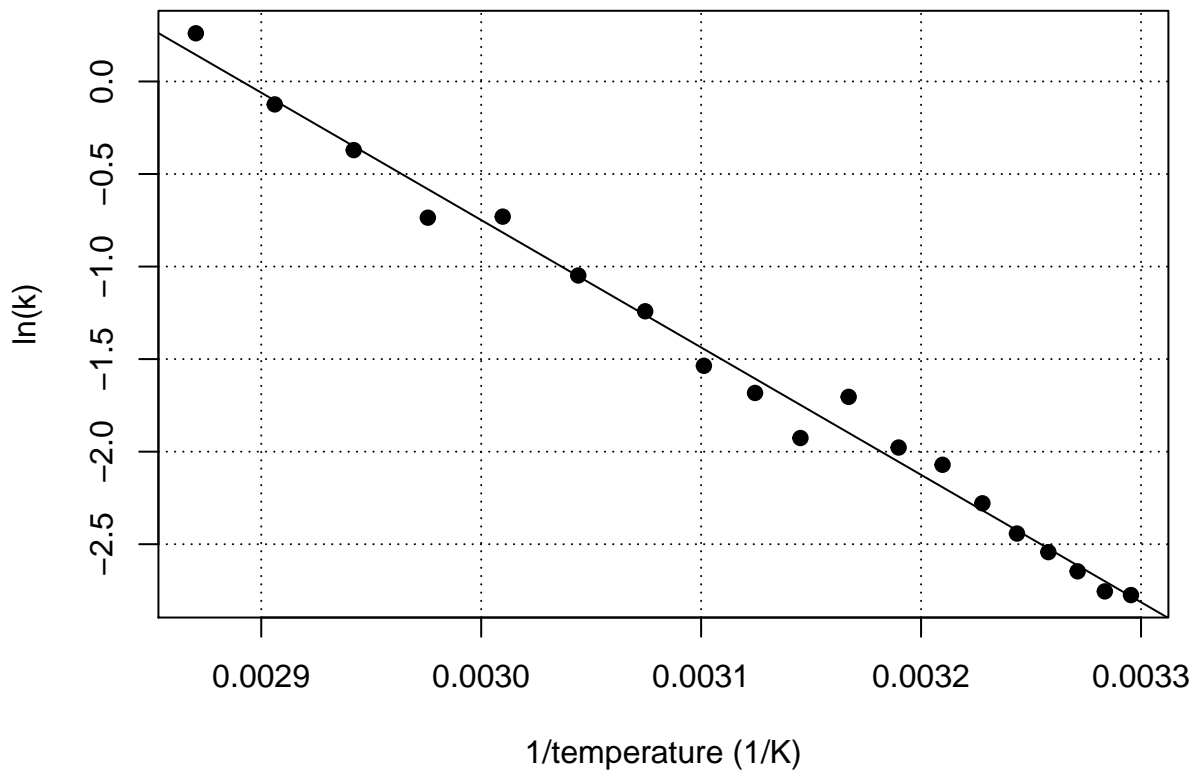
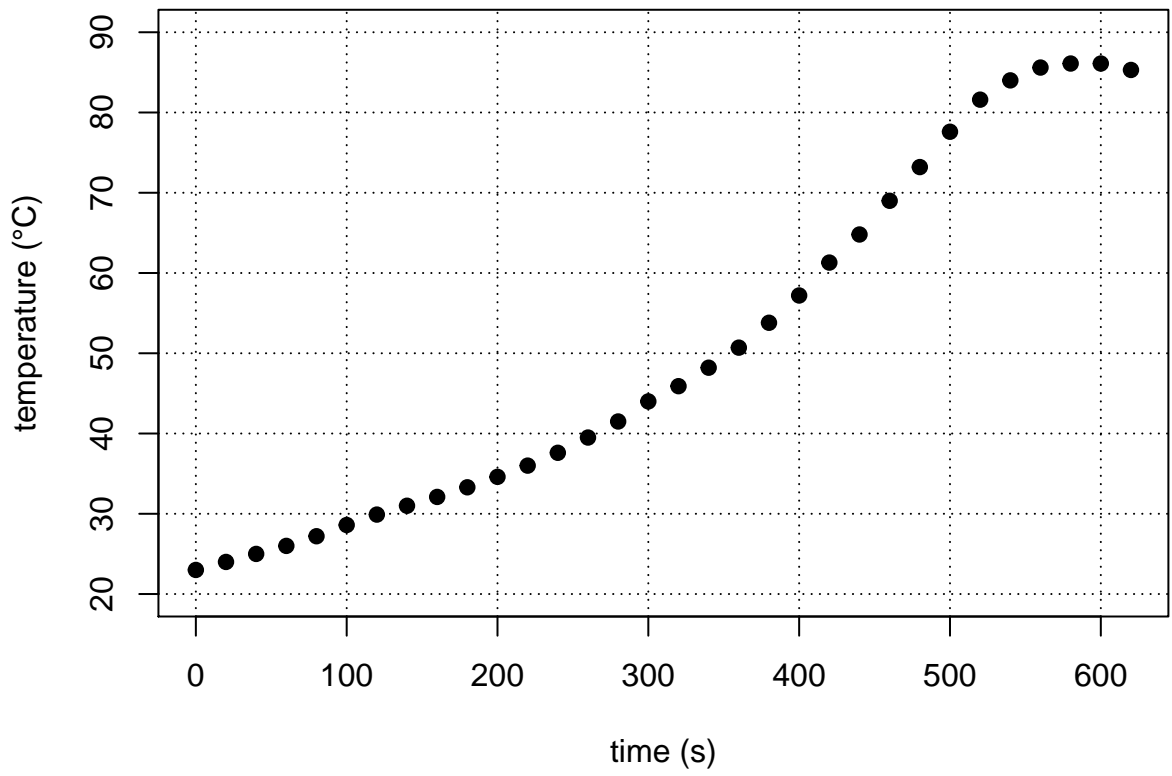
In 2–5 sentences, explain why it was necessary to study this reaction using pseudo-order conditions in which the concentration of dye always is significantly smaller than the concentration of bleach.

Problem 3. The decomposition of H_2O_2 , as we know from our work in lab, is an exothermic reaction with a ΔH 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.

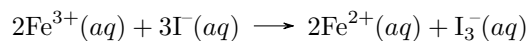
Interestingly, it is possible to estimate the activation energy using data from a single calorimetry experiment—such as that you completed in lab—because the reaction's rate changes as heat is released and the solution warms up. The two plots on the following page, for example, show the original calorimetry data on the left 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 I^- 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.

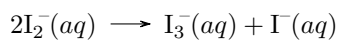
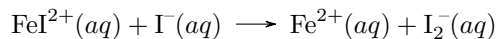
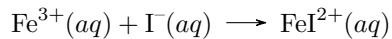
As we discussed in class, the mechanism for this reaction is believed to consist of two steps, the first of which is the rate-determining step in which HOI^- is an intermediate. Draw a reaction energy diagram for this reaction that shows enthalpy on the y -axis. For the x -axis, place the reactants on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



Problem 4. The oxidation of I^- by 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.

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