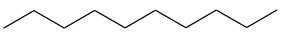
CHEM 331

Problem Set #2: Water Solubility and Partitioning

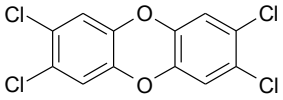
Submit answers to even numbered questions only. Due Wednesday, Feb. 17th

1. Calculate the activity coefficients, γ_w^{sat} and molar water solubility of the following liquids C_w^{sat}(L) at 25°C (*subcooled/superheated, if necessary)*, using the data provided. Rationalize the magnitude of these values using your understanding of the intermolecular interactions that influence water solubility?



n-decane

T_m = -29.7 °C
T_b = 174.1 °C
-log C_w^{sat} (L) = 6.57 (mol L^{-1})
-log P^o (L) = 2.76 (atm)



2,3,7,8-tetrachloro-dibenzo-p-dioxin

T_m = 305 °C
T_b = 421 °C
-log C_w^{sat} (s) = 10.3 (mol L^{-1})
-log P^o (s) = 11.6 (atm)

bromomethane

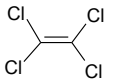
T_m = -93,6 °C
T_b = 3.6 °C
-log $C_w^{1\ atm}$(g) = 0.79 (mol L^{-1})
-log P^o(L) = -0.26 (atm)

2. As can be seen from the data in Appendix C, the aqueous solubility of *n*-hexanol and di-*n*-propylether exceed that of *n*-hexane by more than two orders of magnitude.

a) Calculate the aqueous activity co-efficient for each of these compounds based on C_w^{sat} values given in Appendix C of your textbook.
b) Provide a molecular level description based on intermolecular interactions to explain the differences in C_w^{sat}.
c) Use Eqn 5-22 (Schwarzenbach) to evaluate the various factors that determine the aqueous solubilities of the three compounds. You will find all necessary data in Tables 4.3, 5.5 and Appendix C.

Note that the refractive index values (n_D) are 1.418, 1.381 and 1.375 for *n*-hexanol, di-*n*-propylether and *n*-hexane, respectively.

3. Because of the growing concern over atmospheric contamination by organic pollutants, researchers have focused attention on the composition of rainwater. Assume that PCE and 2-methoxyphenol are present in the atmosphere at low concentrations. Consider a drop of water (volume = 0.1 mL, pH = 6.0) in a volume of 100 L of air (corresponding to the approximate volume ratios in a cloud). Calculate the fraction of each compound present in the water drop at 25°C at equilibrium. How will your answer change if the temperature is 5°C?

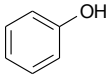


perchloroethene (PCE)

T_m = -19 °C
T_b = 121 °C
- log P^o = 1.60 (atm)
- log C_w^{sat} = 3.04 (mol L^{-1})
log K_H = 1.44 (atm M^{-1})

methyl-*t*-butylether (MTBE)

T_m = -109 °C
T_b = 55.2 °C
- log P^o = 0.496 (atm)
- log C_w^{sat} = 0.34 (mol L^{-1})
log K_H = -0.152 (atm M^{-1})



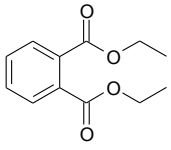
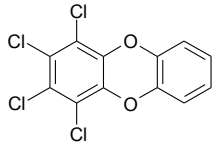
phenol

T_m = 43 °C
T_b = 181.7 °C
- log P^o(L) = 3.41 (atm)
- log C_w^{sat}(L) = 0.02 (mol L^{-1})
log K_H = -3.39 (atm M^{-1})

4. Use the characteristic atomic molar volumes, experimental water solubility and the fragment contributions of Hine and Mookerjee on the attached tables to estimate the following. In each case, comment on how your estimates compare to literature values?

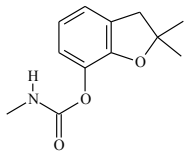
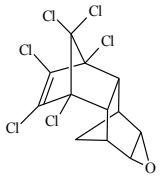
a) The aqueous molar solubility of isooctane (2,2,4-trimethylpentane).
b) The unitless Henry's Law constant, K_H' (K_{aw}) for *lindane* (hexachlorocyclohexane) and pentachlorophenol.
c) Convert your answer in part a) to a mole fraction concentration and your answer in part b) to kPa m^3 mol^{-1}.

5. a) The structures of diethylphthalate and 1,2,3,4-tetrachlorodibenzodioxin are shown below. Describe which of these compounds will have a greater tendency to be i) transported from surface water to the atmosphere
ii) less soluble in seawater than freshwater, iii) bio-accumulated by aquatic organisms
Use the chemical structure and physio-chemical data below to justify your answer.

	-log P° (Pa)	-log C_w^{sat} (M)	-log K_{aw}	log K_{ow}
diethyl phthalate	0.66	2.4	4.6	2.4
1,2,3,4-tetrachlorodibenzo-*p*-dioxin	5.2	8.8	2.8	6.6

b) Comment on the environmental distribution of the following pesticides between organic rich sediments and the water column from the following information. Explain your reasoning and justify.

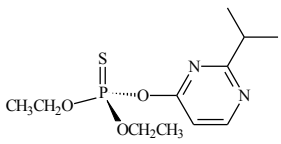
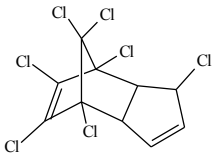
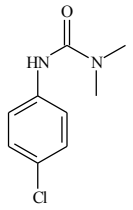



Carbofuran
log K_{ow} = 1.6

Dieldrin
log K_{ow} = 5.5

6. Calculate Henry's Law Constant in units of atm.M^{-1} (at 25°C) for each of the pesticides from the following vapor pressures and solubilities at 25°C. Convert each of these to a unitless K_{aw} value and calculate the fraction of each compound in the air in equilibrium with an equal volume of aqueous solution.

Pesticide	Molar Mass (g.mol^{-1})	Vapour Pressure (mPa)	Solubility (mg.L^{-1})
Diazinon	304	16.0	40.0
Heptachlor	373	22.0	5.60 x 10^{-3}
Monuron	199	2.30 x 10^{-2}	2.60 x 10^{2}

Diazinon Heptachlor Monuron

7. C_1 and C_2 halocarbons of natural and anthropogenic origin are ubiquitous in the atmosphere and marine ecosystems. For example, the compound 1,1,1-trichloroethane (TCE) is found in the northern hemisphere at typical concentrations of 0.9 mg m^{-3} in air and 2.5 mg m^{-3} in surface seawater. Using these concentrations, evaluate whether there is a net flux of TCE between the air and the surface seawater assuming a temperature of 25°C. If there is a net flux, indicate it's direction (i.e., air to sea or sea to air). Use total salt conc of 0.5 M in seawater. How would you expect your answer to change in the Arctic with an average temperature of 5°C?

T_m = -30.4°C; T_b = 74.1 °C; -log P^o = 0.78 (atm); -log C_w^{sat} = 2.07 (mol L^{-1})

K^{sw} = 0.35

8. A colleague who works in oceanography bets you that both the solubility and the activity coefficient of naphthalene are larger in seawater (35‰ salinity) at 25 °C, than in distilled water at 5 °C. Estimate C_w^{sat} and γ_w^{sat} for naphthalene in both solutions and discuss this apparent contradiction. Assume the average enthalpy of solution (ΔH_{soln} for the aqueous dissolution of the solid) of naphthalene is 30 kJ/mol. All other data can be found in Tables 5.3, 5.7 and Appendix C of Schwarzenbach?

PS #2, Question 4:

Estimating Molar Volume from Structure. In the absence of density information, molar volumes can be estimated using a simple atomic volume contribution approach proposed by Abraham and McGowan. In this method, each element is assigned a characteristic atomic volume (table below) and the total volume is calculated by summing up all atomic volumes and subtracting 6.56 cm^3 mol^{-1} for each bond no matter whether single, double or triple. Thus, the molar volume for benzene is calculated as (6)(16.35) + (6)(8.71) –(12)(6.56) = 71.6 cm^3 mol^{-1}.

Characteristic Atomic Volumes in cm^3 mol^{-1}

C	H	O	N	P	F	Cl	Br	I	S
16.35	8.71	12.43	14.39	24.87	10.48	20.95	26.21	34.53	22.91

Water Solubility of Gasoline Components

Compound	MW ($g\ mol^{-1}$)	T_b (^oC)	Solubility (25^oC) ($mg\ L^{-1}$)
1-pentene	70.1	30.0	148
2-methyl-1-pentene	84.2	60.7	78
1-hexene	84.2	63.4	50
4-methyl-1-pentene	84.2	53.9	48
2,2-dimethylbutane	86.2	49.7	12.8
2,2-dimethylpentane	100.2	79.2	4.4
2,2,3-trimethylbutane	100.2	80.9	4.4
3-methylhexane	100.2	92.0	3.3
1-octene	112.2	121.3	2.7
2-methylheptane	114.2	117.6	0.85
1-nonene	126.3	146.9	1.12
3-methyloctane	128.3	143.0	1.42
2,2,5-trimethylhexane	128.3	124.0	1.15

Structural Unit Contributions of Hine and Mookerjee to estimate Log K_H' (unitless)

Bond	Contribution	Bond	Contribution
C-H	+0.12	C_{ar}-H	+0.15
C-F	+0.42	C_{ar}-Cl	+0.02
C-Cl	-0.33	C_{ar}-Br	-0.25
C-Br	-0.82	C_{ar}-O	+0.35
C-I	-1.01	C_{ar}-S	-0.63
C-O	-1.09	C_{ar}-C_{ar}	-0.26
C-S	-1.11	C_{ar}-N_{ar}	-1.63
C-N	-1.30	=C-H	+0.10
C-C	-0.12	=C-Cl	-0.04
C-C=	-0.06	C=C	-0.10
C-C≡	-0.54	≡C-H	0.00
C-C_{ar}	-0.16	S-H	-0.23
O-H	-3.23	N-H	-1.28