CEE 697K

Environmental Reaction Kinetics

Homework #1

1. Chapter 2, problem 1 in Brezonik (pg.102).

Mass

15 g total weight

$[^{40}K] = 15g*(0.5/100)*(0.00118/100) = 8.85 \times 10^{-7}$ g $= 2.21 \times 10^{-8}$ M

$= 6.028 \times 10^{23}$ atoms/M x 2.21×10^{-8} M

$= 1.33 \times 10^{16}$ atoms

Rate:

T ½ = 1.28×10^{9} years $= 6.73 \times 10^{14}$ min

K= ln(2)/ t ½ $= 0.693 / 6.73 \times 10^{14} = 1.0296 \times 10^{-15}$ min^{-1}

Disintegrations = 1.33×10^{16} atoms x 1.0296×10^{-15} min^{-1}

= 13.72 dpm

2. Using the kinetic plot and data for the hydrolysis of Benzyl Chloride as presented in class (refer to posted slides), determine the following:

a. The expected concentration of benzyl chloride after 72 hours (@25°C), when the initial concentration was 33µg/L.

0.923 µg/L

b. The expected concentration of benzyl chloride after 72 hours (@25°C), when the initial concentration was 7.9µg/L.

0.221 µg/L

c. The expected concentration of benzyl chloride after 72 hours (@0.1°C), when the initial concentration was 33µg/L.

29.6 µg/L

3. It has been known for some time that concentrated solutions of aqueous chlorine lose strength with time. Accompanying this is the accumulation of chlorate ion. Early chemical studies have determined this to be a second order reaction in hypochlorite. The stoichiometry is as follows:

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

Bolyard and co-workers [1992, Env. Sci. Technol. 26(8)1663-1665] found that chlorate is being inadvertently added to drinking water when aqueous chlorine is used as a disinfectant. Data collected at 14 sites showed that raw water chlorate levels were 0.02 mg/L or below. However, finished water levels were as high as 0.66 mg/L, apparently due to contamination from the chlorine stocks. Gordon and Adam [Water Disinfection News, 5:1, Novatek] have subsequently studied this reaction. They determined that a 2.776 M chlorine stock solution (15.89% FAC, d=1.239 g/mL) has a 61.7 day half-life at 25°C and pH 13. Based on this information answer the following questions.

a. What is the 2nd order rate constant for this reaction in units of $M^{-1}s^{-1}$?

$2.25 \times 10^{-8}\ M^{-1}s^{-1}$ if the rate is defined in terms of chlorate formation
$6.76 \times 10^{-8}\ M^{-1}s^{-1}$ if the rate is defined in terms of hypochlorite loss

b. Calculate the concentration of chlorate in the stock after 40 days holding time at 25°C

0.364 M

c. What is the dosed concentration (mg/L) of chlorate if sufficient stock (aged 40 days at 25°C) is added to a finished drinking water to achieve a free chlorine dose of 2.5 mg/L?

0.636 mg/L

d. Repeat "c", but assume that the chlorine stock was diluted by a factor of 4 prior to holding for 40 days. Assume that dilution does not change the value of the rate constant [we will find out later that it will change a bit due to the change in ionic strength].

0.158 mg/L

e. Consider an MCLG (maximum contaminant level goal) of 0.2 mg/L for chlorate. Determine the amount of dilution of the chlorine stock, which will just allow compliance after 40 days holding time at 25°C.

Dilution Factor = 3.2

Assigned: 28 Feb 08
Due: 11Mar 08