Fall 2005
CEE 432/532 Fate and Transport of Pollutants
Midterm #1 (Time 90 minutes)

<u>Instructions</u>

Write your Name - NOW.

Please turn in your exam after 90 minutes.

Each subpart of a particular problem may or may not be independent. For example, you may need correct answer of (ii) to calculate the correct answer of (iii).

In order to get partial credits, you must show your method/calculations.

Most problems require that you calculate answers in specified units; please read the problem and answer carefully.

1. The aqueous ethylbenzene concentration in groundwater near a leaking underground storage tank is 0.5 mg/L (K_{oc} for ethylbenzene = 1.1 x 10^3 mL/gm). Assume sorption follows the following linear model:

$$S = K_d * C$$

where,   S = mass sorbed per mass sorbent (mg/kg)
          K_d = partition or distribution coefficient (mL/gm)
          C = concentration in groundwater at equilibrium (mg/L)

(i) The distribution coefficient in the above equation describes the equilibrium between:
    (A) solid and the liquid phase
    (B) solid and the gas phase
    (C) solid and fish tissue
    (D) solid and fugacity constant.

(ii) The S versus C curve for the above equation is:
    (A) straight line
    (B) concave downwards
    (C) concave upwards
    (D) perfect ellipse

(iii) Assuming a silty soil containing 0.1% organic carbon, the distribution coefficient (K_d) for of ethylbenzene (in mL/gm) is most nearly:
    (A) 2
    (B) 1.1
    (C) 110
    (D) none of the above

$$K_d = K_{oc} * f_{oc}$$
$$= (1.1 \times 10^3) \frac{mL}{gm} * 0.001$$
$$= 1.1 \frac{mL}{gm}$$

(iv) Assuming $K_d = 4.0$, the expected concentrations of ethylbenzene sorbed to a silty soil (in mg/kg) is most nearly:
    (A) 8
    (B) 4
    (C) 2
    (D) none of the above

$$\frac{mL}{gm}$$

$$S = K_d * C$$
$$= \left(4 \frac{mL}{gm} * 0.5 \frac{mg}{L}\right) * \frac{L}{1000\,mL}$$
$$= 2.0 \frac{mg}{kg}$$

2. If 765 mg of trichloroethene or TCE (MW = 131.4 gm/mole and aqueous solubility = 1000 mg/L) is added to 1.0 L of water in a 11.0 L sealed bottle. The dimensionless Henry's Law constant is 4.2 x 10⁻¹.

(i) At equilibrium, the solvent will form a
      (A) Light Non Aqueous Phase Liquid (LNAPL)
      (B) Dense Non Aqueous Phase Liquid (DNAPL)
      Ⓒ Completely dissolved phase
      (D) fugacity phase

(ii) The aqueous phase concentration of TCE (in mg/L) is most nearly:
      Ⓐ 147.1
      (B) 182.7
      (C) 1821.0
      (D) 2000.0

Handwritten work:

$$4.2 \times 10^{-1} = C_{air}/C_{water} = \frac{\frac{765-x}{10}}{x}$$

$$\Rightarrow 0.42\,x = \frac{765-x}{10}$$

$$\Rightarrow 4.2\,x + 1x = 765$$

$$\Rightarrow x = 765/5.2 = 147.1 \text{ mg}$$

$$\text{or } 147.1\,\frac{mg}{L}$$

(iii) The gas phase concentration of TCE (in mg/L) is most nearly:
      (A) 618.0
      Ⓑ 61.7
      (C) 765.0
      (D) 0.42

Handwritten work:

Amt. in air = 765 - 147.1
              = 617.9 mg in 10 L air

Conc. 61.79 mg/L

(iv) TCE is a common contaminant typically found in:
      (A) bottled water
      Ⓑ groundwater
      (C) Delaware River water
      (D) Rain Water

3. A first-order chemical reaction is 40% complete in 50 minutes.

(i) The reaction rate constant (k) (in min^{-1}) is most nearly:

    (A) 0.0182

    (B) 0.0102

    (C) 0.0022

    (D) none of the above

$$\frac{C}{C_o} = 0.6 = e^{-kt}$$
$$\Rightarrow -0.51 = -k * 50$$
$$\Rightarrow k = 0.0102 \; min^{-1}$$

(ii) The half-life (in minutes) is most nearly:

    (A) 37.8

    (B) 67.8

    (C) 97.8

    (D) none of the above

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0102}$$
$$= 67.94 \; min$$

(iii) The time required (in minutes) for 80% completion is most nearly:

    (A) 157.78

    (B) 134.33

    (C) 123.20

    (D) 111.00

20% remaining
$$0.2 = e^{-kt} = e^{-0.0102 * t}$$
$$\Rightarrow -1.609 = -0.0102 x$$
$$\Rightarrow x = 157.78 \; min$$

(iv) If the reaction temperature increases the reaction rate will:

    (A) increase

    (B) decrease

    (C) not change

    (D) double

4. A groundwater sample collected from a contaminated site is found to contain 10^{-8} M hydrogen (H^+), 10^{-1} M chloride (Cl^-), 2×10^{-1} M sodium (Na^+), and 5×10^{-2} M sulfate (SO_4^{-2}). The concentration of cupric ion detected (Cu^{2+}) in the water is 10^{-7} M.

(i) Strictly speaking, pH is defined as:
   (A) $-\log_{10}\{H^+\}$
   (B) $-\log_{10}[H^+]$
   (C) $-\log_e\{H^+\}$
   (D) $-\log_e[H^+]$

*[ ] indicates molar concentration and { } indicates activity

(i) The pH of the water is most nearly:
   (A) -8
   (B) 8
   (C) 10^{-8}
   (D) 10^8

(ii) The ionic strength of the solution (in M) is most nearly:
   (A) 0.15
   (B) 0.25
   (C) 0.35
   (D) 0.45

$$I = [(-1)^2(10^{-1}) + (1)^2(2\times10^{-1}) + (-2)^2(5\times10^{-2}) + (2)^2(10^{-7})$$
$$+ (1)^2(10^{-8}) + (-1)^2(10^{-6})]$$

$$= 0.25$$

(iii) Assuming ionic strength of the solution is 0.5 M, the activity of copper (in M) is most nearly:
   (A) 1.0×10^{-7}
   (B) 2.2×10^{-8}
   (C) 5.2×10^{-8}
   (D) 6.2×10^{-8}
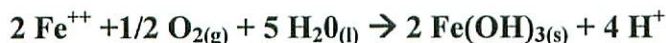
For $I = 0.5 M$

$-\log_{10} \gamma = 0.6$

$\Rightarrow \gamma = 0.25$

$\{Cu^{++}\} = \gamma [Cu^{++}] = 0.25 \times 10^{-7}$

$= 2.5 \times 10^{-8}$ M

5. The ΔG^o of the reactants and products of the following reaction at $25^o C$ are given below.

$$2\ Fe^{++} + 1/2\ O_{2(g)} + 5\ H_2O_{(l)} \rightarrow 2\ Fe(OH)_{3(s)} + 4\ H^+$$

Specie	ΔG^o, kCal/mole
Fe^{++}	-20.3
$O_{2(g)}$	0
$H_2O_{(l)}$	-56.7
$Fe(OH)_{3(s)}$	-166.0
H^+	0

(i) The value of ΔG^o (in kCal/mole) for the reaction is most nearly:

    (A) 7.9

    (B) -7.9

    (C) 48.5

    (D) -48.5

ΔG^o = products - reactants

$= [4*0 + 2*(-166.0)] - [2*(-20.3) + \frac{1}{2}*0 + 5*(-56.7)]$

$= -7.9$ kcal/mole

(ii) The value of K is most nearly:

    (A) 610,260.00

    (B) 6.1×10^{-5}

    (C) 1.01

    (D) 7.6×10^5

Correct
T. A.

$\Delta G^o = -RT \ln K$

$\Rightarrow \ln K = \Delta G^o / -RT$

$= \dfrac{-7.9 * 1000}{-1.99 * 298}$

$= 13.32$

$\Rightarrow K = 6.1 \times 10^5$

(iii) The the ΔG is negative for certain concentrations of reactants and products, the reaction:

    (A) will proceed from left to right

    (B) will proceed from right to left

    (C) is at equilibrium

    (D) none of the above

(iv) Gibbs free energy of the chemical system provides information on:

    (A) both the direction in which a chemical reaction will proceed and how fast the reaction will proceed.

    (B) both the direction in which a chemical reaction will proceed and the rate-limiting step in the reaction.

    (C) both the molar concentrations of reactants and the final equilibrium composition of the system.

    (D) both the direction in which a chemical reaction will proceed and the final equilibrium composition of the system.

6. A large tank of water containing 500 ppm of sodium chloride (NaCl, MW = 58.5 gm/mole) is connected to a large tank of distilled water with a narrow tube 10 cm long. The pressures are adjusted so that there is no bulk fluid flow and the system reaches steady state.

(i) The concentration of NaCl (in mmoles/L) is most nearly:
    (A) 50.0
    (B) 500.0
    (C) 58.5
    (D) 8.54

Conc. $= 500$ ppm $= 500$ mg/L $* \dfrac{mmole}{58.5\ mg}$

$= 8.54$ mmole/L

(ii) At steady state, the transfer of chemical through the tube is due to:
    (A) pressure differential
    (B) advection
    (C) concentration gradient
    (D) convection.

(iii) Assuming diffusion coefficient = 10^{-5} cm^2/sec, the flux of salt (in mg/cm^2-sec) in the tube due to molecular diffusion is most nearly:
    (A) 5×10^{-2}
    (B) 5×10^{-3}
    (C) 5×10^{-4}
    (D) 5×10^{-7}

$J = \left(10^{-5}\ \dfrac{cm^2}{sec}\right) \left(\dfrac{500 - 0}{10}\right) \dfrac{mg}{L} \cdot \dfrac{1}{cm} \cdot \dfrac{1 L}{1000\ cm^3}$

$= 5 \times 10^{-7}\ \dfrac{mg}{cm^2 - sec}$

(iv) If the diameter of the tube is 3 inch, the mass flow rate of salt (in mg/sec) is most nearly:
    (A) 3.53×10^{-6}
    (B) 2.28×10^{-5}
    (C) 1.98×10^{-4}
    (D) 1.22×10^{-3}

Area of the pipe $= \dfrac{\pi}{4} (3 * 2.54)^2$

$= 45.6\ cm^2$

Flux $= 5 \times 10^{-7}\ \dfrac{mg}{cm^2 - sec} * 45.6\ cm^2$

$= 2.28 \times 10^{-5}\ \dfrac{mg}{sec}$