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.

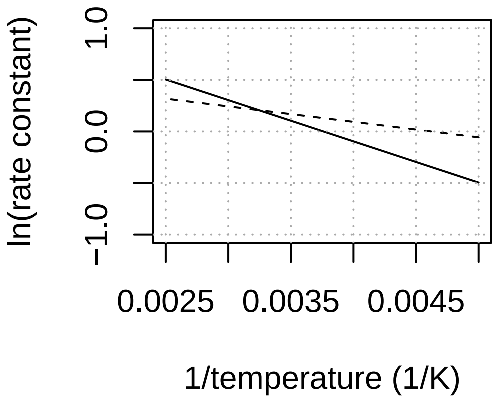
Problem	Points	Maximum	Problem	Points	Maximum
1		12	4		30
2		16	5		15
3		12	6		15
			Total		100

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 • °C
- the gas constant (R) is 8.314 J/mol$_{\text{rxn}}$ • K
- Faraday's constant (F) is 96,485 J/V • mol e$^-$
- water's dissociation constant (K_w) is 1.00×10^{-14}

Part A: Three Problems That Require No Calculations

Problem 1. The diagram below shows a plot of $\ln(k)$ as a function of T^{-1} for two reactions: A (the solid line) and B (the dashed line). Which reaction has the greater activation energy? Explain your reasoning in 1–3 sentences.



Problem 2. The reaction in the atmosphere between molecular chlorine, $Cl_2(g)$, and chloroform, $CHCl_3(g)$, leads to the formation of carbon tetrachloride, $CCl_4(g)$, and hydrogen chloride, $HCl(g)$

$$Cl_2(g) + CHCl_3(g) \longrightarrow CCl_4(g) + HCl(g)$$

The following mechanism has been proposed for this reaction

$$Cl_2(g) \longrightarrow 2Cl(g)$$

$$Cl(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_3(g)$$

$$CCl_3(g) + Cl(g) \longrightarrow CCl_4(g)$$

If the second step is the rate-determining step, then what is the reaction's expected rate law?

Problem 3. Draw a reaction energy diagram for the mechanism outlined in Problem 2, placing Cl_2 on the left and CCl_4 on the right. Assume each step in the mechanism is exothermic. In 2–4 sentences, explain how you arrived at your reaction energy diagram.

Part B: Three Problems That Require Calculations

Problem 4. When exposed to air, a freshly cleaned surface of iron quickly oxidizes to iron oxide

$$4\mathrm{Fe}(s) + 3\mathrm{O_2}(g) \longrightarrow 2\mathrm{Fe_2O_3}(s)$$

The kinetic behavior of this system is studied by taking a sample of iron, cleaning to remove its outer layer of iron oxide, placing the sample in a reaction vessel filled with air, and monitoring the partial pressure of O_2 as a function of time. The pseudo-order rate law for the reaction is

$$\text{rate} = k_{\text{obs}}\,(P_{\mathrm{O_2}})^{\alpha}$$

where k_{obs} is a function of the mass of iron

$$k_{\text{obs}} = k(\text{g Fe})^{\beta}$$

and where k is the reaction's true rate constant. The figures on the exam's last page show three different views of the results of two experiments, one where the mass of iron is 15.0 g and one where the mass of iron is 30.0 g. Given this data, report the reaction's rate law by (a) determining the reaction order, α, for O_2, by (b) determining the reaction order, β, for Fe, and by (c) determining the value of the reaction's true rate constant, k, with units. To ensure maximum credit, organize your work into three parts, one each for (a), (b), and (c), include appropriate calculations where needed, and provide a few sentences to explain your answers.

Problem 5. Many compounds undergo a simple dimerization reaction in which two molecules bind together. Isomers often dimerize at different rates, which provides a means for studying the relationship between structure and chemical reactivity. For example, consider the two compounds A and B, which dimerize according to the reactions $2A \longrightarrow A_2$ and $2B \longrightarrow B_2$.

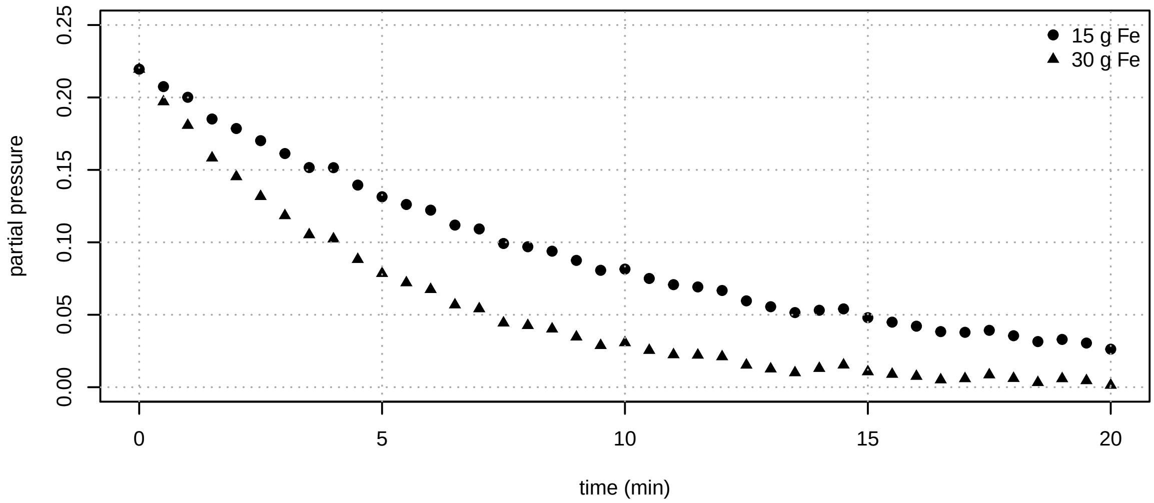
The kinetics of both reactions are second order with, respectively, rate constants of k_A and of k_B. When 1.22×10^{-2} moles of A are introduced into a 250.0 mL reaction flask the concentration of A after 3.00 min is found to be 6.90×10^{-3} M. What is the value of k_A for this reaction (with units)?

Equimolar solutions of A and of B are allowed to dimerize and after 3.00 min the concentration of B_2 is found to be less than that of A_2. What, if anything, can you conclude about the value of k_B? Explain your reasoning in 1–3 sentences.

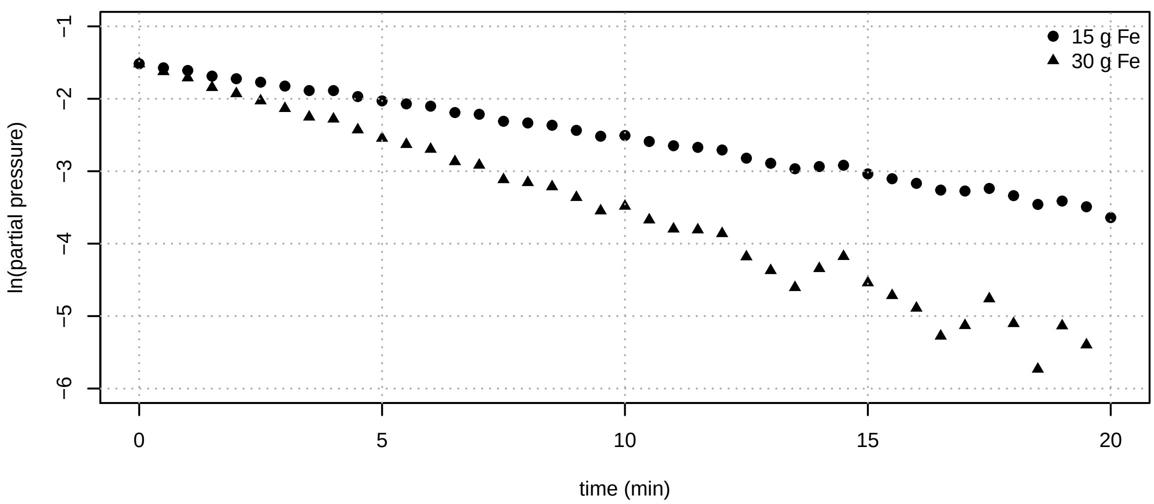
Problem 6. In lab you studied the decomposition of hydrogen peroxide

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

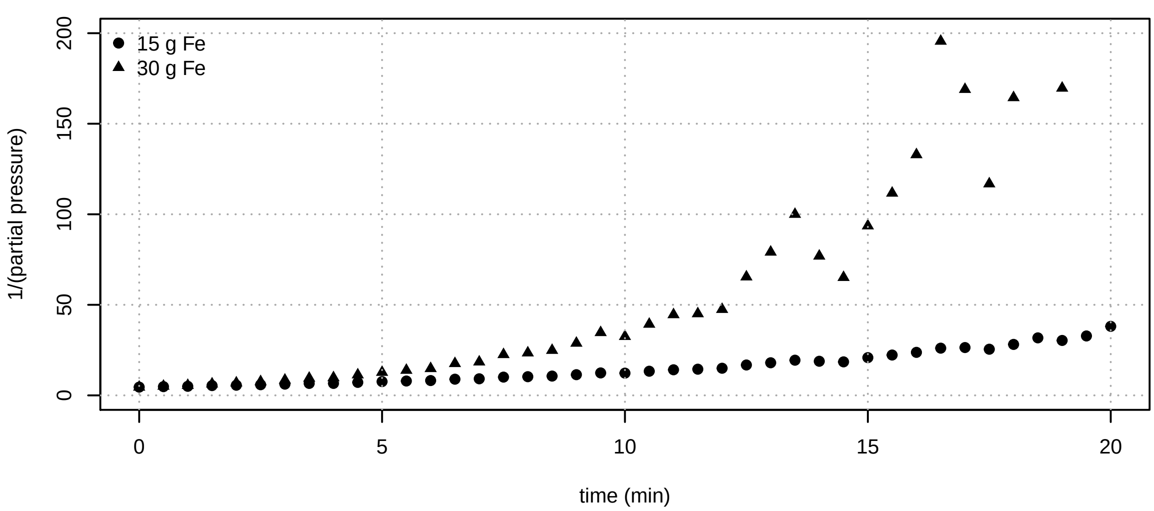
As you observed, the rate of this reaction is very slow in the absence of a catalyst: in the presence of Fe^{3+} the activation energy is 42.0 kJ/mol$_{rxn}$; without a catalyst, the activation energy is 70.0 kJ/mol$_{rxn}$. At a temperature of 20°C, how many times greater is the reaction's rate constant, k, in the presence of a catalyst? You may assume that the factor A in the Arrhenius equation is the same for both reactions.



partial pressure
0.00
0.05
0.10
0.15
0.20
0.25
15 g Fe
30 g Fe
0
5
10
15
20
time (min)



ln(partial pressure)
−1
−2
−3
−4
−5
−6
15 g Fe
30 g Fe
0
5
10
15
20
time (min)



1/(partial pressure)
0
50
100
150
200
15 g Fe
30 g Fe
0
5
10
15
20
time (min)