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	21.7	25	4	13.6	17
2	15.9	17	5	14.4	17
3	13.2	17	6	12.9	17
			Total	91.6	110

average score	high score	scores 100–90	scores 89–80	scores $\leq$ 79
83.3	90.9	1	11	2

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}

Problem 1. One treatment for thyroid cancer is the radioactive isotope ^{131}I, which, when ingested, is taken up by the thyroid where it remains while it undergoes radioactive decay through the emission of beta particles. Radioactive decay is known to occur by a first-order process. In one study of its radioactive decay, the following data were obtained using a standard sample of ^{131}I.

time (days)	concentration (µg/mL)
4	11.99
8	8.48
12	6.01
16	4.24
20	2.98

In 1–2 sentences, explain why this data supports the claim of first-order kinetics.

Answer. The easiest way to show that this is first-order kinetics is to examine half-lives and show that they are constant in value. There are three such half-lives in this data, all of which are eight days: from day 4 to day 12; from day 8 to day 16; and from day 12 to day 20.

What is the value of the rate constant, with units, for the radioactive decay of ^{131}I?

Answer. For a first-order process we know that $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{8\text{ d}} = 0.0866\text{ d}^{-1}$.

Someone forgot to record the initial concentration of ^{131}I! What was that concentration?

Answer. For a first-order process we know that $\ln[^{131}\text{I}]_t = \ln[^{131}\text{I}]_\text{o} - kt$. Using, for example, the result at 4 days gives $\ln[^{131}\text{I}]_\text{o} = \ln(11.99\text{ d}^{-1}) + 0.0866\text{ d}^{-1} \times 1\text{ d}$, or $[^{131}\text{I}]_\text{o} = 16.95$ µg/mL. Other choices of data give similar results.

What percentage of ^{131}I will remain after five weeks?

Answer. For a first-order process we know that $\ln[^{131}\text{I}]_t = \ln[^{131}\text{I}]_\text{o} - kt$, which we can rearrange to $\ln\left(\frac{[^{131}\text{I}]_t}{[^{131}\text{I}]_\text{o}}\right) = -kt$. Substituting in our value of k and 35 for the number of days and solving for the ratio $\frac{[^{131}\text{I}]_t}{[^{131}\text{I}]_\text{o}}$ gives its value as 0.0483; thus, 4.83% remains after five weeks.

Problem 2. Consider the hypothetical reaction $A + B \longrightarrow$ products. A kinetic analysis of this reaction produces the following set of observations:

- when the initial concentrations of A and of B are each 1.00×10^{-3} M, the reaction's initial rate is 1.46×10^{-3} M/s
- halving the initial concentration of A while maintaining the initial concentration of B at its original level, gives an initial rate of 7.28×10^{-4} M/s
- doubling the initial concentrations of both A and of B gives an initial rate of 1.17×10^{-2} M/s.

Report the rate law and the rate constant for this reaction (with units) and, in 2–4 sentences, explain how you arrived at this rate law.

Answer. From the first two experiments we see that cutting the concentration of A in half cuts the rate in half; thus, the reaction is first-order in A. From the first and the third experiments, we see that doubling the concentrations of A and of B results in an 8-fold increase in the rate. The reaction order for A accounts for a doubling of the rate; thus, the effect of B is to quadruple the rate, which means the reaction is second-order in B and the rate law is $R = k[A][B]^2$. Substituting in the data from any one experiment and solving for k gives its value as $1.46 \times 10^6\text{ M}^{-2}\text{s}^{-1}$.

Problem 3. Consider the hypothetical reaction $C + D \longrightarrow$ products. Because C is red in color and D is colorless, it is easy to follow the reaction's rate by monitoring the reaction mixture's absorbance (abs) as a function of time. A kinetic analysis of this reaction produces the following set of observations:

- when the concentration of C is 1.00×10^{-6} M and the concentration of D is 0.25 M, a plot of abs^{-1} as a function of time is linear with a slope of 0.135 min^{-1}
- when the concentration of C is 2.00×10^{-6} M and the concentration of D is 0.50 M, a plot of abs^{-1} as a function of time is linear with a slope of 0.540 min^{-1}

Report the rate law and the rate constant for this reaction (with units) and, in 2–4 sentences, explain how you arrived at this rate law.

Answer. This is an experiment run under pseudo-order conditions in which the concentration of D is many orders of magnitude greater than the concentration of C. We know that the rate of change in absorbance is second-order in C because a plot of $(\text{abs})^{-1}$ vs. time is a straight-line. The observed rate constant is related the true rate constant by the equation $k_{\text{obs}} = k[D]^{\beta}$. As doubling the concentration of D increases k_{obs} by a factor of 4, we know that $\beta = 2$. Substituting in results for either experiment gives k as 2.16 M^{-3} s^{-1}.

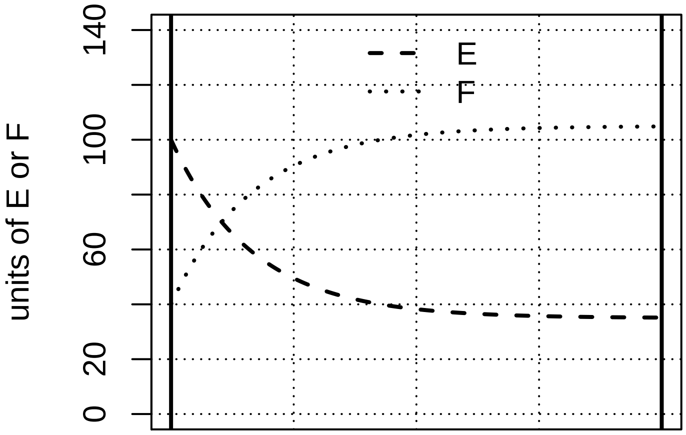
Problem 4. Consider the hypothetical equilibrium reaction $E \rightleftharpoons F$ where the forward reaction is first-order in E with a rate constant of 3.0×10^{-3} s^{-1} and where the reverse reaction is first-order in F with a rate constant of 1.0×10^{-3} s^{-1}.

What is the equilibrium constant for this reaction?

Answer. At equilibrium, we know that $k_{E \longrightarrow F}[E] = k_{F \longrightarrow E}[F]$. Solving for $K = \frac{[F]}{[E]}$ gives its value as $\frac{k_{E \longrightarrow F}}{k_{F \longrightarrow E}} = 3.0$.

Suppose you place 100 units of E and 40 units of F in a flask and allow the system to react until it reaches equilibrium. Use the axes below to show how the concentrations of E and of F will change as a function of time. The solid vertical line on the left is time = 0 and the solid vertical line on the right is the time where equilibrium is first established. Be sure your plot clearly distinguishes between E and F.

Answer. Using an ICE table, we can show that the equilibrium condition must satisfy the relationship $\frac{40+x}{100-x} = 3.0$. Solving gives x as 65 and the equilibrium concentrations are 105 for F and 35 for E; note that the total is 140 units, at required by a conservation of matter. The resulting concentration vs. time curves are shown below.



Problem 5. A kinetic study of the reaction $G + H_2 \longrightarrow GH + H$ shows that the reaction's rate is directly proportional to the concentration of H_2, independent of the concentration of G, and directly proportional to the concentration of I. Propose a two-step mechanism that is consistent with this information **and** explain, in 2–4 sentences, why your mechanism is plausible.

Answer. The rate depends on the concentration of I—which is not in the overall stoichiometry and is a catalyst—and on the concentration of H_2. Because the rate does not depend on the concentration of G, it must appear after the RDS, which, for a two-step mechanism, means that the first step is rate-determining. This is all we need to know to propose that the first step is $H_2 + I \longrightarrow HI + H$ and that the second step is $HI + G \longrightarrow HG + I$. The two steps add up to the overall reaction and the rate law for the first step—the rate-determining step—matches the experimental rate law.

Problem 6. Suppose you are studying the reaction $J + K \longrightarrow$ products under pseudo-order conditions where the reaction's rate law is first order in J. Based on some theoretical modeling of the reaction's energetics you have reason to believe the activation energy is 58.4 $\text{kJ/mol}_{\text{rxn}}$. A kinetic analysis of the reaction at a temperature of 298 K gives a pseudo-first-order rate constant of 0.502 d^{-1}. Suppose you wish to run the reaction so that just 1% of J remains after 24 hrs. What is the minimum temperature you can use?

Answer. To determine the minimum temperature, we need to know the smallest value of k that will satisfy the requirement that just 1% of J remain after 24 hours (1 day). To find the value for k we note that for a first-order reaction we have

$$\ln(0.01) = \ln(1) - k \times 1 \text{ d}$$

and solve for k obtaining a alue fo 4.605 d^{-1}. Substituting this back into the equation

$$\ln\left(\frac{4.605}{0.502}\right) = \frac{E_a}{R} \times \left(\frac{1}{298} - \frac{1}{T_2}\right)$$

and solving gives the minimum temperature as 329 K.