Seoul National University

457.620.001

Water Contaminants

FINAL EXAMINATION

TIME ALLOWED: 120 MINUTES

May 31, 2018

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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.

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

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

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

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

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

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

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

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

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

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)

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)

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

3. **<u>Determine the H_2 partial pressure</u>** 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)

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

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

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

k_A	k_N	k_B
$8.5\times10^{-5}\ M^{-1}s^{-1}$	$2.1\times10^{-7}\ s^{-1}$	$1.4\times10^{2}\ M^{-1}s^{-1}$

k_A = 2^{nd} order acid-catalyzed hydrolysis rate constant
k_N = pseudo 1^{st} order neutral hydrolysis rate constant
k_B = 2^{nd} order base-catalyzed hydrolysis rate constant
(15 points)

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 10 g sediment (in dry weight), 0.5 g activated carbon, 30 cm^3 water, and a piece of PE passive sampler. 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} ($atm\cdot cm^3/mole$)	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 mass of 2-methyl naphthalene in the PE passive sampler to be less than 0.5% of the total compound mass in the vial, because otherwise the sediment-AC-water equilibrium may be affected by the presence of the PE passive sampler. **What would be the maximum value of PE mass he could add to the vial?** Use the fugacity approach. Assume that equilibrium for PAH mass distribution had been established within the vial, all phase equilibrium processes followed linear partitioning and partitioning to the headspace (gas phase) is negligible.

(20 points)

6. The K_La value for oxygen in an aerobic bioreactor is determined to be 5.0 hr^{-1}. **<u>What would be the K_La value for nitrous oxide</u>** (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)