Seoul National University

457.620.001

Water Contaminants

FINAL EXAMINATION

TIME ALLOWED: 120 MINUTES

May 31, 2018

---

1. Students may use two double-sided, A4 notes prepared in their own handwriting. Mechanical or electronic reproduction of any notes are not allowed.

2. Students should bring their own calculator which is not pre-programmed with formulae from the class.

3. Be aware that the cheated student will get 80% of the lowest score in class! There is no tolerance at all.

4. Make sure your answers include units if appropriate. Watch your units! Prepare your answers in a logical, easy-to-follow format.

5. If needed, use the following constants:
   Ideal gas constant, $R = 8.21 \times 10^{-2}\ L-atm/mole-K = 8.31 \times 10^{-3}\ kJ/mole-K$
   Faraday constant, $F = 96500\ Coulomb/mole = 96.5\ kJ/mole-V$

6. **Assume 25℃, 1 atm and activity = molarity in an aqueous solution unless specified in the question.**

1. Mark T or F for the following statements. (2 points each)

1) A metal ion located at the center of a complex ion is a Lewis acid.

Answer) T

2) BTEX content is higher in gasoline than in diesel.

Answer) F

3) The pK_a value of 3-chlorophenol is higher than that of 2-chlorophenol.

Answer) T

4) Tertiary amine acts as a hydrogen (bond) donor in an aqueous solution.

Answer) F

5) The molecular volume of a humic substance in an aqueous solution increases as the ionic strength of the solution increases.

Answer) F

6) The COD/TOC ratio of ethanol (C_2H_5OH) is higher than that of acetic acid (CH_3COOH).

Answer) T

7) By halogenation of a hydrocarbon, oxidation reaction becomes more thermodynamically favorable.

Answer) F

8) The rate of an S_N1-type nucleophile substitution reaction does not depend on the property of a leaving group.

Answer) T

9) By hydrolysis of 2-bromobutane, the two enantiomers of 2-butanol are produced at 1:1 ratio.

Answer) F

10) For a pulse input of a tracer, the maximum concentration at time t after the pulse input is inversely proportional to t.

Answer) F

2. Answer the following questions on organic molecules.

1) List all structural isomers of butanol (C_4H_9OH) and provide systematic name for each. Mark one of the structural isomer which has a pair of enantiomers (optical isomers).
* note: exclude ethers (e.g., CH_3-CH_2-O-CH_2-CH_3)

(9 points)

Answer)

CH_3-CH_2-CH_2-CH_2OH	*1-butanol*
CH_3-CH_2-CH(OH)-CH_3	*2-butanol*
CH_3-C(CH_3)(OH)-CH_3	*2-methyl-2-propanol*
CH_3-CH(CH_3)-CH_2OH	*2-methyl-1-propanol*

2-butanol has a pair of enantiomers.

2) List roles that dissolved organic matter plays in the fate of chemicals in the aquatic environment. (+1 for a correct item, -1 for an incorrect one; max. 6 points)

Answer)

- *Reduce the rate of direct photolysis by light attenuation*
- *Involved in indirect photolysis; excited by sunlight and produce PPRIs*
- *Increase the apparent solubility of hydrophobic organic compounds by sorbing the compounds*
- *Facilitate the transport of hydrophobic organic compounds by sorbing the compounds such that the compounds can be transported along with DOM*

- *Coat minerals such that the chemical interaction of the mineral surface with the aqueous phase is inhibited*
- *Sorb metals by chelation, electrostatic force, etc. to reduce the bioavailability of the metals*
- *Sorb metals by chelation, electrostatic force, etc. such that the metal transport mechanism is governed by DOM transport rather than the transport of the free metal (ion) phase in water*

and a lot more

3) Describe what the Stark-Einstein Law implies to the mechanism of photochemical reactions. (5 points)

Answer)

[Stark-Einstein Law] For each photon of light absorbed by a chemical system, only one molecule is activated.

Implication: A single atom should have sufficient energy to activate a molecule, which is a prerequisite for an occurrence of a photochemical reaction. In other words, the wavelength of light should be short enough such that the energy that a photon provides is large enough to induce excitation of a molecule.

3. Determine the H_2 partial pressure of an air bubble at thermodynamic equilibrium with water having a pH of 8.0 at a temperature of 25℃. The O_2 partial pressure of the air bubble is 0.21 atm. Use the following half reactions. (15 points)

$$O_2(g) + 4H^+ + 4e^- = 2H_2O \qquad E_H^0 = +1.23\ V$$

$$2H^+ + 2e^- = H_2(g) \qquad E_H^0 = 0.00$$

Answer)

Overall reaction:

$$2H_2(g)+O_2(g)=2H_2O \qquad E_H^0=+1.23-0.00=+1.23\ V$$

$$E_H=E_H^0-\frac{RT}{nF}\ln Q_r=1.23\ V-\frac{8.31\times10^{-3}\ kJ/mole-K\times298\ K}{4\times96.5\ kJ/mole-V}\ln Q_r=1.23\ V-6.415\times10^{-3}\ V\times\ln Q_r$$

For thermodynamic equilibrium, E_H should be zero.

$$Q_r=\exp\left(\frac{1.23\ V}{6.415\times10^{-3}\ V}\right)=1.866\times10^{83}$$

$$Q_r=\frac{1}{P_{O_2}P_{H_2}^2}=\frac{1}{0.21P_{H_2}^2}=1.866\times10^{83}$$

$$P_{H_2}=5.05\times10^{-42}\ atm$$

4. Using the following rates constants for methyl chloroacetate ($CH_2ClCOOCH_3$), determine the hydrolysis half-life at i) pH=4.0 and iii) pH=10.0.

k_A	k_N	k_B
8.5×10^{-5} $M^{-1}s^{-1}$	2.1×10^{-7} s^{-1}	1.4×10^{2} $M^{-1}s^{-1}$

k_A = 2nd order acid-catalyzed hydrolysis rate constant
k_N = pseudo 1st order neutral hydrolysis rate constant
k_B = 2nd order base-catalyzed hydrolysis rate constant

(15 points)

Answer)

Pseudo 1st order hydrolysis rate constant,

$$k_h=k_A[H^+]+k_N+k_B[OH^-],\ \ t_{1/2}=\frac{\ln 2}{k_h}$$

$$pH=4.0:\ k_h=8.5\times10^{-5}\ M^{-1}s^{-1}\cdot10^{-4}\ M+2.1\times10^{-7}\ s^{-1}+1.4\times10^{2}\ M^{-1}s^{-1}\cdot10^{-10}\ M$$

$$=2.33\times10^{-7}\ s^{-1}$$

$$t_{1/2} = \frac{\ln 2}{2.33\times 10^{-7}\ s^{-1}} = 2.97\times 10^{6}\ s = 34.4\ d$$

$$pH = 10.0:\ k_h = 8.5\times 10^{-5}\ M^{-1}s^{-1}\cdot 10^{-10}\ M + 2.1\times 10^{-7}\ s^{-1} + 1.4\times 10^{2}\ M^{-1}s^{-1}\cdot 10^{-4}\ M$$

$$= 1.40\times 10^{-2}\ s^{-1}$$

$$t_{1/2} = \frac{\ln 2}{1.40\times 10^{-2}\ s^{-1}} = 49.5\ s$$

5. During his Ph.D. study, Prof. Choi used polyethylene (PE) passive samplers to determine the aqueous equilibrium concentration of 2-methyl naphthalene, an alkylated polycyclic aromatic hydrocarbon (PAH), in a sediment slurry amended with activated carbon (AC). In a 40-mL amber vial, he added **<u>10 g sediment (in dry weight), 0.5 g activated carbon, 30 cm^3 water, and a piece of PE passive sampler.</u>** After 12 months of continuous mixing, he sampled the PE passive sampler to determine the 2-methyl naphthalene concentration therein, which could be used to calculate the aqueous concentration of the compound. From the literature and his previous laboratory works he obtained following partitioning coefficients.

Parameter	H_{pc} (atm·cm^3/mole)	K_d (cm^3 water/g sed.)	K_{PE} (cm^3 water/g PE)	K_{AC} (cm^3 water/g AC)
Value	520	2.9×10^3	2.2×10^3	1.3×10^5

K_d: sediment-water partitioning coefficient
K_{PE}: PE-water partitioning coefficient
K_{AC}: AC-water partitioning coefficient

He wanted the **<u>mass of 2-methyl naphthalene in the PE passive sampler to be less than 0.5% of the total compound mass in the vial</u>**, because otherwise the sediment-AC-water equilibrium may be affected by the presence of the PE passive sampler. **<u>What would be the maximum value of PE mass he could add to the vial?</u>** Use the **<u>fugacity approach</u>**. Assume that **<u>equilibrium for PAH mass distribution had been established</u>** within the vial, all phase equilibrium processes followed linear partitioning and **<u>partitioning to the headspace (gas phase) is negligible.</u>**

(20 points)

Answer)

Calculate the Z (or Z) values and Z×V (or Z*×M) for each phase:*

	Water	Sediment	PE	AC
Volume (cm^3)	30	-	-	-
Mass (g)	-	10	M_{PE}	0.5
Z (mole/atm/cm^3)	1.92×10^{-3}			
Z* (mole/atm/g)		5.58	4.23	250
ZV or Z*M (mole/atm)	0.0577	55.8	$4.23M_{PE}$	125

Note $Z_{water} = \frac{1}{H_{pc}}$ *and* $Z_s^* = C_s^*/H_{pc}$ *(s can be sediment, PE, or AC)*

$$\frac{M_{PE}^{2-NAPH}}{M_{tot}} = \frac{Z_{PE}^* M_{PE}}{\sum ZV \text{ or } Z^* M} = 0.005$$

$$4.23M_{PE} = 0.005 \times (0.0577 + 55.8 + 4.23M_{PE} + 125)$$

$$M_{PE} = 0.225\ g$$

6. The K_La value for oxygen in an aerobic bioreactor is determined to be 5.0 hr^{-1}. What would be the K_La value for nitrous oxide (N_2O), a greenhouse gas that may be produced by biological reactions, in the bioreactor? Use the following data and assumptions.

* H_{cc} (oxygen) = 30; H_{cc} (nitrous oxide) = 1.7
* Surface renewal theory applies to the gas-liquid mass transfer.
* $k_G/k_L \fallingdotseq 100$.
* Less than 5% error is negligible.
* Diffusion coefficient in water, D_L
D_L (oxygen) = 2.0×10^{-9} m^2/s; D_L (nitrous oxide) = 1.6×10^{-9} m^2/s

(10 points)

Answer)

As $R_G = \frac{1}{k_G H_{cc}} < \frac{1}{100}\frac{1}{k_L} = \frac{1}{100} R_L$ *for both oxygen and nitrous oxide,*

Liquid phase boundary layer controls the gas-liquid mass transfer for both compounds

If surface renewal theory holds, $k_L \propto D_L^{0.5}$.

So: $K_L \propto D_L^{0.5}$ *and so does* $K_L a$ *because* a *is a constant for the same bioreactor.*

K_La *(nitrous oxide)* $= 5.0\,hr^{-1} \times \left(\frac{1.6 \times 10^{-9}\ m^2/s}{2.0 \times 10^{-9}\ m^2/s}\right)^{0.5} = 4.5\,hr^{-1}$