CE4501 Environmental Engineering Chemical Processes, Fall 2008
Problem Set 7

Due: Wednesday, 12/10 by 5 p.m.
Solutions will be posted on the Web. Problem sets will be graded for completeness, and one problem (selected at random) will be graded in detail. Each problem set contributes 2.5% towards your final grade.

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1. The accident at the nuclear power plant in Chernobyl released a number of radioisotopes to the environment. All of these isotopes ultimately ended up in soils and sediments. Two of the isotopes released were ^{134}Cs and ^{129}I. The half-lives for these isotopes are 2.06 yr and 1.56×10^7 yr, respectively. In villages 10 km from Chernobyl, the concentrations of these two isotopes in the soil were raised approximately 250x background. How long will it take for concentrations in the soil to return to within 10x background levels?

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2. You wish to design a reactor for the microbial degradation of pentachlorophenol (PCP). Laboratory experiments reveal the following kinetics for disappearance of the PCP:

Time (min)	PCP conc. (μg/L)
0	170
20	161
60	140
150	95
280	30

A) What is the order of the reaction?
B) What is one possible mechanism that could explain the reaction order?
C) How long will be required to reduce the concentration to the Maximum Contaminant Level of 1 μg/L?

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3. The reaction

$$2CH_3NHCl \Longrightarrow CH_3NCl_2 + CH_3NH_2$$

may proceed either directly (as written) or by the mechanism:

$$CH_3NHCl + H_2O \Longrightarrow CH_3NH_2 + HOCl \quad \text{(slow)}$$
$$CH_3NHCl + HOCl \Longrightarrow CH_3NCl_2 + H_2O \quad \text{(fast)}$$

The first mechanism leads to a second-order reaction; the second mechanism leads to a first-order reaction. In an experiment at pH 3.5 with $[CH_3NHCl] = 5.5 \times 10^{-4}$ M, the following results were obtained:

Time (min):	0	10	20	30	40
$[CH_3NHCl]$ (μM)	500	312	228	179	147

Determine the reaction order (and apparent mechanism) of the reaction. Also determine the reaction rate constant and the half-life.

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4. Microbial nitrification (the oxidation of ammonium to nitrate) can be modeled as a two-step, consecutive, first-order process:

$NH_4^+ + 1.5O_2 \Rightarrow NO_2^- + H_2O + 2H^+$

$NO_2^- + 0.5O_2 \Rightarrow NO_3^-$

(It is really higher order, but we will assume that the concentration of O_2 remains constant, and treat the reaction as pseudo-first order.) Model the time course of the three nitrogen forms for the following conditions:

$[NH_4^+]_o = 2.0$ mM

$[NO_2^-]_o = [NO_3^-]_o = 0$

The rate constant for the first reaction is 0.2 d^{-1} and that for the second reaction is 1.0 d^{-1}.

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5. Experiments were conducted in the lab to determine that rate at which dibromopropane (DBP, a soil fumigant) is broken down in water. To get results in a reasonable amount of time, the experiments were conducted at elevated temperatures. From the results below, calculate the first order rate constant and half life at 25°C.

Temperature (°C)	Rate constant (s^{-1})
76	4.4×10^{-5}
61	0.69×10^{-5}
45	0.10×10^{-5}

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6. Problem 22.6 in the text (p. 517)