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		13	4		20
2		14	5		20
3		13	6		20
			Total		100

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 • °C
- the gas constant (R) is 8.314 J/mol_{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 With Short Written Answers and/or With Short Calculations

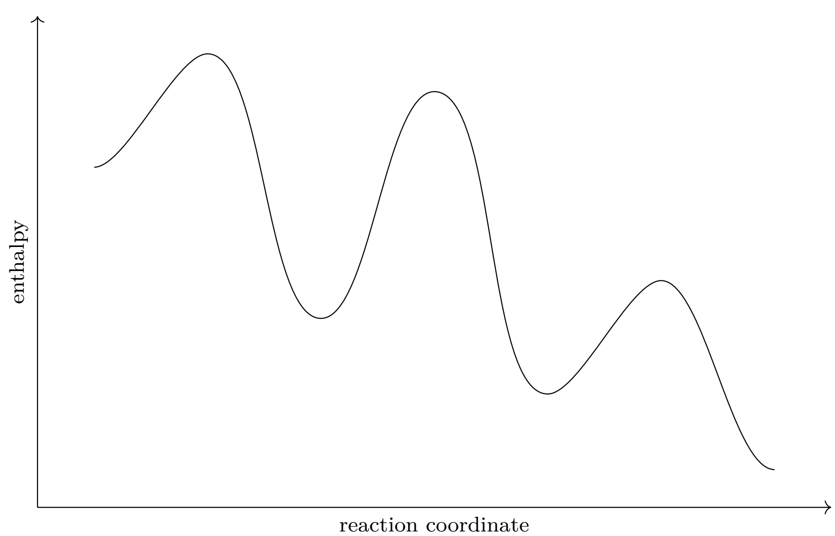
Problem 1. The decomposition of $N_2O_5(g)$ occurs by one of these overall reactions

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g) \quad \text{or} \quad 2\,N_2O_5(g) \longrightarrow 4\,NO(g) + 3\,O_2(g)$$

Between 300 s and 400 s the average rate of decomposition for N_2O_5 is 1.9×10^{-5} mol N_2O_5/s and the average rate of formation for O_2 is 9.5×10^{-6} mol O_2/s. Based on these average rates, is the other product in the reaction NO_2 or NO. Explain your choice in 1–3 sentences.

Problem 2. Radon, which can outgas from bedrock and enter into a home's basement, is a hazard because one of its isotopes, ^{222}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 6.022×10^{23} atoms of ^{222}Rn. How many days will it take until there are 6022 atoms of ^{222}Rn remaining?

Problem 3. The figure below shows a reaction energy diagram for the reaction R $\longrightarrow$ 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.



Part B: Three Problems With More Involved Calculations

Problem 4. The oxidation of $Mn^{2+}(aq)$ to $MnO_2(s)$ by $O_2(g)$ is important in the geochemical cycling of manganese. A kinetic study of this reaction at 298 K yields the following information

experiment	$Mn^{2+}(aq)$ (M)	pH	$P_{O_2(g)}$ (atm)	$R = \frac{d[Mn^{2+}]}{dt}$ (M/day)
1	1.5×10^{-4}	10.0	0.20	0.00258
2	3.0×10^{-4}	10.0	0.20	0.00519
3	1.5×10^{-4}	11.0	0.20	0.25600
4	1.5×10^{-4}	10.0	0.10	0.00131

What is the rate law for this reaction in terms of the concentration of Mn^{2+}, the concentration of H_3O^+, and the partial pressure of 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.

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

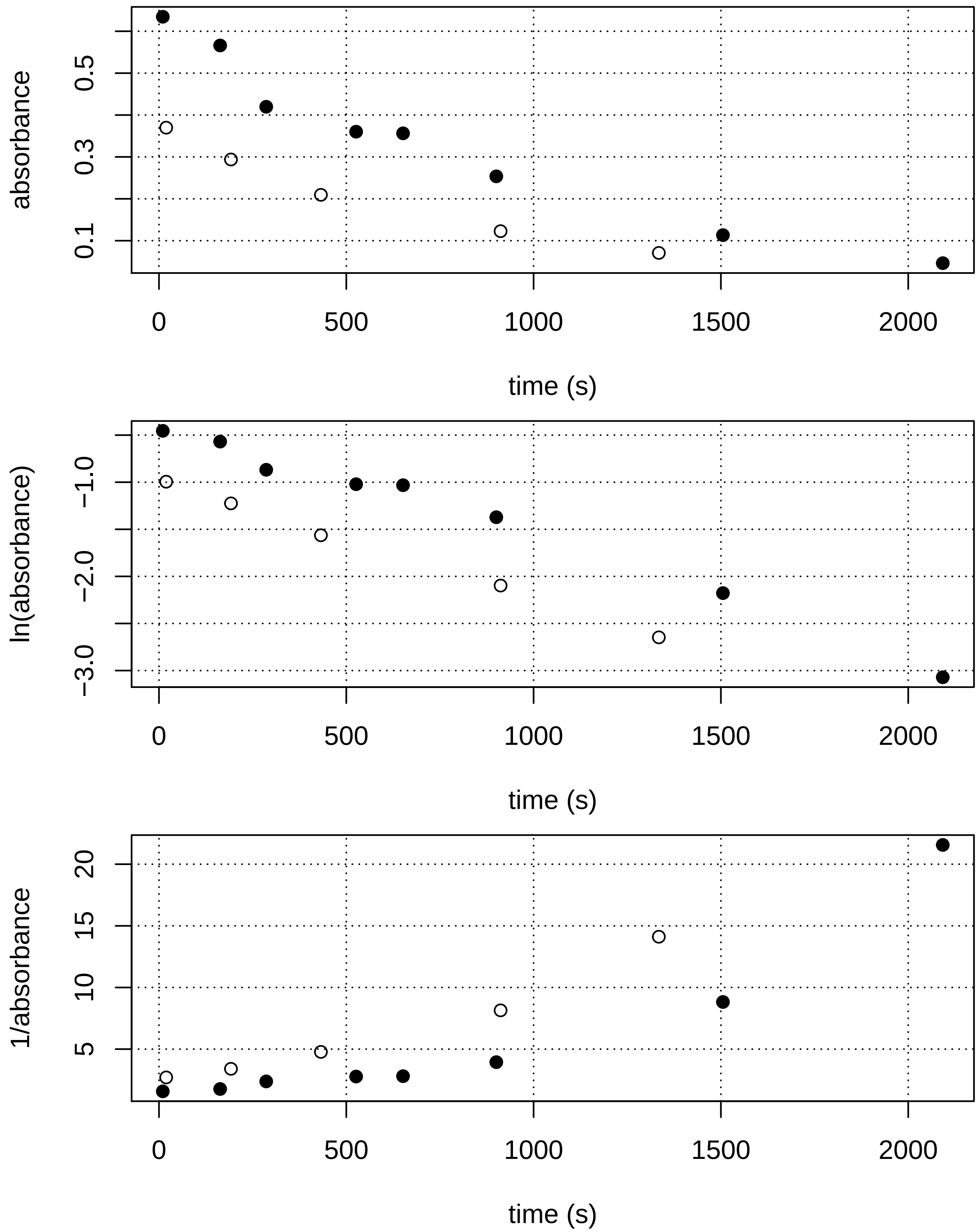
$$\mathrm{Fe(phen)_3^{2+}}(aq) + 3\,\mathrm{H_3O^+}(aq) \longrightarrow \mathrm{Fe^{2+}}(aq) + 3\,\mathrm{phenH^+}(aq) + 3\,\mathrm{H_2O}(l)$$

Because ferroin 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 condtions where $[\mathrm{Fe(phen)_3^{2+}}] << [\mathrm{H_3O^+}]$. The figures on the following page shows three views of kinetic data collected using two sets of conditions:

filled circles: 60 µM $\mathrm{Fe(phen)_3^{2+}}$ and 0.50 M H_2SO_4

open circles: 30 µM $\mathrm{Fe(phen)_3^{2+}}$ and 0.050 M H_2SO_4

If the general form of the reaction's rate law is $R = k[\mathrm{Fe(phen)_3^{2+}}]^\alpha[\mathrm{H_2SO_4}]^\beta$, what are the values of the reaction orders α and β, 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.


absorbance
0.1
0.3
0.5
0
500
1000
1500
2000
time (s)
ln(absorbance)
−3.0
−2.0
−1.0
0
500
1000
1500
2000
time (s)
1/absorbance
5
10
15
20
0
500
1000
1500
2000
time (s)

Problem 6. Commerical lightsticks (and fireflies!) use a chemical reaction to generate light, a process called chemiluminesence. 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 s^{-1} was obtained at a temperature of 310 K and a rate constant of 129.9 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.