

Kinetics Practice Exam

Note: All problems included in this practice exam are drawn from problems used in previous semesters. Exams typically include 7 or 8 problems that are a mixture of qualitative problems calling for written explanations and quantitative problems that involve calculations and, in some cases, written explanations.

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	5		16
2		12	6		16
3		12	7		16
4		16	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}

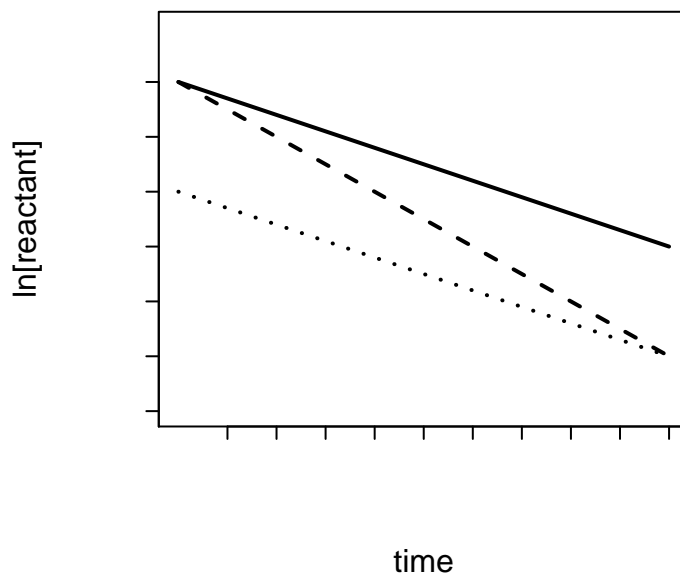


Figure 1: Experiment 1: solid line; Experiment 2: dashed line; Experiment 3: dotted line

Problem 1. Figure 1 shows results for three experiments run under conditions where the reaction's kinetics depend on a single reactant. Two experiments were run at the same temperature and a third experiment was run at a different temperature. Which experiment was run at a different temperature?

Answer. The slope of a plot of $\ln[\text{reactant}]$ vs. time is equal to $-k$. Lines of equal slope have the same rate constant and, because k depends on temperature, $k = e^{-E_a/RT}$, must have the same temperature; thus, the second experiment (shown as the dashed line) has the unique temperature because its slope is different from the other two experiments.

Problem 2. Consider the reaction $\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)$, which is first order in H_2 and in I_2 . For each of the following, predict whether the stated action will increase, decrease, or leave unchanged the reaction's rate and support each answer in a single sentence.

Answer. The factors that affect a reaction's rate are the rate constant, k , and the concentrations of $\text{H}_2(g) + \text{I}_2(g)$. The rate constant, in turn, is a function of temperature and activation energy.

an increase in the reaction's temperature **increases** its rate because the molecules are moving faster resulting in more collisions and more collisions that exceed the activation energy

an increase in the volume of the reaction vessel **decreases** its rate because the concentrations $\text{H}_2(g) + \text{I}_2(g)$ decrease

the addition of a catalyst **increases** the rate because it decreases the activation energy and, therefore, increases the rate constant

the addition of an inert gas, such as Ar, has **no effect** on the rate as it does not affect the rate constant, nor does it affect the concentrations of $\text{H}_2(g) + \text{I}_2(g)$

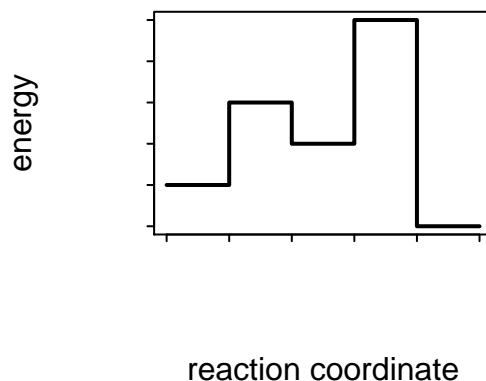


Figure 2: One possible reaction energy diagram for Problem 3; A is on the left and C is on the right.

Problem 3. The following information is known to you about a reaction in which A first reacts to form B, which, in turn, reacts to form C:

- the reaction $A \rightarrow C$ is exothermic
- the reaction's rate-determining step is $B \rightarrow C$

Draw a reaction energy diagram that is consistent with this information.

Answer. There are many possible solutions, each of which has the following features: (a) the absolute energy of A is greater than that of C because the reaction is exothermic; (b) the activation energy for $B \rightarrow C$ is greater than that for $A \rightarrow B$ because the second step is slower than the first step; and (c) the absolute energy of B is greater than that of C because C is the final thermodynamic product. Note there is no requirement on the absolute energy of B relative to that of A. Figure 2 shows one possible reaction energy diagram that is consistent with these features.

Problem 4. Americium-241, ^{241}Am , is a radioactive isotope used in some smoke detectors. The first-order rate constant for its radioactive decay is $1.63 \times 10^{-3} \text{ yr}^{-1}$. What percentage of the ^{241}Am originally present in a smoke detector remains after 34.0 months?

Answer. For a first-order reaction we know that $\ln[^{241}\text{Am}]_t = \ln[^{241}\text{Am}]_0 - kt$. Rearranging this equation and solving shows us that 99.5% of the ^{241}Am remains.

$$\ln\left(\frac{[^{241}\text{Am}]_t}{[^{241}\text{Am}]_0}\right) = (-1.63 \times 10^{-3} \text{ yr}^{-1})\left(\frac{34.0 \text{ m}}{12 \text{ m/yr}^{-1}}\right) = -0.00462$$

$$\left(\frac{[^{241}\text{Am}]_t}{[^{241}\text{Am}]_0}\right) = 0.995$$

Problem 5. *Mycobacterium avium* is a human pathogen responsible for some respiratory infections. Although it is sometimes found in hot tubs and swimming pools, adding a disinfectant to the water destroys the pathogen. When using ClO_2 as a disinfectant, the rate constant for the pathogen's inactivation is $0.267 \text{ L/mg} \cdot \text{min}$ at a temperature of 5°C and $3.45 \text{ L/mg} \cdot \text{min}$ at a temperature of 30°C . What is the activation energy for the pathogen's destruction?

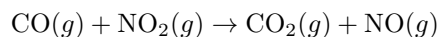
Answer. We know that $k = e^{-E_a/RT}$ where E_a is the activation energy and T is the temperature. If we measure k at two temperatures, then

$$\frac{k_2}{k_1} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

Substituting $0.267 \text{ L/mg} \cdot \text{min}$ for k_1 , $3.45 \text{ L/mg} \cdot \text{min}$ for k_2 , 278 K for T_1 , and 303 K for T_2 , and solving for E_a gives its value as $71,700 \text{ J/mol}_{\text{rxn}}$, or $71.7 \text{ kJ/mol}_{\text{rxn}}$.

Problem 6. An important reaction in atmospheric chemistry is the oxidation of carbon monoxide to carbon dioxide using nitrogen dioxide



The following data were gathered during a kinetic study of this reaction at 540 K.

$[\text{CO}]_0$ (M)	$[\text{NO}_2]_0$ (M)	Initial Rate (M/hr)
5.1×10^{-4}	3.5×10^{-5}	3.4×10^{-8}
5.1×10^{-4}	7.0×10^{-5}	6.8×10^{-8}
5.1×10^{-4}	1.8×10^{-5}	1.7×10^{-8}
1.0×10^{-3}	3.5×10^{-5}	6.8×10^{-8}
1.5×10^{-3}	8.5×10^{-5}	

Using this data, determine the rate law for the reaction and the value of the rate constant (with appropriate units). When you are done, fill in the missing rate in the data table.

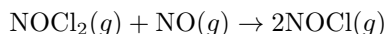
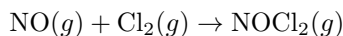
Answer. Comparing the first and second experiment we note that doubling the concentration of NO_2 doubles the rate; thus, the reaction is first-order in NO_2 . Comparing the first and fourth experiments, we note that doubling the concentration of CO doubles the rate; thus, the reaction is first-order in CO . Substituting into the rate law the data from the first experiment and solving for k gives its value as

$$k = \frac{\text{rate}}{[\text{NO}_2][\text{CO}]} = \frac{3.4 \times 10^{-8} \text{ M/hr}}{(5.1 \times 10^{-4} \text{ M})(3.5 \times 10^{-5} \text{ M})} = 1.90 \text{ M}^{-1}\text{hr}^{-1}$$

The rate for the last experiment is

$$\text{rate} = k[\text{NO}_2][\text{CO}] = (1.90 \text{ M}^{-1}\text{hr}^{-1})(1.5 \times 10^{-3})(8.5 \times 10^{-5}) = 2.4 \times 10^{-7} \text{ M/hr}$$

Problem 7. The reaction $2\text{NO}(g) + \text{Cl}_2(g) \rightarrow 2\text{NOCl}(g)$ is one of many reactions important in atmospheric chemistry. Under conditions where the partial pressure of Cl_2 is significantly greater than the partial pressure of NO , a plot of $(P_{\text{NO}})^{-1}$ as a function of time is linear. The following mechanism is proposed for this reaction



Is this a plausible mechanism for this reaction? In a paragraph of four to six sentences, provide a convincing explanation for your decision.

Answer. We know that the reaction is pseudo-second order in NO because a plot of $(P_{\text{NO}})^{-1}$ as a function of time is a straight-line; thus, the rate law is $R = k_{\text{obs}}[\text{NO}]^2$ where $k_{\text{obs}} = k[\text{Cl}_2]^\beta$ and where β is unknown to us. We also know that the first step is not the rate-determining step as it predicts that the rate law is first-order in NO . If the second step is the rate-determining step, then the rate law is $R = k[\text{NOCl}_2][\text{NO}]$. If we assume that the first step is at equilibrium, then $[\text{NOCl}_2] = K[\text{NO}][\text{Cl}_2]$. Substituting back gives $R = kK[\text{NO}]^2[\text{Cl}_2] = k_{\text{obs}}[\text{NO}]^2$ where $k_{\text{obs}} = kK[\text{Cl}_2]$. This is a plausible mechanism as it predicts correctly that the reaction is second-order in NO . Note: because the reaction is run under pseudo-order conditions, we have no information regarding the reaction's rate with respect to Cl_2 ; thus, we have no reason to reject the mechanism simply because it predicts a rate law that includes the concentration of Cl_2 .