# Homework #3 - Solutions

Due: May 26 (Tue) 23:59

Question set I: Photochemical reactions

1. You made a phenanthrene solution in distilled water in a transparent bottle and placed the bottle under an ultraviolet light with an intensity of 1×10^{-5} millieinstein/cm^2-s and a (single) wavelength of 320 nm for 5 hours until use. Your lab-mate, who took this class a year ago, discovered the bottle. (S)he told you should not have done so and had to make a new phenanthrene solution.

1) Briefly describe the reason why your lab-mate told you so. Consider the chemical structure of phenanthrene shown below. (8 points)

 <phenanthrene>
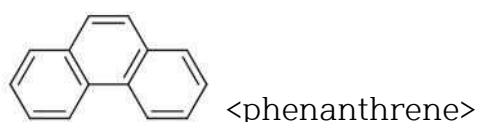
Answer)

Phenanthrene may be susceptible to UV light because its resonance structure may act as a good chromophore.

2) Calculate how much fraction of phenanthrene would have lost due to direct photolysis. Assume that the UV light absorption by phenanthrene is negligible compared to the UV light absorption by water. Also assume that only very little change of UV light

intensity occurs when the light passes the bottle containing the phenanthrene-dissolved water. The molar extinction coefficient for phenanthrene at 320 nm wavelength is $10^{2.4}$ $M^{-1}cm^{-1}$ and the reaction quantum yield is 0.01. The distribution function, $D(\lambda) = \alpha_D(\lambda)/\alpha(\lambda)$, is 1.02. (22 points)

Answer)

By the two assumptions, this situation satisfies the "negligible light absorption" case we discussed in the lecture:

$$k_p^o = \frac{2.303\, W_0(\lambda)\alpha_D^0(\lambda)\epsilon_i(\lambda)\Phi_{ir}(\lambda)}{\alpha(\lambda)} = 2.303\, W_0(\lambda)D^0(\lambda)\epsilon_i(\lambda)\Phi_{ir}(\lambda)$$

$$= 2.303 \cdot 10^{-5}\, millieinistein/cm^2 - s \cdot 1.02 \cdot 10^{2.4}\, M^{-1}cm^{-1} \cdot 0.01$$

$$= 5.90 \times 10^{-5}\, s^{-1} = 0.21\, h^{-1}$$

$$\frac{C}{C_0} = e^{-kt} = \exp(-0.21\, h^{-1} \cdot 5\, h) = 0.35$$

65% of phenanthrene is lost

Question set II: Phase equilibrium

You want to examine the ability of activated carbon to remove benzene in water. For this purpose, you are designing the following experimental procedure: i) add deionized water and activated carbon at a volume to weight ratio of 1000 mL/g (=1000 L/kg) in a bottle, ii) spike a certain amount of benzene into the bottle, iii) agitate the bottle until the inner content of the bottle reaches equilibrium with respect to benzene partitioning, and iv) sample the aqueous phase to determine the aqueous concentration at equilibrium.

Assuming that the mass of benzene in the headspace of the bottle is negligible at equilibrium, you can set up the following mass balance for the system:

$$M^T = M^{AC} C_{eq}^{AC} + V^{aq} C_{eq}^{aq} \tag{1}$$

where M^T = mass of benzene spiked to the bottle, mg

M^{AC} = mass of activated carbon added to the bottle, g

V^{aq} = volume of deionized water added to the bottle, mL

C_{eq}^{AC} = equilibrium concentration of benzene in activated carbon, μg/kg

C_{eq}^{aq} = equilibrium concentration of benzene in the aqueous phase, μg/L

Rearrangement of this mass balance equation enables us to determine the equilibrium concentration of benzene in activated carbon, C_{eq}^{AC}, using the experimentally determined value of C_{eq}^{aq}:

$$C_{eq}^{AC} = \frac{M^T - V^{aq} C_{eq}^{aq}}{M^{AC}} \tag{2}$$

If you repeat this procedure for various deionized water volume-to-activated carbon weight ratios, you get multiple C_{eq}^{aq}-C_{eq}^{AC} pairs, which allows you to construct a sorption isotherm plot.

Answer the questions below that are related to the design of this experiment. Assume that the experiments are to be conducted at standard condition (25 ℃, 1 atm).

1) Determine the maximum headspace-to-water volume ratio allowed for neglecting the mass of benzene in the headspace of the bottle at equilibrium, in other words, for Equation (1) to be valid. Assume you accept a maximum benzene mass fraction of 1% in the headspace relative to the total amount in the system (i.e., $M_{eq}^{air} \leq 0.01M^T$; where M_{eq}^{air} is the mass of benzene in the headspace (air) at equilibrium). Use fugacity approach and the following data/assumptions. (45 points)

   i) Henry's law constant of benzene, H_{pc} = 5.50 L-atm/mol

   ii) octanol-water partition coefficient of benzene, K_{ow} = 148

   iii) K_{ow}-K_{oc} relationship, $K_{oc} = 0.63K_{ow}$ (K_{oc} in L/kg)

   iv) Assume the K_{oc} value of activated carbon is 100 times greater than the K_{oc} value of natural organic matter [which is derived from iii)] and the organic carbon content of activated carbon is 0.8.

Answer)

First, determine the activated carbon-water partition coefficient of benzene, K_{AC}:

$K_{oc} = 0.63K_{ow} = 93.24 \ L/kg$

$K_{oc,AC} = 100K_{oc} = 9324 \ L/kg$ *($K_{oc,AC}$ = K_{oc} value of activated carbon)*

$$K_{AC} = f_{oc,AC}K_{oc,AC} = 0.8 \times 9324 \ L/kg = 7459 \ L/kg$$

Now, determine the Z values for each phase:

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

$$Z^{water} = \frac{1}{H_{pc}} = \frac{1}{5.50 \ L-atm/mol} = 0.182 \ mol/L-atm$$

$$Z^{AC*} = \frac{K_{AC}}{H_{pc}} = \frac{7459 \ L/kg}{5.50 \ L-atm/mol} = 1356 \ mol/kg-atm$$

Construct a table as follows:

Phase	Volume or Mass (L or kg)	Z^i or Z^{i*} (mol/L-atm or mol/kg-atm)	$Z^i \times V^i$ or $Z^{i*} \times M^i$ (mole/atm)	$(Z_i \times V_i)/\Sigma(Z_i \times V_i)$	mass (µg)
Air	V^{air}	0.0409	$0.0409V^{air}$	?	M_{eq}^{air}
Water	V^{aq}	0.182	$0.182V^{aq}$	?	M_{eq}^{aq}
AC	M^{AC}	1356	$1356M^{AC}$	?	M_{eq}^{AC}
Total	–	–	–	?	M^T

We have:

$$V^{aq} = 1000M^{AC}$$

$$M_{eq}^{air} \leq 0.01M^T$$

$$\sum(Z^i \times V^i) = 0.0409\,V^{air} + 0.182\,V^{aq} + 1356M^{AC} = 0.0409\,V^{air} + 0.182\,V^{aq} + 1356 \times \frac{V^{aq}}{1000}$$

$$= 0.0409\,V^{air} + 1.538\,V^{aq}$$

$$\frac{M_{eq}^{air}}{M^T} = \frac{Z^{air} \times V^{air}}{\sum(Z^i \times V^i)} = \frac{0.0409\,V^{air}}{0.0409\,V^{air} + 1.538\,V^{aq}} \leq 0.01$$

$$0.01538\,V^{aq} \geq 0.04049\,V^{air}$$

$$\frac{V^{air}}{V^{aq}} \leq 0.380$$

2) From the result in 1), you determined to use a 100-mL bottle and to add 95 mL of deionized water in it, leaving 5 mL of headspace for conservativeness. Deionized water volume-to-activated carbon weight ratio of 1000 mL/g will be applied as planned. Now your concern is if you will be able to quantify the aqueous equilibrium concentration of benzene by an analytical instrument in your laboratory. The limit of quantification (LOQ) for the analysis of aqueous benzene concentration is 10 μg/L using the instrument. What is the minimum amount of benzene you need to spike to the bottle ($M_{T,\min}$) for the estimated aqueous equilibrium concentration of benzene (C_{eq}^{aq}) to be 10 times higher than the LOQ value? (25 points)

Answer)

So, $C_{eq}^{aq} \geq 100\,\mu g/L$ should hold.

Because the gas phase can safely be neglected, the system can be reduced to a two-phase system where Equation (1) [$M^T = M^{AC}C_{eq}^{AC} + V^{aq}C_{eq}^{aq}$] holds. This equation can further be modified and then be as

$$M^T = M^{AC}K_{AC}C_{eq}^{aq} + V^{aq}C_{eq}^{aq}$$

$$= \frac{V^{aq}K_{AC}C_{eq}^{aq}}{1000\ L/kg} + V^{aq}C_{eq}^{aq} = \left(1 + \frac{K_{AC}}{1000\ L/kg}\right)V^{aq}C_{eq}^{aq}$$

$$= \left(1 + \frac{7459\ L/kg}{1000\ L/kg}\right) \times 0.095\ L \times C_{eq}^{aq} = (0.8036\ L) \times C_{eq}^{aq}$$

$$C_{eq}^{aq} = \frac{M^T}{0.8036\ L} \geq 100\,\mu g/L$$

$$M^T \geq 80.4\,\mu g$$