CHEM 331

Problem Set #2: Water Solubility and Partitioning

Hand in all worked solutions in a neat and organized format. Not all questions will be graded.

Due: Friday, Feb 16th.

1. Provide the missing information from Appendix C of your textbook and calculate the aqueous activity coefficients, γ_w^{sat} for the following compounds at 25°C (*subcooled/superheated, if necessary)*. Rationalize the magnitude of these values using your understanding of the intermolecular interactions that influence water solubility? Which of these compounds will have the greatest air-octanol partition constant (K_{ao})?

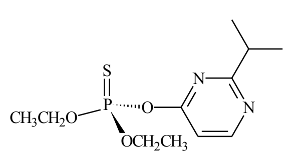
	chlorobenzene	hexachlorobenzene	p,p'-DDT
T_m / °C			**109**
log P^o / Pa			**-4.70**
-log C_w^{sat} / M			**7.80**
-log K_{aw}			**3.30**
logK_{ow}			**6.36**

2. Calculate the activity coefficients for trichloroethene in water and in 1-octanol (water-saturated) at 25°C given $C_w^{sat} = 8.32 \times 10^{-3}$ M and $K_{ow} = 2.63 \times 10^2$. Rationalize the relative magnitude of these activity coefficients?

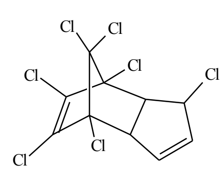
3. a) Estimate the molar volumes for di-*n*-butylphthalate and 2,4,6-trichlorophenol using the atomic volume contribution approach proposed by Abraham and McGowan (attached data table).
b) Estimate the Henry's Law constant for these same compounds using the fragment contribution approach of Hine and Mookerjee (attached data table) and report your estimated K_H in units of atm M^{-1}
c) How do your K_H estimates compare to values estimated based on the vapour pressure and water solubility reported in Appendix C of Schwarzenbach?

4. 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 aqueous solution of equal volume.

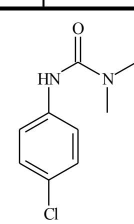
Pesticide	Molar Mass (g.mol^{-1})	Vapour Pressure (mPa)	Solubility (mg.L^{-1})
Diazinon	304	16.0	40.0
Heptachlor	373	22.0	5.60×10^{-3}
Monuron	199	2.30×10^{-2}	2.60×10^{2}



Diazinon



Heptachlor



Monuron

5. Consider a 100. mL aqueous standard solution containing 100. μg/L of iodomethane that is stored in a well sealed 1 L flask (i.e., 900. mL of air). The following data is provided for iodomethane;

$$P^o = 53{,}700 \text{ Pa}, C_w^{sat} = 0.0977 \text{ mol L}^{-1}, K_H = 542 \text{ Pa m}^3 \text{ mol}^{-1}$$

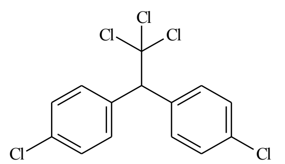
a) Calculate the concentration of iodomethane in the water and headspace of the bottle at equilibrium at 25°C.
b) If the bottle is opened after equilibration and all of the air in the headspace is flushed out and replaced by fresh air, what will the concentration of iodomethane be in the aqueous solution after the equilibrium is re-established?
c) Calculate the fraction of iodomethane present in the liquid water of a cloud aerosol characterized by $V_{H2O(l)}$ = 0.10 mL per 100. L air. How will your answer change if the temperature is 5°C?

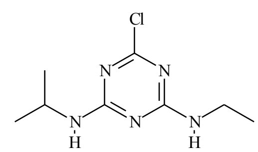
6. Using the chemical structure and physio-chemical data below to justify your answer, indicate which of these compounds will;

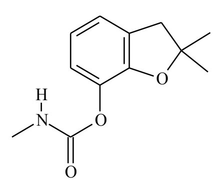
i) be the most hydrophobic as measured by their aqueous activity co-efficient
ii) be most likely to partition from surface water to the atmosphere
iii) exhibit the greatest reduction in water solubility in seawater compared to freshwater
iv) exhibit the greatest tendency to bio-accumulate in aquatic organisms
v) exhibit the greatest aqueous concentration in equilibrium with organic rich sediments in the water column

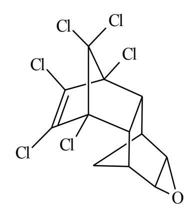
Explain your reasoning with reference to corroborating evidence from your text (Schwarzenbach).

	$-\log P°$ (atm)	$-\log C_w^{sat}$ (M)	$\log K_{ow}$
DDT	9.87	7.85	6.36
Carbofuran			1.60
Atrazine	9.05	3.81	2.56
Dieldrin			5.50


DDT


Atrazine


Carbofuran


Dieldrin

7. Within a given class of apolar or weakly polar compounds (e.g., alkanes, chlorobenzenes, PCBs), the variation in the air-octanol partition constants (K_{ao}) is much larger than the variation in the corresponding air-water partition constants (K_{ow}). For example, the K_{ao} values for chlorobenzens vary between $10^{-3.5}$ (chlorobenzene) and 10^{-7} (hexachlorobenzene), whereas the K_{aw} values for this series of compounds are all within the same order of magnitude. Explain.

8. 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 → sea or sea → 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

PS #2, Question 3:

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

Structural Unit Contributions of Hine and Mookerjee to estimate Log K_H' (unitless) at 25 ^oC

Bond	**Contribution**	**Bond**	**Contribution**
C-H	+0.120	C_{ar}-H	+0.154
C-F	+0.418	C_{ar}-Cl	+0.0241
C-Cl	-0.334	C_{ar}-Br	-0.245
C-Br	-0.819	C_{ar}-O	-0.347
C-I	-1.01	C_{ar}-OH	-0.597
C-O	-1.09	C_{ar}-C_{ar}	-0.264
C-S	-1.11	C_{ar}-N_{ar}	-1.63
C-N	-1.30	=C-H	+0.101
C-C	-0.116	=C-Cl	-0.0426
C-C=	-0.0635	C=C	-0.100
C-C≡	-0.538	≡C-H	0.004
C-C_{ar}	-0.162	S-H	-0.225
C_{ar}-CO	-1.24	CO-O	-0.071
O-H	-3.23	N-H	-1.28

See further Table 6.4 (Schwarzenbach)