Seoul National University

457.620.001

Water Contaminants

FINAL EXAMINATION - SOLUTIONS

TIME ALLOWED: 75 MINUTES

November 28, 2022

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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 NOT get any credits for the course! 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.

1. Mark O or X (or T or F) for the following statements.

(+2 points for correct answers; -2 points for incorrect answers)

1) Ethylene (ethene) has a dipole moment of zero.

Answer) O

2) The COD/TOC ratio of ethylene (ethene) is smaller than the COD/TOC ratio of acetylene (ethyne).

Answer) X

3) Ethylbenzene is a planar molecule.

Answer) X

4) The pK_a of o-cresol (systematic name: 2-methylphenol) is greater than the pK_a of 2-(trifluoromethyl) phenol.

Answer) O

5) Phthalates are hydrogen bond acceptors.

Answer) X

6) Polychlorinated biphenyls are conservative compounds.

Answer) X

7) The hydrolysis rate constant of CH_3Br is greater than the hydrolysis rate constant of CH_3Cl. (Assume reaction conditions, e.g., temperature and pH, are the same)

Answer) O

8) The resistance at the liquid phase boundary layer dominates the overall resistance of mass transfer at the air-water interface for highly volatile compounds.

Answer) O

2. Answer the followings.

1) Arrange the following molecules in the order of decreasing water solubility. Explain your rationale. (8 points)

pentane (C_5H_{12})	perfluoropentane (dodecafluoropentane; C_5F_{12})
cyclopentane (C_5H_{10})	methyl tert-butyl ether [1,1-dimethylethyl methyl ether; $(CH_3)_3COCH_3$]

Answer)

$WS_{cyclopentane}$ > $WS_{pentane}$ because both are nonpolar and the molecular volume of the cyclic compound should be smaller

WP_{MTBE} the greatest because it is the only polar among the four C5 molecules

$WP_{perfluoropentane}$ the smallest because of the full fluorination

Thus, MTBE > cyclopentane > pentane > perfluoropentane

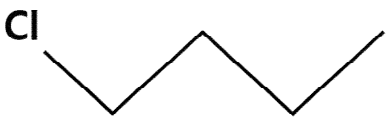
** Literature water solubility values:*

MTBE, 26 g/L; cyclopentane, 156 mg/L; pentane, 40 mg/L; perfluoropentane, 0.456 mg/L

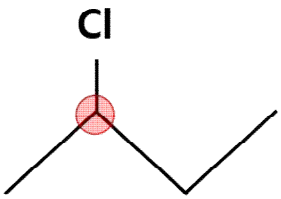
2) Draw the molecular structure (i.e., molecular constitution) of the following chemicals. Mark all chiral centers. (8 points)

1-chlorobutane	2-chlorobutane
2-chloro-2-methylpropane	1,2-dichloro-2-methylbutane

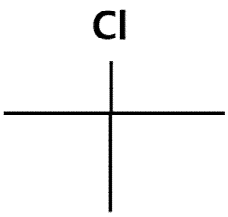
Answer)



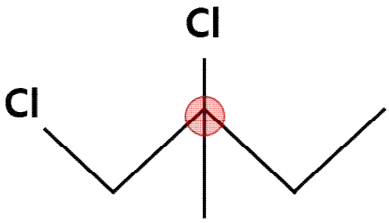
1-chlorobutane



2-chlorobutane



2-chloro-2-methylpropane



1,2-dichloro-2-methylpropane

3) Briefly describe the possible fates of a molecule that has been excited by light absorption. (6 points)

Answer)

- *undergoes chemical transformation (direct photolysis)*
- *transfers the energy to other molecules (photosensitization)*
- *loss of energy by heat or light emission*

4) A cube-sized crystal is being dissolved in a cup of water. How fast will the dissolution rate change right after cutting the crystal into eight smaller cubes? Show your reasoning. (5 points)

Answer)

Because the surface area doubles while the volume stays the same by the cutting, the $K_L a = K_L(A/V)$ *doubles.*

3. The reductive dechlorination reaction of trichloromethane is written as

$$CHCl_3(aq) + H_2(g) = CH_2Cl_2(aq) + H^+(aq) + Cl^-(aq)$$

with half reactions of

$$CHCl_3(aq) + H^+(aq) + 2e^-(aq) = CH_2Cl_2(aq) + Cl^-(aq), \qquad E_H^0 = +0.68\ V$$

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

Determine the molar ratio of aqueous CH_2Cl_2 and $CHCl_3$ at thermodynamic equilibrium at the following condition.

Use the Faraday constant, F, of 96500 J/mol-V and the ideal gas constant, R, of 8.31 J/mol-K. Assume activity = molarity.

(14 points)

Answer)

$$Q_r = \frac{[CH_2Cl_2][H^+][Cl^-]}{[CHCl_3]P_{H_2}} = \frac{10^{-6.0} \cdot 10^{-3.0} \cdot [CH_2Cl_2]}{10^{-5.0} \cdot [CHCl_3]} = 10^{-4.0}\frac{[CH_2Cl_2]}{[CHCl_3]}$$

$$E_H = E_H^0 - \frac{RT}{nF}\ln Q_r = 0 \quad \text{(at equilibrium)}$$

$$Q_r = \exp\left(\frac{nFE_H^0}{RT}\right)$$

$$\frac{[CH_2Cl_2]}{[CHCl_3]} = 10^{4.0} \times \exp\left(\frac{nFE_H^0}{RT}\right) = 10^{4.0} \times \exp\left(\frac{2 \cdot 96500\ J/mol-V \cdot 0.68\ V}{8.31\ J/mol-K \cdot 298\ K}\right)$$

$$\frac{[CH_2Cl_2]}{[CHCl_3]} = 1.04 \times 10^{27}$$

4. You have a UV-visible light spectrophotometer that can differentiate down to 0.03-unit

difference in absorbance. Determine the minimum difference of aqueous concentration of phenol that can be differentiated by this device. The molar extinction coefficient of phenol is 1500 /M-cm at the maximum absorption wavelength of 275 nm. The light path length of the spectrophotometer is 1 cm. Assume the light absorption by water constituents other than phenol is exactly the same.

(8 points)

Answer)

$\Delta A = \epsilon \cdot \Delta C \cdot l$

$\Delta C = \frac{0.02}{1500\ /M-cm \times 1\ cm} = 2 \times 10^{-5}\ M$

5. Estimate the half life of 1,2-bromoethane in the hypolimnion of the Lower Mystic Lake, MA, USA. Use the following data and assumptions.

Nucleophiles	Lake water chemistry	$n_{Nu,\,CH_3Br}$
Cl^-	0.4 M	3.0
HS^-	3 × 10^{-3} M	5.1
S_4^{2-}	9 × 10^{-5} M	7.2
OH^-	6.3 × 10^{-8} M	4.2

- The neutral hydrolysis rate, k_N, is 3.5 × 10^{-9} s^{-1}.
- Assume the sensitivity constant, s, as 1.0.
- The temperature is 25 ℃.

(15 points)

Answer)

$k_{obs} = k_{H_2O}\left([H_2O] + 10^{n_{Cl^-CH_3Br}}[Cl^-] + 10^{n_{HS^-CH_3Br}}[HS^-] + 10^{n_{S_4^{2-}CH_3Br}}[S_4^{2-}] + 10^{n_{OH^-CH_3Br}}[OH^-]\right)$

$= k_{H_2O}\{55.3 + 10^{3.0} \cdot (0.4\ M) + 10^{5.1} \cdot (3 \times 10^{-3.0}) + 10^{7.2} \cdot (9 \times 10^{-5}) + 10^{4.2} \cdot (6.3 \times 10^{-8}\ M)\}$

$$k_N = k_{H_2O}[H_2O] = 55.3k_{H_2O}$$

$$k_{obs} = k_N \times \frac{k_{H_2O}\{55.3 + 10^{3.0} \cdot (0.4\ M) + 10^{5.1} \cdot (3\times10^{-3}) + 10^{7.2} \cdot (9\times10^{-5}) + 10^{4.2} \cdot (6.3\times10^{-8}\ M)\}}{55.3k_{H_2O}}$$

$$k_{obs} = 0.024\ s^{-1}$$

$$t_{1/2} = \frac{\ln 2}{0.024\ s^{-1}} = 28.9\ s$$

6. You are asked to determine the equilibrium freely dissolved concentration (C_{free}) of benzo(a)pyrene[a] in the pore-water of sediment in a lake contaminated with polycyclic aromatic hydrocarbons (PAHs). You plan to use an ex-situ polyethylene (PE) passive sampling technique to complete this task. In detail, you plan to add 10-g lake sediment (in dry mass), 30-mL water, and a piece of clean PE sheet in a 40-mL vial, which will be agitated vigorously for four weeks at 25 ℃ to ensure equilibrium. After the agitation, the PE will be collected, wiped clean to remove any sediment particles, and then submitted for benzo(a)pyrene concentration analysis. The equilibrium C_{free} of benzo(a)pyrene will be determined by $C_{free}=C_{PE}/K_{PE}$, where C_{PE} is the benzo(a)pyrene concentration in PE and K_{PE} is the PE-water partition coefficient.

   You find from the literature that for ex-situ passive sampling the mass of analyte (benzo(a)pyrene in this case) accumulated in the passive sampler is recommended not to exceed 0.5% of the total analyte mass in the system (vial in this case). **Determine the maximum amount of PE passive sampler you can add into the 40-mL vial** to conform to this recommendation. Use the following information.

   Benzo(a)pyrene K_{PE} = 1.2 × 10^6 L/kg (@ 25 ℃)
   Benzo(a)pyrene K_{oc} = 2.0 × 10^6 L/kg (@ 25 ℃)[b]
   Benzo(a)pyrene Henry's constant = 4.57 × 10^{-4} L-atm/mol (@ 25 ℃)[b]
   Benzo(a)pyrene vapor pressure: negligible (@ 25 ℃)
   Sediment f_{oc} = 0.025[c]

[a] A member of PAHs
[b] organic carbon-water partition coefficient
[c] total organic carbon fraction in sediment

(20 points)

Answer)

We do not need to account for the benzo(a)pyrene in the headspace (air) because its vapor pressure is negligible.

To use fugacity approach, calculate the Z values first.

$$Z^{aq} = \frac{1}{H_{pc}} = \frac{1}{4.57\times10^{-4}\ L-atm/mol} = 2188\ mol/L-atm$$

$$K_p = f_{oc}K_{oc} = 5.0\times10^{4}\ L/kg$$

$$Z^{sed}* = \frac{K_p}{H_{pc}} = \frac{5.0\times10^{4}\ L/kg}{4.57\times10^{-4}\ L-atm/mol} = 1.1\times10^{8}\ mol/kg-atm$$

$$Z^{PE}* = \frac{K_{PE}}{H_{pc}} = \frac{1.2\times10^{6}\ L/kg}{4.57\times10^{-4}\ L-atm/mol} = 2.6\times10^{9}\ mol/kg-atm$$

The recommendation is mathematically written as

$$\frac{Z^{PE}*M^{PE}}{Z^{PE}*M^{PE}+Z^{sed}*M^{sed}+Z^{aq}V^{aq}} \le 0.005$$

$$\frac{(2.6\times10^{9}\ mol/kg-atm)M^{PE}}{(2.6\times10^{9}\ mol/kg-atm)M^{PE}+(1.1\times10^{8}\ mol/kg-atm)(0.01\ kg)+(2188\ mol/L-atm)(0.03\ L)} \le 0.005$$

$$M^{PE} \le \frac{0.005\times\{(1.1\times10^{8}\ mol/kg-atm)(0.01\ kg)+(2188\ mol/L-atm)(0.03\ L)\}}{0.995\times(2.6\times10^{9}\ mol/kg-atm)}$$

$$M^{PE} \le 2.13\times10^{-6}\ kg = 2.13\ mg$$