Seoul National University

457.620.001

Water Contaminants

FINAL EXAMINATION

TIME ALLOWED: 75 MINUTES

May 18, 2016

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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, $F = 96500\, Coulomb/mole = 96.5\, kJ/mole-V$

1. Mark O or X for the following statements.

(+2.5 points for correct answers; -1 points for incorrect answers)

i) Boron fluoride (BF_3) molecule has a net dipole moment of zero.

Answer) O

ii) In a metal complex ion, ligand is a Lewis acid attached to the metal ion in the center (Lewis base).

Answer) X

iii) The pK_a value for 2-nitrophenol is smaller than that for 3-nitrophenol. (Note: nitro group is a strong electron withdrawing group)

Answer) O

iv) Tertiary amines can act as both hydrogen donors and acceptors.

Answer) X

v) Molecular volume of a dissolved humic substance is generally greater at higher pH.

Answer) O

vi) When a linear concentration gradient is developed for a dissolved species between spatial locations A and B in a water body, there will be no net diffusive transport of the species between the two locations.

Answer) X

vii) The rate for a nucleophile substitution reaction following S_N2 mechanism does not depend on the property of a leaving group.

Answer) X

viii) Direct photolysis will not occur if the energy of a single photon is not enough to activate a single molecule.

Answer) O

2. For the chemicals below, answer the following questions.

acetic acid, CH_3COOH

2-butanol, $CH_3CH(OH)CH_2CH_3$

glyceraldehyde, $CH_2(OH)CH(OH)CHO$

2-chloropropane, $CH_3CHClCH_3$

i) Identify all compounds that have enantiomers (optical isomers).

(4 points)

Answer)

Selecting those having a carbon singly bonded to four different entities:

2-butanol and glyceraldehyde

ii) Compare the theoretical COD/TOC ratios of the compounds.

(6 points)

Answer)

Compare the mean oxidation number of carbons:

acetic acid: 0; 2-butanol: -2; glyceraldehyde: 0; 2-chloropentane: -2

2-butanol = 2-chloropentane > acetic acid = glyceraldehyde

3. Calculate the $E_H^0(W)$ values for the following half reactions:

i) $C_6H_5NO_2 + 6e^- + 6H^+ \Leftrightarrow C_6H_5NH_2 + 2H_2O, \; \Delta_r G^0 = -479.3\ kJ/mole$

ii) $SO_4^{2-}+9H^++8e^-\Leftrightarrow HS^-+4H_2O,\ \Delta_rG^0=193.0\ kJ/mole$

(10 points)

Answer)

i)

$$E_H^0=-\frac{\Delta_rG^0}{nF}=-\frac{-479.3\ kJ/mole}{6\cdot 96.5\ kJ/mole-V}=0.828\ V$$

$$E_H^0(W)=E_H^0-\frac{2.303RT}{nF}logQ_r=E_H^0-\frac{0.059\ V}{n}logQ_r$$

$$E_H^0(W)=0.828\ V-\frac{0.059\ V}{6}log\frac{\{C_6H_5NH_2\}}{\{C_6H_5NO_2\}\{H^+\}^6}=0.828\ V-\frac{0.059\ V}{6}log\frac{1}{(10^{-7})^6}=0.42\ V$$

ii)

$$E_H^0=-\frac{\Delta_rG^0}{nF}=-\frac{193.0\ kJ/mole}{8\cdot 96.5\ kJ/mole-V}=-0.25\ V$$

$$E_H^0(W)=-0.25\ V-\frac{0.059\ V}{8}log\frac{\{HS^-\}}{\{SO_4^{2-}\}\{H^+\}^9}=-0.25\ V-\frac{0.059\ V}{8}log\frac{1}{(10^{-7})^9}=-0.71\ V$$

4. The hydrolysis rate constants for methyl chloroacetate ($CH_2(Cl)COOCH_3$) are determined as follows. Determine the half lives of this compound at i) pH=3.0 and ii) pH=9.0 at 25℃ (K_w = 10^{-14}).

$k_A=8.5\times10^{-5}\ M^{-1}s^{-1}$

$k_N=2.1\times10^{-7}\ s^{-1}$

$k_B=1.4\times10^{2}\ M^{-1}s^{-1}$

(10 points)

Answer)

$k_h=k_a[H^+]+k_N+k_B[OH^-]$

i) pH = 3.0

$k_h = 8.5 \times 10^{-5}\ M^{-1}s^{-1} \cdot 10^{-3.0}\ M + 2.1 \times 10^{-7}\ s^{-1} + 1.4 \times 10^{2}\ M^{-1}s^{-1} \cdot 10^{-11.0}$

$= 2.96 \times 10^{-7}\ s^{-1}$

$$t_{1/2} = \frac{\ln 2}{2.96 \times 10^{-7}\ s^{-1}} = 2.3 \times 10^{6}\ s = 27\ days$$

ii) pH = 9.0

$k_h = 8.5 \times 10^{-5}\ M^{-1}s^{-1} \cdot 10^{-9.0}\ M + 2.1 \times 10^{-7}\ s^{-1} + 1.4 \times 10^{2}\ M^{-1}s^{-1} \cdot 10^{-5.0}$

$= 1.40 \times 10^{-3}\ s^{-1}$

$$t_{1/2} = \frac{\ln 2}{1.40 \times 10^{-3}\ s^{-1}} = 495\ s = 8.25\ \min$$

5. Calculate the half life of nitrobenzene in a well-mixed aqueous solution subject to a UV light (wavelength = 320 nm) with an intensity of 1.0×10^{-5} millieinstein/cm^2-s. Assume the followings:

   a) The light absorbed by the aqueous solution is negligible compared to the incoming light (i.e., $\alpha_D \cdot z_{mix} < 0.02$)

   b) The light absorbed by nitrobenzene is negligible compared to the light absorbed by other constituents in the aqueous solution

   Use a molar extinction coefficient of 800 $M^{-1}cm^{-1}$ and a reaction quantum yield of 2.9×10^{-5} for nitrobenzene at a wavelength of 320 nm, and assume the distribution function $D(\lambda) = \alpha_D(\lambda)/\alpha(\lambda)$ is 1.02.

(15 points)

Answer)

The near surface direct photolysis rate is expressed as

$k_p^o = 2.303 I_o(\lambda) D(\lambda) \epsilon_i(\lambda) \Phi_{ir}(\lambda)$

$= 2.303 \cdot 1.0 \times 10^{-5}\, milliE/cm^2 - s \cdot 1.02 \cdot 800\, L/mole - cm \cdot 2.9 \times 10^{-5}\, mole/E$

$= 5.45 \times 10^{-7}\, s^{-1}$

$$t_{1/2} = \frac{\ln 2}{5.45 \times 10^{-7}\, s^{-1}} = 1.27 \times 10^{6}\, s = 14.7\, days$$

6. The pesticide DDT (MW = 354.5) has the following properties:

Vapor pressure = $10^{-9.87}$ atm (25℃)
Aqueous solubility = $10^{-7.85}$ mole/L (25℃)
Octanol-water partitioning coefficient, $K_{ow} = 10^{6.36}$

i) Calculate the Henry's constant at 25℃ expressed as a dimensionless concentration ratio, H_{CC}.

(5 points)

Answer)

$$H_{PC} = \frac{P^{sat}}{C^{sat}} = \frac{10^{-9.87}\, atm}{10^{-7.85}\, mole/L} = 9.55 \times 10^{-3}\, atm - L/mole$$

$$H_{CC} = \frac{H_{PC}}{RT} = \frac{9.55 \times 10^{-3}\, atm - L/mole}{8.21 \times 10^{-2}\, L - atm/mole - K \cdot 298\, K} = 3.90 \times 10^{-4}$$

ii) In a 40-mL vial, you added 5 g sediment and 20 mL water, spiked some DDT, and agitated the contents until equilibrium was established. The air volume in the vial was 17 mL. Determine how much fraction of the spiked DDT mass will partition into the gas phase. The sediment distribution coefficient, K_d, is estimated to be 1.5×10^5 L/kg.

(15 points)

Answer)

$$Z^{air} = \frac{1}{RT} = 0.0409\ mole/L-atm$$

$$Z^{water} = \frac{1}{H_{PC}} = \frac{1}{9.55\times10^{-3}\ atm-L/mole} = 105\ mole/L-atm$$

$$Z^{sed*} = \frac{K_d}{H_{PC}} = \frac{1.5\times10^{5}\ L/kg}{9.55\times10^{-3}\ atm-L/mole} = 1.57\times10^{7}\ mole/kg-atm$$

$$\sum ZV = 0.0409\ mole/L-atm\cdot 0.017\ L + 105\ mole/L-atm\cdot 0.020\ L + 1.57\times10^{7}\ mole/kg-atm\cdot 0.005\ kg$$

$$= 7.85\times10^{4}\ mole/atm$$

$$\frac{Z^{air}V^{air}}{\sum ZV} = \frac{0.0409\ mole/L-atm\cdot 0.017\ L}{7.85\times10^{4}\ mole/atm} = 8.86\times10^{-9}$$

7. You obtained overall mass transfer coefficient K_L values as shown in the table for the gas-liquid transfer of oxygen and phenol in a well-mixed reactor. Assuming that i) film theory is applicable, ii) liquid phase controls the mass transfer for oxygen, and iii) gas phase controls the mass transfer for phenol, estimate the K_L values for 1,4-dichlorobenzene.

Compounds	K_L (m/s)	H_{CC}	D_L (m^2/s)	D_G (m^2/s)
Oxygen	2.0×10^{-5}	30	2.1×10^{-9}	2.3×10^{-5}
Phenol	3.3×10^{-8}	3.0×10^{-5}	9.1×10^{-10}	8.3×10^{-6}
1,4-dichlorobenzene	-	0.091	7.9×10^{-10}	6.9×10^{-6}

D_L = aqueous diffusion coefficient; D_G = gas diffusion coefficient

(15 points)

Answer)

For oxygen: $K_L = k_L = 2.0\times10^{-5}\ m/s$

For phenol: $K_L = H_{CC}\times k_G = 3.3\times10^{-8}\ m/s,\ k_G = 1.1\times10^{-3}\ m/s$

$$k_L = \frac{D_L}{\delta_L},\ \ k_G = \frac{D_G}{\delta_G}$$

Therefore, for 1,4-dichlorobenzene:

$$k_L = 2.0\times 10^{-5}\, m/s \times \frac{7.9\times 10^{-10}}{2.1\times 10^{-9}} = 7.5\times 10^{-6}\, m/s$$

$$k_G = 1.1\times 10^{-3}\, m/s \times \frac{6.9\times 10^{-6}}{8.3\times 10^{-6}} = 9.1\times 10^{-4}\, m/s$$

$$H_{CC}\times k_G = 9.1\times 10^{-4}\, m/s \cdot 0.091 = 8.3\times 10^{-5}\, m/s$$

So, for 1,4-dichlorobenzene, liquid phase resistance is more significant than gas phase resistance, but gas phase resistance cannot be safely neglected.

$$K_L = \frac{k_L k_G H_{CC}}{k_L + k_G H_{CC}} = \frac{7.5\times 10^{-6}\cdot 8.3\times 10^{-5}}{7.5\times 10^{-6} + 8.3\times 10^{-5}} = 6.9\times 10^{-6}\, m/s$$