

Key for 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	10.0	12	4	23.9	30
2	12.5	16	5	12.8	15
3	10.6	12	6	13.0	15
			Total	82.0	100

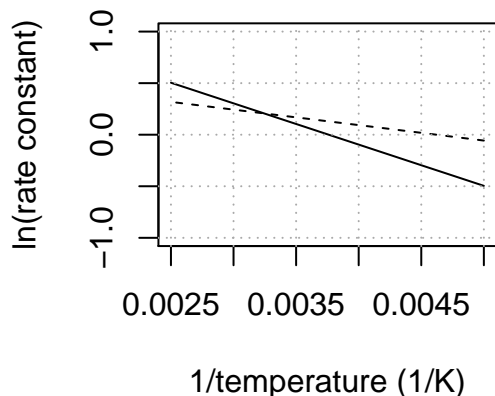
high score	scores 100–90	scores 89–80	scores ≤ 79
100	6	6	9

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}

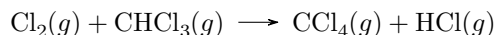
Part A: Three Problems That Require No Calculations

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.

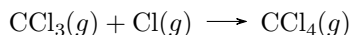
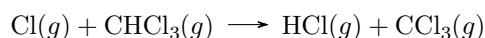
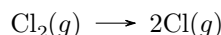


Answer. We know that the relationship between k and T is given by the Arrhenius equation, $k = Ae^{-E_a/RT}$, where A is the rate constant's maximum value and E_a is the reaction's activation energy. Linearizing the equation, $\ln(k) = \ln(A) - E_a/RT$, shows us that the slope of a plot of $\ln(k)$ vs. T^{-1} is directly proportional to the activation energy (slope = $-E_a/R$). Reaction A (the solid line) has the steeper slope and, therefore, it has the greater activation energy.

Problem 2. The reaction in the atmosphere between molecular chlorine, $\text{Cl}_2(g)$, and chloroform, $\text{CHCl}_3(g)$, leads to the formation of carbon tetrachloride, $\text{CCl}_4(g)$, and hydrogen chloride, $\text{HCl}(g)$



The following mechanism has been proposed for this reaction



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

Answer. The rate law for the rate-determining step is $\text{rate} = k_2[\text{Cl}][\text{CHCl}_3]$ and is defined in terms of one of the reactants, CHCl_3 , and an intermediate, Cl . To remove the intermediate from the rate law, we assume the first step is at equilibrium and solve for $[\text{Cl}]$; thus

$$K_1 = \frac{[\text{Cl}]^2}{\text{Cl}_2}$$

$$[\text{Cl}] = K_1^{1/2} \times [\text{Cl}_2]^{1/2}$$

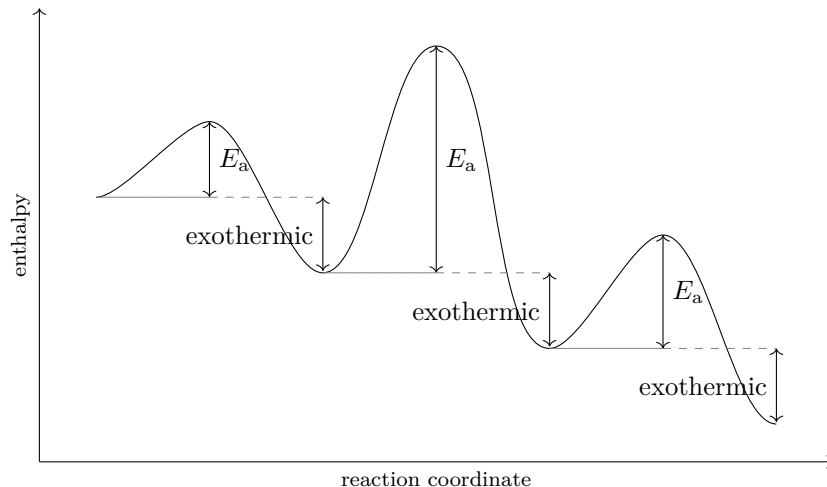
Substituting back gives the rate law as

$$\text{rate} = k_2 K_1^{1/2} [\text{CHCl}_3][\text{Cl}_2]^{1/2} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

The reaction, therefore, is first-order in CHCl_3 and is $\frac{1}{2}$ -order in Cl_2 .

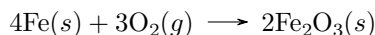
Problem 3. Draw a reaction energy diagram for the mechanism outlined in Problem 2, placing Cl_2 on the left and CCl_4 on the right. Assume each step in the mechanism is exothermic. In 2–4 sentences, explain how you arrived at your reaction energy diagram.

Answer. The energy diagram is shown below. There are three essential features that your diagram must show: (a) there must be three activation energy barriers, shown here by the arrows labeled E_a , one for each step; (b) the second of the three activation energy barriers must be larger than the first or the third because the second step is the rate-determining step; and (c) the change in enthalpy for each step must show, as indicated here by the arrows labeled exothermic, a decrease in absolute enthalpy that represents an exothermic process.



Part B: Three Problems That Require Calculations

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



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

$$\text{rate} = k_{\text{obs}} (P_{\text{O}_2})^\alpha$$

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.

Answer. *Note: The data on the answer key's last page and the values provided below differ slightly from those on the original exam because the raw data is generated anew each time the document is saved to a pdf format. Nevertheless, the raw data is designed in a way that does not change the resulting values for α , β , and k .*

For part (a), we note that the plot of $\ln(\text{partial pressure})$ vs. time is linear, which means the reaction is first-order in O_2 ; the other two ways of viewing the data clearly are not straight-lines.

For part (b), we note that the two plots of $\ln(\text{partial pressure})$ vs. time have different slopes, which means the mass of Fe must affect the rate. To determine the reaction order for Fe, we need values for the two

observed rate constants, k_{obs} , which are given by the slopes of the two plots of $\ln(\text{partial pressure})$ vs. time (slope = $-k_{\text{obs}}$); these are 0.103 when using 15.0 g of Fe and 0.218 when using 30.0 g of Fe. Thus, we see that doubling the amount of Fe from 15.0 to 30.0 g increases the rate by a factor of 2.1, which means the reaction is first order in Fe. An alternative approach is to use the data in the figure at the top to find the half-lives when using 15.0 g of Fe and 30.0 g of Fe, and then convert the half-lives to rate constants using the equation $t_{1/2} = 0.693/k$.

For part (c), we note that $k_{\text{obs}} = k(\text{g Fe})^1$; thus, using the value of k_{obs} for 15.0 g Fe gives k as 0.00688 and using the value of k_{obs} for 30.0 g Fe gives k as 0.00728; the average of the two values for k is 0.00708. The units for k are $\text{min}^{-1} \text{g Fe}^{-1}$, which yields the correct units of atm/min implied by the original kinetic data.

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 $2\text{A} \rightarrow \text{A}_2$ and $2\text{B} \rightarrow \text{B}_2$.

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)?

Answer. For a second-order reaction we know that

$$\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + kt$$

Substituting in the known values for $\frac{1}{[\text{A}]_t}$ and for $\frac{1}{[\text{A}]_0}$ at, respectively, $t = 3.00$ min and $t = 0$ min gives

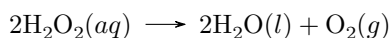
$$\frac{1}{6.90 \times 10^{-3} \text{ M}} = \frac{1}{(1.22 \times 10^{-2} \text{ mol})/0.250 \text{ L}} + k(3.00 \text{ min})$$

Solving for k gives its value as $41.5 \text{ M}^{-1} \text{ min}^{-1}$.

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.

Answer. If the concentration of B_2 is less than the concentration of A_2 , then we know that the rate for the reaction $2\text{B} \rightarrow \text{B}_2$ is less than the rate for the reaction $2\text{A} \rightarrow \text{A}_2$; in turn, this means that the rate constant k_{B} must be less than the rate constant k_{A} .

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



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 $42.0 \text{ kJ}/\text{mol}_{\text{rxn}}$; without a catalyst, the activation energy is $70.0 \text{ kJ}/\text{mol}_{\text{rxn}}$. 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.

Answer. From the Arrhenius equation we know that $k = Ae^{-E_a/RT}$. Letting k_{cat} be the rate constant for the catalyzed reaction and letting k_{uncat} be the rate constant for the uncatalyzed reaction, we find that

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{Ae^{-E_{a,\text{cat}}/RT}}{Ae^{-E_{a,\text{uncat}}/RT}} = \frac{e^{-42000/(8.314 \times 293)}}{e^{-72000/(8.314 \times 293)}} = 98,150$$

