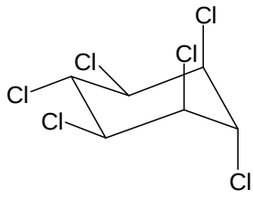
CHEM 331: ENVIRONMENTAL ORGANIC CHEMISTRY

Mid-Term Test 1
Total Marks = 36

1. Provide one example of an *environmentally relevant* organic compound in each of the following classes; (i) halogenated alkene (ii) polybrominated diphenyl ether (iii) polyaromatic hydrocarbon. Draw the structure and predict whether each compound is a solid, liquid or gas at room temperature. [3]

2. a) One of the most widely used and frequently detected organochlorine pesticides is known commonly as *lindane* (γ-HCH). Use the information below to estimate an upper limit of the vapour pressure of the *sub-cooled* liquid state at 25 ^{o}C. [3]

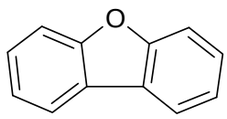


MW = 291 g mol^{-1}
C_w^{sat}(L) = 1.9 x 10^{-4} M
T_m = 113 ^{o}C
T_b > 250 ^{o}C

b) Will the vapour pressure of solid *lindane* be higher or lower than that of the *sub-cooled* liquid state? Why? [2]

c) Estimate the value of the air-water partition constant (K_{aw}). [2]

3. The water solubility of dibenzofuran (MW = 168 g/mol) is reported to be 5 mg/L at 25^{o}C. Calculate the saturated aqueous activity co-efficient at this temperature, using the information below. [4]



T_m = 86 ^{o}C
T_b = 287 ^{o}C
log C_w^{sat} = - 4.5

4. Briefly answer any **TWO** of the following. *You may use equations or examples to illustrate your answer*. [5]

a) What is the effect of dissolved salt on the water solubility of organic compounds? How is the magnitude of this effect related to the structure of the organic solute?

b) What is the effect of temperature on water solubility of organic solutes? How does the phase of the pure solute influence this temperature dependence and why?

c) What is the dominant factor determining the organic solvent - water partitioning of the majority of organic compounds of environmental concern? Why is *n*-octanol used choosen as surrogate for natural organic phases as opposed to some other organic solvent?

5. Assuming that the refractive index, molar volume and dipolarity/polarizability term (π) of the substituted benzenes listed below are roughly the same, rank them in terms of increasing water solubility and octanol-water partition constant (K_{ow}). Use your understanding of the intermolecular interactions present and the multi-parameter linear free energy equation given below to justify your answer (no calculations necessary). [4]

$$\ln \gamma_w = -\ln P^o(L) - 0.6\left[\overline{V}_i^{2/3}\left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2}\right)\right] - 6(\pi_i) - 9(\alpha_i) - 11(\beta_i) + 0.05\,\overline{V}_i + 9.5$$

Compound	$-\ln P^o$ (L) / atm	α_i	β_i
chlorobenzene	4.2	0	0.04
methylbenzene	3.3	0	0.15
hydroxybenzene	7.4	0.60	0.31
methoxybenzene	5.4	0	0.45

6. An accidental spill of 20 mL of a cleaning solution of 1,1,1-trichloroethane (TCE; MW = 133 g/mol, density = 1.3 g/mL) in your kitchen results in the solvent evaporating into the 30 m^3 of room air. During the clean up you discover a 2L container of olive oil that had been left open on the counter. Assuming that all of the TCE has evaporated into the closed room and equilibrated with the olive oil and ignoring adsorption to other phases/surfaces present, calculate the concentration (mol/L) of TCE in the olive oil. [6]

You find the following information for TCE in your textbook and although you cannot find the partition coefficient between air – olive oil, to your amazement you discover a one parameter linear free energy relationship between the unitless air – olive oil and air – octanol partition coefficients for haloalkanes.

$$\log K_{a\text{-olive oil}} = 1.15 \log K_{ao} + 0.16$$

T_m (^{o}C)	T_b (^{o}C)	$\log P^o$ (Pa)	$\log C_w^{sat}$ (M)	$\log K_{aw}$	$\log K_{ow}$
-31	74	4.2	-2.0	0.15	2.5

7. A number of quantitative estimation methods based on *molecular fragment/atom contributions* have been developed to predict partition coefficients, such as K_H' and K_{ow} for a diverse array of organic molecules. Provide several reasons why it is important to the field of Environmental Organic Chemistry to be able to <u>predict</u> (rather than measure) such properties. Briefly describe any assumptions and limitations inherent in this approach. [4]

8. The chemical structures and physico-chemical properties diethyl phthalate and 1,2,3,4-tetrachlorodibenzo-*p*-dioxin are given below. Using this data to justify your response, describe which of these compounds a greater tendency to be; [3]

a) transported from seawater to the atmosphere
b) a mobile groundwater contaminant
c) bio-accumulated by aquatic organisms

	-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