Homework #2

1. How many grams of anhydrous Sodium Sulfate (Na₂SO₄) must be added to a liter of water so that the ionic strength equals 0.01M?

$$\mu = \frac{1}{2} \sum C_i z_i^2$$

for a solution of sodium sulfate at a molar concentration of "C", we have "C" moles of sulfate (a divalent ion) and "2C" moles of sodium (a monovalent ion). Therefore,

$$\mu = \frac{1}{2} \left(2C(1)^2 + C(2)^2 \right)$$
$$\mu = 3C$$
$$C = \frac{1}{3} \mu = \frac{1}{3} (0.01) = 3.33 \times 10^{-3} M$$

since the GFW of Na_2SO_4 is (2x23)+32+(4x16)=142

$$C = 3.33 \times 10^{-3} M (142 \frac{g}{mole}) = 0.473 g / L$$

- 2. The pesticide, parathion, undergoes photolytic degradation (destruction by absorption of energy from the sun's rays) in natural waters. This is a first order process with a rate constant of 8x10⁻⁷s⁻¹.
 - a. What is the half-life for parathion based on this degradation process?

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$
$$t_{\frac{1}{2}} = \frac{0.693}{8x10^{-7}s^{-1}} = 866,250s = 14,438\min = 241hr = 10d$$

b. How long will it take for 90% of the parathion to degrade?

$$C = C_o e^{-kt}$$

$$C_o = e^{-kt}$$

$$\ln\left(C_o\right) = -kt$$





$$t = -\frac{1}{k} \ln \left(\frac{C}{C_o} \right)$$

$$t = -\frac{1}{8x 10^{-7} s^{-1}} \ln(0.1) = 2,878,000 s = 47,970 \min = 800 hr = 33.3d = 4.76 wks$$

c. How long will it take for 99% of the parathion to degrade?

$$t = -\frac{1}{k} \ln \left(\frac{C}{C_o} \right)$$

$$t = -\frac{1}{8x10^{-7}s^{-1}}\ln(0.01) = 5,756,000s = 95,940\min = 1,600hr = 66.6d = 9.52wks$$

- Hypochlorous acid (HOCI) reacts with phenol (C₆H₅OH) to produce a wide range of products including highly offensive chlorophenols. The rate of this reaction is second order, overall (first order in each reactant). The rate constant is 2x10³ M⁻¹s⁻¹. In this problem you have 1.2 ppb of phenol in water, and to this you add 0.1 mM hypochlorous acid.
 - a. How long will it take to destroy 50% of the phenol?

First, calculate molar phenol concentration.

$$Molarity = \frac{\frac{grams_{L}}{GFW}}{GFW}$$

$$GFW = (6x12) + (6x1) + 16 = 94$$

$$Molarity = \frac{\frac{1.2x10^{-6}g_{L}}{94}}{94} = 1.27x10^{-8}M = 0.0000128mM$$

1 point

Although this is a <u>second order kinetic</u> problem, one of the reactants (hypochlorous acid) is present at a very large molar excess (e.g., 0.1 mM vs 0.0000128mM). Therefore, this reactant will not become depleted as the reaction proceeds, and the overall reaction takes on the form of pseudo-first order kinetics.

So the following equation will hold:

$$C = C_o e^{-k't}$$

Where:

$$k' = k[HOCl] = 2x10^{3} M^{-1} s^{-1} (10^{-4} M) = 2x10^{-1} s^{-1}$$

and now we can simply used the re-arranged form of the first order kinetic equation as developed in question #2 above.

$$t = -\frac{1}{k'} \ln \left(\frac{C}{C_o} \right)$$

$$t = -\frac{1}{2x10^{-1}s^{-1}}\ln(0.5) = 3.47s$$

b. How long will it take to destroy 99.99% of the phenol?

And using the same equation again:

$$t = -\frac{1}{k'} \ln\left(\frac{C}{C_o}\right)$$
$$t = -\frac{1}{2x10^{-1}s^{-1}} \ln(0.0001) = 46.1s$$

4. Calculate the ThOD of the following wastewaters

a. 45 mg/L of methanol

The balanced stoichiometric equation is:

$$\underbrace{CH_3OH}_{32} + \underbrace{1\frac{1}{2}O_2}_{48} \rightarrow 1CO_2 + 2H_2O$$

The ThOD is then:

$$ThOD = 45 \frac{mg - CH_3OH}{L} \times \left(\frac{48mg - O_2}{32mg - CH_3OH}\right)$$



b. 10 mg/L of glucose

The balanced stoichiometric equation is:

$$\underbrace{C_6H_{12}O_6}_{180} + \underbrace{6O_2}_{192} \rightarrow 6CO_2 + 6H_2O$$

The ThOD is then:

$$ThOD = 10 \frac{mg - C_6 H_{12} O_6}{L} \times \left(\frac{192mg - O_2}{180mg - C_6 H_{12} O_6}\right)$$
$$ThOD = 10.7 \frac{mg - O_2}{L}$$

c. 45 mg/L of methanol with 10 mg/L glucose

The ThOD of the two components are calculated in parts a and b. The answer is the sum of the two, or:

$$ThOD = 67.5 \frac{mg - O_2}{L} + 10.7 \frac{mg - O_2}{L}$$
$$ThOD = 78.2 \frac{mg - O_2}{L}$$

d. 10⁻⁴ M acetic acid

First, the mass-based concentration is:

$$C_{HAc} = 10^{-4} \frac{mol - HAc}{L} \times \left(\frac{60g - HAc}{mol - HAc}\right) \times \left(\frac{1000mg}{g}\right) = 6 \frac{mg - HAc}{L}$$

The balanced stoichiometric equation is:

$$\underbrace{CH_3COOH}_{60} + \underbrace{2O_2}_{64} \rightarrow 2CO_2 + 2H_2O$$

The ThOD is then:

$$ThOD = 6 \frac{mg - CH_3COOH}{L} \times \left(\frac{64mg - O_2}{60mg - CH_3COOH}\right)$$
$$ThOD = 6.4 \frac{mg - O_2}{L}$$

e. 5 mg/L of trichloroethane

The balanced stoichiometric equation is:

$$\underbrace{Cl_3CCH_3}_{133.5} + \underbrace{2O_2}_{64} \rightarrow 2CO_2 + 3HCl$$

The ThOD is then:

$$ThOD = 5 \frac{mg - CCl_3CCH_3}{L} \times \left(\frac{64mg - O_2}{133.5mg - CCl_3CCH_3}\right)$$
$$ThOD = 2.4 \frac{mg - O_2}{L}$$

Don't forget to check that all elements are balanced as well as the charge

5. Nitrogen occurs at a variety of oxidation states in water environments. Balance the following oxidation-reduction reaction which is important in wastewater treatment:

$$NH_3 + O_2 \rightarrow NO_3^- + H_2O$$

1 point

Show all steps.

Oxidation: $3H_2O + \overset{-III}{N}H_3 \rightarrow \overset{+V}{N}O_3^- + 9H^+ + 8e^-$ Reduction: $\overset{0}{O}_2 + 4H^+ + 4e^- \rightarrow 2H_2 \overset{-II}{O}$

Multiply the reduction reaction by 2x and adding the two we get:

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O$$