

# 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	11.5	13	4	16.3	20
2	12.9	14	5	15.4	20
3	11.4	13	6	17.7	20
Total				85.2	100

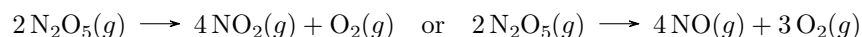
high score	scores 100–90	scores 89–80	scores $\leq 79$
100	8	12	4

A few constants are shown below; other information is included within individual problems. A periodic table and a sheet of equations also are available.

- 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  $1.00 \times 10^{-14}$

### Part A: Three Problems With Short Written Answers and/or With Short Calculations

**Problem 1.** The decomposition of  $\text{N}_2\text{O}_5(g)$  occurs by one of these overall reactions



Between 300 s and 400 s the average rate of decomposition for  $\text{N}_2\text{O}_5$  is  $1.9 \times 10^{-5}$  mol  $\text{N}_2\text{O}_5/\text{s}$  and the average rate of formation for  $\text{O}_2$  is  $9.5 \times 10^{-6}$  mol  $\text{O}_2/\text{s}$ . Based on these average rates, is the other product in the reaction  $\text{NO}_2$  or  $\text{NO}$ . Explain your choice in 1–3 sentences.

**Answer.** The average rate of decomposition for  $\text{N}_2\text{O}_5$  of  $1.9 \times 10^{-5}$  mol  $\text{N}_2\text{O}_5/\text{s}$  is  $2\times$  greater than the average rate of formation for  $\text{O}_2$  of  $9.5 \times 10^{-6}$  mol  $\text{O}_2/\text{s}$ . This tells us that we lose 2 molecules of  $\text{N}_2\text{O}_5$  for every molecule of  $\text{O}_2$  that we make, a 2:1 stoichiometry. This is consistent with the first of the two possible reactions, which means  $\text{NO}_2$  is the other product.

**Problem 2.** Radon, which can outgas from bedrock and enter into a home's basement, is a hazard because one of its isotopes,  $^{222}\text{Rn}$ , is radioactive with a half-life of 3.82 days. As with all radioactive decay processes, it follows first-order kinetics. Suppose a basement contains  $6.022 \times 10^{23}$  atoms of  $^{222}\text{Rn}$ . How many days will it take until there are 6022 atoms of  $^{222}\text{Rn}$  remaining?

**Answer.** With a half-life of 3.82 days, the first-order rate constant is

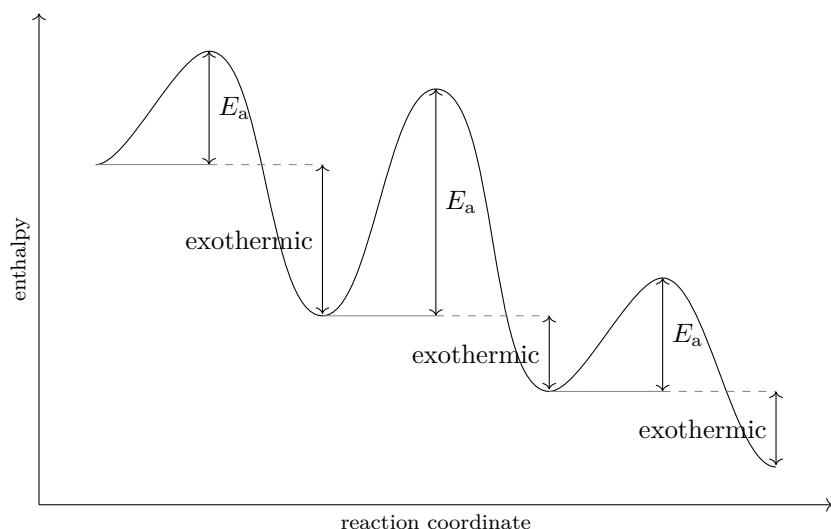
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.82 \text{ d}} = 0.1814 \text{ d}^{-1}$$

Next, we use the integrated first-order rate law,  $\ln[^{222}\text{Rn}]_t = \ln[^{222}\text{Rn}]_0 - kt$ , to find time

$$\ln(6022) = \ln(6.022 \times 10^{23}) - (0.1814 \text{ d}^{-1}) \times t$$

Solving for  $t$  gives its value as 254 days. Note that we can use numbers of atoms in place of concentration as the volume remains constant and there is a fixed relationship between moles and atoms.

**Problem 3.** The figure below shows a reaction energy diagram for the reaction  $\text{R} \longrightarrow \text{P}$ , which follows a three-step mechanism (with step 1 on the far left). Which step—1, 2, or 3—is the slowest step in the reaction and which step releases the most heat? Explain your choices in 1–3 sentences.



**Answer.** As shown above, each of the three “hills” is the activation energy barrier for one step of the mechanism. The slowest step is that with the greatest difference in energy between the step’s reactants and the top of the energy barrier, which, in this case, is the second step (*note: it is not the step where the absolute energy at the top of the barrier is greatest*). The step that releases the most heat is the first step as this step has the greatest difference in energy between the step’s reactants and its products.

## Part B: Three Problems With More Involved Calculations

**Problem 4.** The oxidation of  $\text{Mn}^{2+}(aq)$  to  $\text{MnO}_2(s)$  by  $\text{O}_2(g)$  is important in the geochemical cycling of manganese. A kinetic study of this reaction at 298 K yields the following information

experiment	$\text{Mn}^{2+}(aq)$ (M)	pH	$P_{\text{O}_2(g)}$ (atm)	$R = \frac{d[\text{Mn}^{2+}]}{dt}$ (M/day)
1	$1.5 \times 10^{-4}$	10.0	0.20	0.00258
2	$3.0 \times 10^{-4}$	10.0	0.20	0.00519
3	$1.5 \times 10^{-4}$	11.0	0.20	0.25600
4	$1.5 \times 10^{-4}$	10.0	0.10	0.00131

What is the rate law for this reaction in terms of the concentration of  $\text{Mn}^{2+}$ , the concentration of  $\text{H}_3\text{O}^+$ , and the partial pressure of  $\text{O}_2$ , and what is the value of the rate constant (with units)? Be sure to organize your work so that it is clear how you arrived at your final answers.

**Answer.** Using experiments 1 & 2, we see that doubling the concentration of  $\text{Mn}^{2+}$  doubles the rate, which means the reaction is first-order in  $\text{Mn}^{2+}$ . Using experiments 4 & 1, we see that doubling the partial pressure of  $\text{O}_2$  doubles the rate, which means the reaction is first-order in  $\text{O}_2$ . To determine the effect on the rate of  $\text{H}_3\text{O}^+$ , we note that for experiments 1, 2, and 4 we have  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-10}$  and that for experiment 3 we have  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-11}$ . Using experiments 3 and 1, we see that increasing the concentration of  $\text{H}_3\text{O}^+$  by a factor of 10, decreases the rate by a factor of 100, which means the reaction is inverse second-order in  $\text{H}_3\text{O}^+$ . The rate law for the reaction is

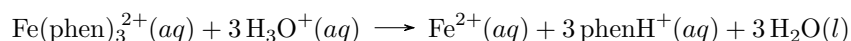
$$R = \frac{k[\text{Mn}^{2+}]P_{\text{O}_2}}{[\text{H}_3\text{O}^+]^2}$$

Substituting in values for any one experiment is sufficient to determine the value of the rate constant; thus

$$0.00258 \text{ M/d} = \frac{k(1.5 \times 10^{-4} \text{ M})(0.20 \text{ atm})}{1.0 \times 10^{-10} \text{ M}}$$

which gives  $k = 8.6 \times 10^{-19} \text{ M}^2/\text{atm} \cdot \text{d}$ .

**Problem 5.** Ferriin is a metal-ligand complex between 1,10-phenanthroline, which we abbreviate as phen, and  $\text{Fe}^{2+}$ . In the presence of acid, ferriin dissociates as shown here

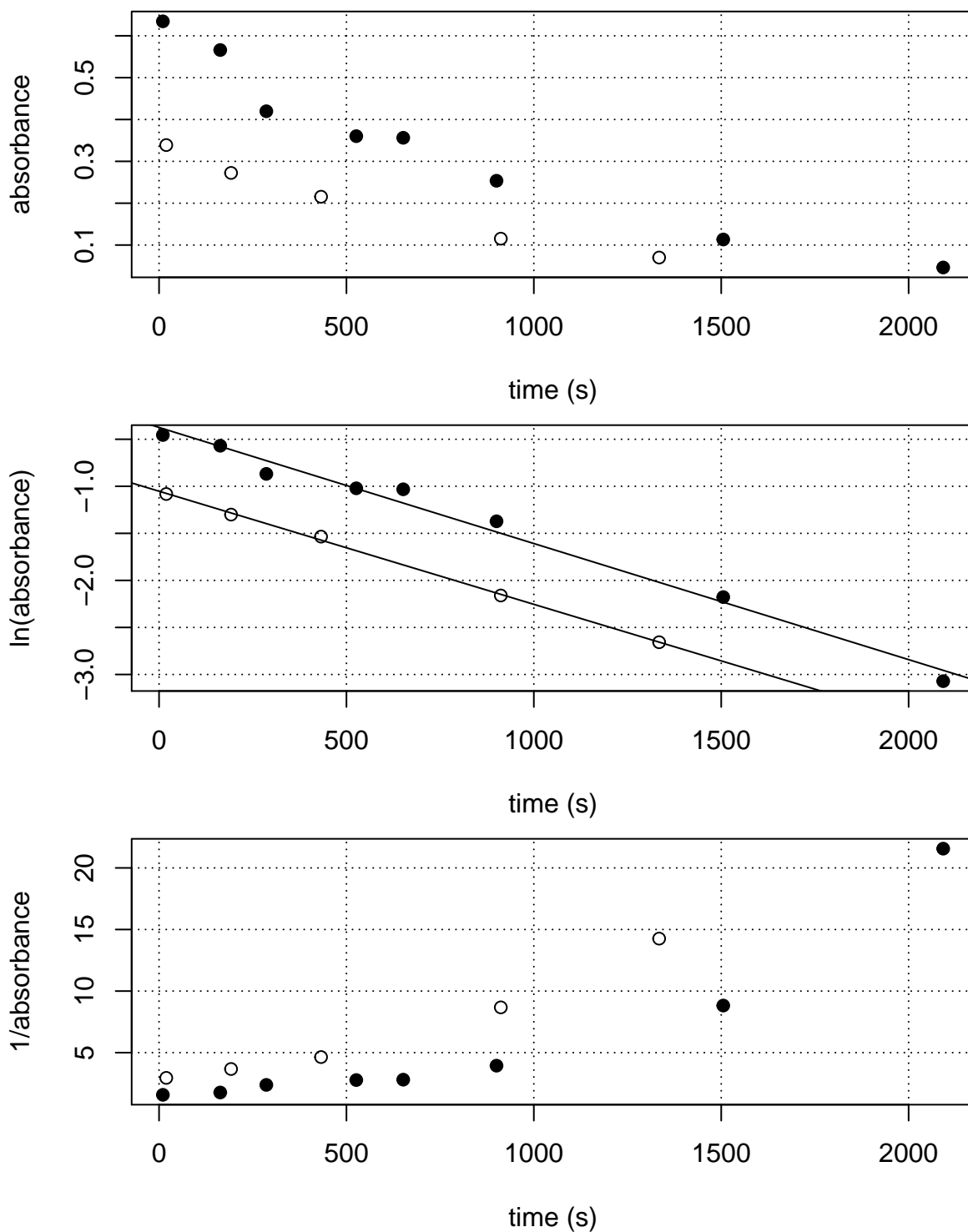


Because ferriin has a distinctive color and all other reactants and products are colorless, it is easy to study the reaction's kinetics by monitoring absorbance as a function of time under pseudo-order conditions where  $[\text{Fe(phen)}_3^{2+}] \ll [\text{H}_3\text{O}^+]$ . The figures on the following page shows three views of kinetic data collected using two sets of conditions:

filled circles: 60  $\mu\text{M}$   $\text{Fe(phen)}_3^{2+}$  and 0.50 M  $\text{H}_2\text{SO}_4$

open circles: 30  $\mu\text{M}$   $\text{Fe(phen)}_3^{2+}$  and 0.050 M  $\text{H}_2\text{SO}_4$

If the general form of the reaction's rate law is  $R = k[\text{Fe(phen)}_3^{2+}]^\alpha[\text{H}_2\text{SO}_4]^\beta$ , where  $\text{H}_2\text{SO}_4$  is the source of hydronium ions, what are the values of the reaction orders  $\alpha$  and  $\beta$ , and what is the value of the rate constant with units? Be sure to organize your work so that it is clear how you arrived at your final answers.



**Answer.** Because the plots of  $\ln(\text{abs})$  vs. time are linear, we know the reaction is first-order in  $\text{Fe}(\text{phen})_3^{2+}$ . To find the observed rate constants for each trial we draw the best straight-line through each set of data and determine their respective slopes, where  $\text{slope} = -k_{\text{obs}} = -k[\text{H}_3\text{O}^+]^\beta$ . The regression lines are included in the figure and the slopes of the two lines are -0.00123 when using 0.50 M  $\text{H}_2\text{SO}_4$  and -0.0012 when using 0.050 M  $\text{H}_2\text{SO}_4$ . Because the two values of  $k_{\text{obs}}$  are nearly identical, we know the concentration of  $\text{H}_2\text{SO}_4$  does not affect the rate and that  $\beta = 0$ . (Note: Even without calculating slopes, we see that the two lines are essentially parallel to each other, which means they have the same slope and, again, we conclude that  $\beta = 0$ .)

The rate constant for the reaction, therefore, is the same as the observed rate constant, or  $k_{\text{obs}}$  of  $0.00122 \text{ s}^{-1}$ .

**Problem 6.** Commercial lightsticks (and fireflies!) use a chemical reaction to generate light, a process called chemiluminescence. A typical lightstick is a plastic tube that contains a solution of phenyl oxalate, a fluorescent dye, and a glass tube that contains hydrogen peroxide. Breaking the glass tube releases the hydrogen peroxide, which initiates the chemiluminescent reaction. To study the kinetics of the system, you simply observe the emission of light as a function of time. In one such study, the reaction's activation energy was determined by running the reaction at different temperatures. For example, a rate constant of  $592.8 \text{ s}^{-1}$  was obtained at a temperature of 310 K and a rate constant of  $129.9 \text{ s}^{-1}$  was obtained at temperature of 300 K. What is the reaction's activation energy in kJ/mol? Be sure to organize your work so that it is clear how you arrived at your final answers.

**Answer.** To find the activation energy we write and solve the following pairs of simultaneous equations

$$k_{310} = 592.8 = Ae^{-E_a/(8.314 \times 310)}$$

$$k_{300} = 129.9 = Ae^{-E_a/(8.314 \times 300)}$$

where the activation energy,  $E_a$  is in Joules/mol. There are many ways to solve this pair of equations for  $E_a$ ; here we will begin by taking the natural log of both sides of each equation; thus

$$\ln(592.8) = \ln(A) - \frac{E_a}{8.314 \times 310}$$

$$\ln(129.9) = \ln(A) - \frac{E_a}{8.314 \times 300}$$

Next, we solve each equation for  $\ln(A)$

$$\ln(A) = \ln(592.8) + \frac{E_a}{8.314 \times 310} = 6.385 + (3.880 \times 10^{-4})E_a$$

$$\ln(A) = \ln(129.9) + \frac{E_a}{8.314 \times 300} = 4.867 + (4.009 \times 10^{-4})E_a$$

and then equate the right sides of the two equations to each other

$$6.385 + (3.880 \times 10^{-4})E_a = 4.867 + (4.009 \times 10^{-4})E_a$$

$$1.518 = (1.29 \times 10^{-5})E_a$$

$$E_a = 117,700 \text{ J/mol}$$

or an activation energy of 117.7 kJ/mol. There are several other mathematical approaches to this problem; each, however, yields the same result.