ENV 6002: Physical & Chemical Principles of Environmental Engineering

Fall 2021   University of South Florida
Homework #7   Civil & Environmental Engineering
Due Tues., Oct. 26, or Thurs., Oct. 28   J.A. Cunningham

Assignment for 2021: Complete any 4 problems. Each is worth 25 points.

1. For part of his PhD research, one of my former students (Hun-Young Wee) studied the catalytic dehalogenation of 1,2,4,5-tetrachlorobenzene (TeCB) to benzene. Below are tables of data he collected under two different sets of conditions, both in batch reactors. For each of the two experiments, determine if the disappearance of TeCB is zero-order, first-order, second-order, or something else. Also specify the value of the rate coefficient for each experiment. Be sure to give the correct units for k!

Experiment 1

time (min)	concentration of TeCB (mg/L)
0	5.0
5	2.93
10	2.06
20	0.61
30	0.28
45	0.057

Experiment 2

time (min)	concentration of TeCB (mg/L)
10	3.02
20	2.51
30	2.16
45	1.59
60	1.07

Wee HY, Cunningham JA, 2008. Palladium-catalyzed hydrodehalogenation of 1,2,4,5-tetrachlorobenzene in water-ethanol mixtures. *Journal of Hazardous Materials*, 155, 1–9.

Wee HY, Cunningham JA, 2011. Remediation of contaminated soil by solvent extraction and catalytic hydrodehalogenation: Semicontinuous process with solvent recycle. *Environmental Progress & Sustainable Energy*, 30(4), 589–598.

2. One of my master's students, Margaret Cone, continued the work of Dr Wee. She studied the sequential reaction TeCB → benzene → cyclohexane. This was an improvement over our earlier work, because cyclohexane is less toxic than benzene. The table below shows one of the data sets collected by Margaret in a batch reactor under a particular set of conditions. We hypothesized that the sequential reactions are both first-order at the conditions tested. Based on this assumption, estimate the two first-order rate coefficients: one for TeCB → benzene, the other for benzene → cyclohexane. Show your work and/or explain your reasoning for how you estimate the values of the rate coefficients. Be sure to include units.

time (min)	C/C_0 for TeCB	C/C_0 for benzene	C/C_0 for cyclohexane
0	1	0	0
1	0.4862	0.1398	0.1899
2	0.2134	0.1223	0.2336
4	0.0623	0.0351	0.6656
6	0.0324	0.0075	0.7095
8	0.0102	0.0108	0.8174
12	0	0	1.0289

Cone M, Osborn C, Ticknor JL, Cunningham JA, 2014. Effects of solvent composition and hydrogen pressure on the catalytic conversion of 1,2,4,5-tetrachlorobenzene to cyclohexane. *Environmental Engineering Science*, 31(3), 156–166.

3. Problems 1 and 2 used real data collected by my students. This one is fictional. The following data were collected from a system believed to follow Monod kinetics (or Michaelis-Menten kinetics). The data were collected in a batch reactor under a particular set of conditions. Estimate the values of k_{max} and K_S for the reaction under these experimental conditions. Specify the units on k_{max} and K_S.

time (hr)	concentration of reactant (mmol/L)
0	1.0
1	0.86
2	0.73
3	0.60
4	0.47
5	0.35
6	0.24
7	0.14
8	0.068
9	0.024
10	0.006

4. Two chemicals, A and B, are known to react with each other when dissolved in water. We don't know the stoichiometry of the reaction, and we don't know the kinetic rate expression. To determine these, we performed the following experiment. We added A and B to water in a batch reactor at known initial concentrations, $[A]_0$ and $[B]_0$. We then allowed the chemicals to react for 10 minutes. After 10 minutes, we quenched the reaction and measured the remaining concentrations $[A]$ and $[B]$. This procedure was repeated for 5 different sets of initial conditions. The table below summarizes the data.

    a. Determine the stoichiometry of the reaction. Hint: for each mole of A that disappears, how much B disappears along with it?

    b. For each of the five experiments, determine the apparent *reaction rate* over the 10-minute interval. Be sure to specify the units on reaction rate.

    c. Determine the reaction *order* with respect to both A and B. Hint: look at your reaction rates from part (b). How does reaction rate vary with concentration of A? How does reaction rate vary with concentration of B?

    d. Determine the reaction rate coefficient. Be sure to specify the units.

Experiment	$[A]_0$ (mmol/L)	$[B]_0$ (mmol/L)	[A] after 10 min (mmol/L)	[B] after 10 min (mmol/L)
1	1.00	2.00	0.97	1.97
2	2.00	2.00	1.88	1.88
3	3.00	2.00	2.74	1.74
4	1.00	4.00	0.94	3.94
5	1.00	6.00	0.91	5.91

5. When we disinfect water using Cl_2 or HOCl, we inadvertently form undesirable chemicals called "disinfection by-products" (DBPs). Some DBPs are toxic and/or carcinogenic. One class of DPBs is trihalomethanes, and one trihalomethane of concern is bromodichloro-methane (BDCM), which has the molecular formula $CHBrCl_2$.

    One of my Master's degree students, Hélène Kassouf, studied the rate of formation of trihalomethanes when municipal wastewater is disinfected with HOCl. She performed experiments at different temperatures and at different doses of HOCl. Below is a table that contains a couple of the data points gathered by Hélène during her research. These data were gathered at a disinfectant dose of 6 mg/L (as Cl_2).

Temperature (°C)	Concentration of BDCM after 15 min (µg/L)
16	17.3
23	20.0
30	25.6

5. continued

The mechanism by which BDCM is formed from HOCl is actually quite complicated. However, we can say that the rate of BDCM formation is approximately first-order in the concentration of HOCl:

HOCl + other contituents → BDCM $r = k_1$ [HOCl]

(This is most certainly an over-simplification, but it's OK for this problem set.)

a.   From the table of data, estimate/calculate the *reaction rate* over the initial 15-minute period for each of the three temperatures. Report your answer in units of μmol/(L·min). You will need to convert from μg/L to μmol/L.

b.   Estimate/calculate the first-order rate coefficient, k_1, at each temperature. Be sure to specify the units on k_1. Note that the concentration of HOCl is reported "as Cl_2" so be sure to account for that. Hint: use your answers from part (a).

c.   Estimate/calculate the activation energy for the formation of BDCM from HOCl. Report your answer in units kJ/mol.

d.   Estimate/calculate the first-order rate coefficient k_1 for BDCM formation at temperatures of 10 °C and 35 °C, assuming an HOCl dose of 6 mg/L (as Cl_2). Then repeat for an HOCl dose of 9 mg/L (as Cl_2).

e.   Estimate/calculate how much BDCM you would expect to see formed in 15 minutes at temperatures of 10 °C and 35 °C, assuming an HOCl dose of 6 mg/L (as Cl_2). Then repeat for an HOCl dose of 9 mg/L (as Cl_2).

f.   What do you conclude about the importance of temperature on DBP formation during wastewater disinfection?

Kassouf H, Cunningham J, Mulford L, Iranipour G, 2018. Chlorine demand and trihalomethane formation during chlorination of wastwater in Hillsborough County, Florida: Effects of temperature and chlorine dose. *ASCE Journal of Environmental Engineering*, 144(8), 04018067.

6. *based on a problem I got from Prof Q Zhang*

An irreversible reaction, $A → B$, is carried out in a batch reactor. For a certain set of conditions, it is found that the reaction is 50 percent complete after 30 min.
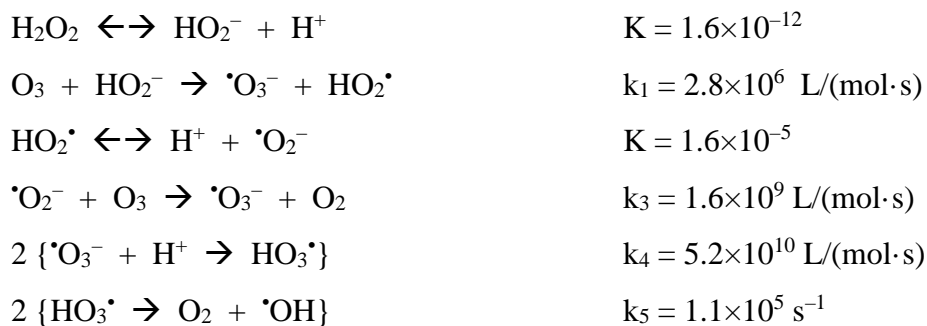
(a)   Assume that the reaction kinetics are first-order. Estimate the value of the reaction rate coefficient, k_1, implied by the data. How much time would be required to reach the same degree of completion (50%) if we doubled the initial concentration of A? How much time would be required to reach the same degree of completion if we doubled the reaction rate coefficient?

6. continued

    (b) Now assume that the reaction kinetics are second-order. Estimate the value of the reaction rate coefficient, k_2, implied by the data. Be sure to specify the units. How much time would be required to reach the same degree of completion (50%) if we doubled the initial concentration of A? How much time would be required to reach the same degree of completion if we doubled the reaction rate coefficient?

7. Advanced oxidation processes (AOPs) are a group of chemical processes used for treating water. AOPs are especially useful when the water contains organic contaminants that are difficult to remove by other (less expensive) processes. Most AOPs rely on the formation of hydroxyl radicals, $^{\bullet}OH$. (It is also sometimes written $HO^{\bullet}$. That is the same thing.) Hydroxyl radicals are highly reactive oxidizing agents that are good at destroying lots of different organic contaminants. One way to form hydroxyl radicals is by adding ozone (O_3) and hydrogen peroxide (H_2O_2) to the water. Ozone and peroxide react to form hydroxyl radicals. The mechanism for $^{\bullet}OH$ formation goes like this.

$$H_2O_2 \longleftrightarrow HO_2^- + H^+ \qquad\qquad K = 1.6 \times 10^{-12}$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}O_3^- + HO_2^{\bullet} \qquad\qquad k_1 = 2.8 \times 10^6 \ L/(mol{\cdot}s)$$

$$HO_2^{\bullet} \longleftrightarrow H^+ + {}^{\bullet}O_2^- \qquad\qquad K = 1.6 \times 10^{-5}$$

$$^{\bullet}O_2^- + O_3 \rightarrow {}^{\bullet}O_3^- + O_2 \qquad\qquad k_3 = 1.6 \times 10^9 \ L/(mol{\cdot}s)$$

$$2 \ \{{}^{\bullet}O_3^- + H^+ \rightarrow HO_3^{\bullet}\} \qquad\qquad k_4 = 5.2 \times 10^{10} \ L/(mol{\cdot}s)$$

$$2 \ \{HO_3^{\bullet} \rightarrow O_2 + {}^{\bullet}OH\} \qquad\qquad k_5 = 1.1 \times 10^5 \ s^{-1}$$

    a. Write the net stoichiometry for the formation of $^{\bullet}OH$ from H_2O_2 and O_3. It's not bad, really. Just "add" all of the above equations and cancel out anything that appears on both the left- and right-hand sides.

    b. This reaction is definitely not an elementary reaction. Show that the overall rate expression for the formation of $^{\bullet}OH$ is

$$\textit{\textbf{r}} = 2 \ k_1 \ [O_3] \ [HO_2^-]$$

To show this, start with $\textit{\textbf{r}} = k_5 \ [HO_3^{\bullet}]$, which comes directly from the last equation. Then, apply the pseudo-state-state approximation (also called stationary-state approximation, or quasi-steady-state approximation, or QSSA) to the four radical species $^{\bullet}O_3^-$, $HO_2^{\bullet}$, $^{\bullet}O_2^-$, and $HO_3^{\bullet}$. Then work through the algebra.

NOTE: When I teach ENV 6519, Physical and Chemical Processes for Groundwater Remediation, we design an AOP system to treat groundwater contaminated with some organic contaminants. We use some of the chemical kinetics from above to estimate/predict the concentration of hydroxyl radicals formed in our treatment system. It's pretty fun!