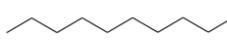
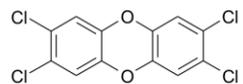


CHEM 331

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 $C_w^{\text{sat}}(\text{L})$ 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?

		CH_3Br
<i>n</i> -decane	2,3,7,8-tetrachloro- dibenzo-p-dioxin	bromomethane
$T_m = -29.7\text{ }^\circ\text{C}$ $T_b = 174.1\text{ }^\circ\text{C}$ $-\log C_w^{\text{sat}}(\text{L}) = 6.57\text{ (mol L}^{-1}\text{)}$ $-\log P^\circ(\text{L}) = 2.76\text{ (atm)}$	$T_m = 305\text{ }^\circ\text{C}$ $T_b = 421\text{ }^\circ\text{C}$ $-\log C_w^{\text{sat}}(\text{s}) = 10.3\text{ (mol L}^{-1}\text{)}$ $-\log P^\circ(\text{s}) = 11.6\text{ (atm)}$	$T_m = -93.6\text{ }^\circ\text{C}$ $T_b = 3.6\text{ }^\circ\text{C}$ $-\log C_w^{\text{sat}}(\text{g}) = 0.79\text{ (mol L}^{-1}\text{)}$ $-\log P^\circ(\text{L}) = -0.26\text{ (atm)}$

Solution:

Recall, for organic solutes the reference state is taken as the pure liquid state and the activity coefficient of a particular solute in water is a measure of its activity in water relative to its activity in the pure liquid (i.e., is given by the $\gamma = \{\text{activity}\}_{\text{aq}}/\{\text{activity}\}_l$) and is a direct quantitative measure of the dissimilarity of the solute and the solvent.

For organic solutes that are liquids at 25 °C, we can write;

$$C_w^{\text{sat}}(\text{L}) = \frac{1}{g_w^{\text{sat}} \bar{V}_w}$$

and hence,

$$g_w^{\text{sat}} = \frac{1}{C_w^{\text{sat}}(\text{L}) \bar{V}_w}$$

So for *n*-decane, the activity coefficient is given by;

$$g_w^{\text{sat}} = \frac{1}{(10^{-6.57} \text{ mol/L}) (0.018 \text{ L/mol})} = 2.06 \times 10^8$$

But, for 2,3,7,8-dibenzodioxin, which is a solid at 25 °C and we have the aqueous solubility $C_w^{\text{sat}}(\text{s})$. Recall, that the aqueous solubility of a solid is always less than that of the *subcooled liquid* state as energy is required to melt the solid prior to dissolution. Hence, we can write;

$$C_w^{\text{sat}}(\text{s}) = C_w^{\text{sat}}(\text{L}) \frac{P^\circ(\text{s})}{P^\circ(\text{L})} \quad \text{and} \quad \frac{P^\circ(\text{s})}{P^\circ(\text{L})} = e^{-6.8\left(\frac{T_m}{T} - 1\right)}$$

Using $T_m = 578 \text{ K}$ and the $C_w^{\text{sat}}(\text{s}) = 10^{-10.3} \text{ M}$, we get $C_w^{\text{sat}}(\text{L}) = 2.98 \times 10^{-8} \text{ M}$ and $\gamma_w^{\text{sat}} = \mathbf{1.86 \times 10^9}$.

For bromomethane, which is a gas at 25 °C, we need to once again take into account a phase change and convert the aqueous solubility of the gas into a solubility of the superheated liquid state.

$$C_w^{\text{sat}}(\text{g}) = C_w^{\text{sat}}(\text{L}) \frac{1 \text{ atm}}{P^\circ(\text{L})} = C_w^{\text{sat}}(\text{L}) \frac{1 \text{ atm}}{10^{0.26} \text{ atm}}$$

So

$$C_w^{\text{sat}}(\text{L}) = \frac{C_w^{\text{sat}}(\text{g})}{1 \text{ atm}} = \frac{10^{-0.79} \text{ mol/L}}{1 \text{ atm} / 10^{0.26} \text{ atm}} = 0.295 \text{ mol/L}$$

$$P^{\circ}(\text{L})$$

$$\gamma_w^{\text{sat}} = 1.88 \times 10^2$$

	<i>n</i> -decane	2,3,7,8-dibenzodioxin	bromomethane
$C_w^{\text{sat}}(\text{L}) \text{ M}$	2.69×10^{-7}	2.98×10^{-8}	0.295
γ_w^{sat} unitless	2.06×10^8	1.86×10^9	1.88×10^2

There are a number of intrinsic molecular properties that influence water solubility, including size (greater energy costs in creating a cavity in the water solvent) polarity and polarizability as indicated in the multi-parameter equation below. *n*-decane is a relatively large, apolar molecule with low polarizability all of which contribute to its low water solubility and large activity co-efficient. Although 2,3,7,8-dibenzodioxin is a monopolar molecule (has H-acceptors, $\beta > 0$) and is more polarizable than *n*-decane (by virtue of its π bonding), it has a much lower vapour pressure resulting from greater inter-molecular forces in the sub-cooled liquid state. Bromomethane on the other hand, is relatively water soluble. It is a relatively small molecule somewhat polar molecule accounting for its relatively small activity coefficient.

$$\ln g_w = -\ln P^{\circ}(\text{L}) + s \frac{\bar{V}^{2/3} (n_D^2 - 1)}{n_D^2 + 2} + a(a) + b(b) + v \bar{V} + \text{Constant}$$

	<i>n</i> -decane	2,3,7,8-dibenzodioxin	bromomethane
$-\ln P^{\circ}(\text{L})$	6.35	20.3	-0.599
$\bar{V}^{2/3} (n_D^2 - 1/n_D^2 + 2)$	1.41	1.656	1.44
α	0	0	0
β	0		
V	195	196	54.6

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.
- Calculate the aqueous activity co-efficient for each of these compounds based on C_w^{sat} values given in Appendix C of your textbook.
 - Provide a molecular level description based on intermolecular interactions to explain the differences in C_w^{sat} .
 - 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.

Solution:

- a) Since all compounds here are liquids at room temperature, we can use

$$g_w^{sat} = \frac{1}{C_w^{sat} (L) \bar{V}_w}$$

The molar water solubilities are provided by Schwarzenbach as 6.2×10^{-2} , 3.2×10^{-2} and 1.5×10^{-4} , for *n*-hexanol, di-*n*-propylether and *n*-hexane, respectively (pg 177). Thus, the activity co-efficients are;

$$\begin{aligned} \gamma_{\square} (n\text{-hexanol}) &= 900 \\ \gamma_{\square} (\text{di-}n\text{-propylether}) &= 1700 \\ \gamma_{\square} (n\text{-hexane}) &= 370,000 \end{aligned}$$

b) On the molecular level, there are several steps involved in the dissolution process. Solutes must overcome the solute:solute interactions in order to separate solute molecules from one another. Solvents must also overcome solvent:solvent interactions in order to create a cavity within which a solute molecule can fit. There are then favourable solute:solvent interactions and some re-organization energy from the 'ice' formation in the solvent shell. The magnitude of the energy associated with each of these processes will depend on the intrinsic properties and structure of the solute. From the structures of the compounds under consideration, we see that they are roughly the same size, so the energy costs of cavity formation are roughly equal. Hexane is apolar and will have the weakest solute:solute interactions (vdW), however it will also have the weakest solute:solvent interactions (dipole-induced dipole) as well. Di-*n*-propylether is monopolar and has a small permanent dipole moment giving rise to both vdW and dipole-dipole forces. The lone pair electrons on oxygen can act as an H-bond acceptor from the surrounding water molecules. Hexanol has a hydrogen atom covalently bonded to a small electronegative oxygen atom and is therefore capable of acting as an H-bond donor. Since the lone pair electrons on oxygen can act as an H-bond acceptor, this molecule is said to be bipolar. Because both dipropylether and hexanol have the more favourable solute:solvent interactions with the water solvent, they are roughly two orders of magnitude more water soluble than hexane.

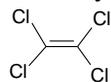
- c) Equation 5-22 is shown below.

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

It has six terms each relating water solubility to intrinsic characteristics of the solute. The first term involving the vapour pressure relates to the magnitude of the solute:solute interactions. The second term involving molar volume and refractive index is related to the strength of the dispersive energy part of the solute:solvent interactions resulting from the polarizability of the solute. The third term is related to the permanent dipole moment (and polarizability) and is related to the dipole-dipole part of the solute:solvent interactions. The third term is related to the contribution of H-bond donating ability to the solute:solvent interactions. The fourth term is related to the H-bond acceptor ability of the solute:solvent interaction. And finally, the fifth term in this expression is related to the energy costs associated with cavity formation in the solvent. The refractive index

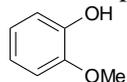
values provided indicate that hexanol and dipropylether are more polarizable than hexane. This is largely due to the lone pair electrons on the oxygen atom. The result is a greater contribution to the dispersive energy part of the solute:solvent interaction. Furthermore, hexane will have a value of zero for the π , α and β terms (Tables 4.3 and 5.5). Since these terms are all negative, the bigger they are, the more negative $\ln \gamma_w$ will be and consequently the more water soluble the solute. Dipropylether has a non-zero value for π and β , so it will be more water soluble than hexane. Hexanol will also have a non-zero value for α , so it will be more water soluble than dipropylether.

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)

$T_m = -22\text{ }^\circ\text{C}$
 $T_b = 121\text{ }^\circ\text{C}$
 $\log P^\circ = 3.40\text{ (Pa)}$
 $-\log C_w^{\text{sat}} = 3.07\text{ (mol L}^{-1}\text{)}$
 $-\log K_{\text{aw}} = -0.08$



2-methoxyphenol

$T_m = 32\text{ }^\circ\text{C}$
 $T_b = 205\text{ }^\circ\text{C}$
 $\log P^\circ(\text{s}) = 1.32\text{ (Pa)}$
 $-\log C_w^{\text{sat}}(\text{s}) = 0.70\text{ (mol L}^{-1}\text{)}$
 $-\log K_{\text{aw}} = 4.38$

Solution:

Given $V_w = 1 \times 10^{-4}\text{ L}$; $V_g = 100\text{ L}$; $K_{\text{aw}}(\text{PCE}) = 1.20$ and $K_{\text{aw}}(\text{2-methoxyphenol}) = 4.2 \times 10^{-5}$ (Appendix C, textbook),

$$\text{The fraction in water} = \frac{\text{amt in water}}{\text{total amt}} = \frac{C_w V_w}{C_w V_w + C_g V_g}$$

Since, K_{aw} can be defined as $= C_g/C_w$, we can write;

$$C_g = K_{\text{aw}} C_w$$

and therefore, $f_w = \frac{C_w V_w}{C_w V_w + K_{\text{aw}} C_w V_g} = \frac{V_w}{V_w + K_{\text{aw}} V_g}$

So, for PCE we calculate that only a trace fraction of **8.3×10^{-7}** (or $8.3 \times 10^{-5}\%$) as the fraction in the aqueous water phase. On the other hand, for 2-methoxyphenol, which has a much smaller K_{aw} value, the fraction in the aqueous phase is calculated to be **0.023** (or 2.3%).

To understand the affect of temperature on the air-water partitioning (K_{aw}), we need to examine the affects on both vapour pressure (P°) and water solubility (C_w^{sat}). In general, P° decreases with decreased temperature and this will be true for all of the compounds examined here. The extent of this decrease will depend on ΔH_{vap} . However, the change in water solubility with temperature will depend on whether the compound is present as a gas, liquid or solid. In general, gaseous organics become more soluble with decreased temperature, solids become less soluble and the solubility of organic liquids is more or less invariant. Consequently, we should deal with each of these phases separately.

Gases: As the temperature decreases from 25 to 5°C, the C_w^{sat} will increase. Coupled with the decrease in P° experienced by all compds, we see that K_{aw} at 5°C will be considerably less than K_{aw} at 25°C. Therefore, a greater fraction will be present in rainwater at 5°C than at 25°C.

Liquids: As the temperature decreases, the water solubility of organic liquids remains relatively constant. So as P° decreases over a 25 to 5°C temperature range, the value of K_{aw} will be lower although the effect will be less than that experienced by gases. We therefore expect a greater fraction of PCE in rainwater at 5°C than at 25°C.

Solids: The water solubility of organic solids generally decreases with decreased temperature. So as both P° and C_w^{sat} decrease over the range of 25 to 5°C, it can be difficult to assess the extent of the change on K_{aw} without further information. However, since P° tends to be more sensitive to temperature than water solubility for solids, we can anticipate the value of K_{aw} will decrease somewhat over the 25 \rightarrow 5 °C range. Hence a greater fraction of 2-methoxyphenol is expected in the rainwater at 5°C.

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?

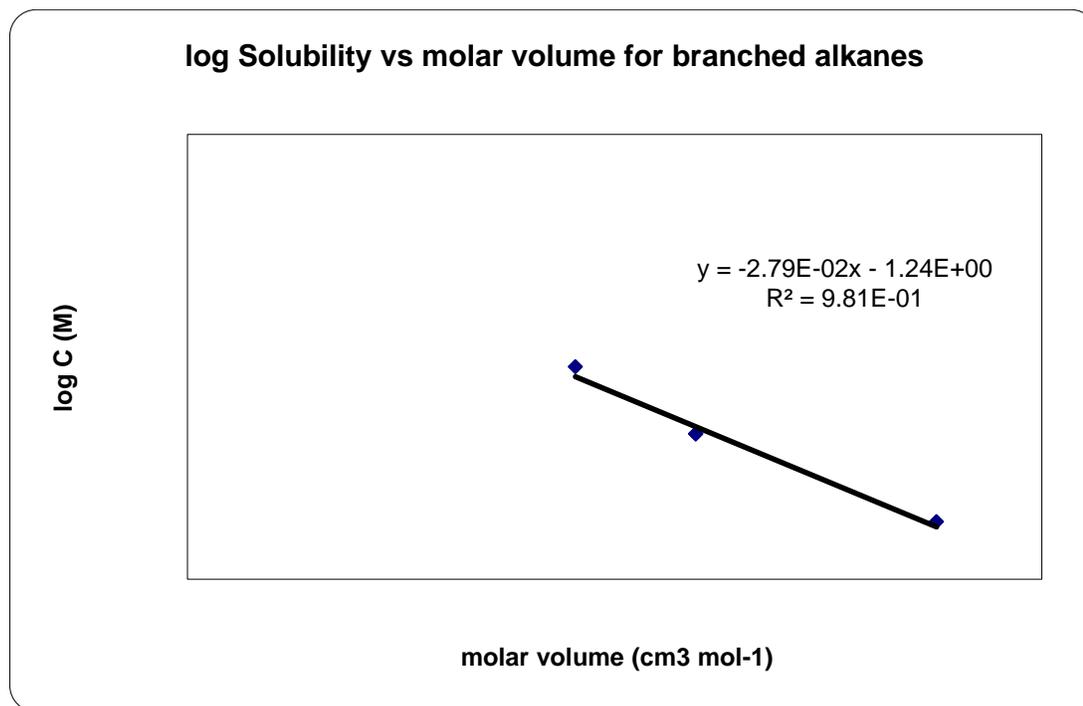
- The aqueous molar solubility of isooctane (2,2,4-trimethylpentane).
- The unitless Henry's Law constant, K_H' (K_{aw}) for *lindane* (hexachlorocyclohexane) and pentachlorophenol.
- Convert your answer in part a) to a mole fraction concentration and your answer in part b) to $\text{kPa m}^3 \text{mol}^{-1}$.

Solution:

a) Since the isooctane is an apolar hydrocarbon, we can use the solubilities of structurally similar compounds to predict its water solubility based on its size (molar volume). We use the data provided to calculate molar solubility and the chemical structures (count the number of carbon atoms, hydrogen atoms and bonds) for molar volume predictions. Plotting $\log C_w^{\text{sat}}$ vs molar volume given a straight line as this is in effect a linear free energy relationship (recall that $C_w^{\text{sat}} = K$, the equilibrium constant for the dissolution of a pure substance).

Branched Alkanes	C (mg/L)	MW	C (M)	log C	#C	#H	#bond	Calc molar vol
2,2-dimethylbutane	12.8	86.2	1.48E-04	-3.828	6	14	19	95.4
2,2-dimethylpentane	4.4	100.2	4.39E-05	-4.357	7	16	22	109.49
2,2,3-trimethylbutane	4.4	100.2	4.39E-05	-4.357	7	16	22	109.49
3-methylhexane	3.3	100.2	3.29E-05	-4.482	7	16	22	
2-methylheptane	0.85	114.2	7.44E-06	-5.128	8	18	25	
3-methyloctane	1.42	128.3	1.11E-05	-4.956	9	20	28	
2,2,5-trimethylhexane	1.15	128.3	8.96E-06	-5.048	9	20	28	137.67
2,2,4-trimethylpentane	2.00	114.2	1.75E-05	-4.757	8	18	25	123.58
2,2,4-trimethylpentane	2.34	114.2	2.05E-05	-4.688	8	18	25	123.58

(using all branches)
(using only di and tri branched alkanes)



Depending on the choice of alkanes used in generating the correlation, the aqueous solubility of 2,2,4-trimethylpentane is estimated between **18 and 21 μM** . If we limit our choice of alkanes to only those di- and tri methyl groups ($n=4$), the correlation is quite good;

$$\log C (\text{M}) = -2.8 \times 10^{-2} V_m - 1.2 \quad (R^2 = 0.98)$$

b) The method of Hine and Mookerjee yields **$\log K_H'$ (unitless) as -1.98** for lindane. Therefore, $K_{aw} (\text{lindane}) = 1.05 \times 10^{-2}$.

The method of Hine and Mookerjee yields **$\log K_H'$ (unitless) as -3.69** for phenol. Therefore, $K_{aw} (\text{phenol}) = 2.04 \times 10^{-4}$.

c) Conversion to mole fraction (χ), where $M \cong \frac{\text{mole fraction concentration}}{\text{molar volume solvent}}$

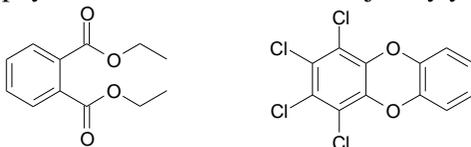
$$\text{Therefore, } \chi_{\text{isooctane}} = (20 \times 10^{-6} \text{ mol/L}) (0.018 \text{ L/mol}) = 3.6 \times 10^{-7}$$

Conversion to SI units ($\text{Pa m}^3 \text{ mol}^{-1}$) using $K_H = K_H' \times RT$, where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T = 298\text{K}$. Then divide by 10^3 to convert to $\text{kPa m}^3 \text{ mol}^{-1}$.

$$\text{Therefore } K_H (\text{lindane}) = (-1.98) (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (298\text{K}) / (1000 \text{ Pa kPa}^{-1}) = 2.59 \times 10^{-2} \text{ kPa m}^3 \text{ mol}^{-1}$$

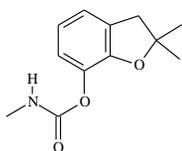
$$\text{Similarly, } K_H (\text{phenol}) = 5.05 \times 10^{-4} \text{ kPa m}^3 \text{ mol}^{-1}$$

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.

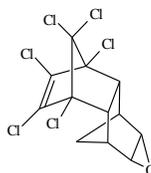


	$-\log P^{\circ}$ (Pa)	$-\log C_w^{\text{sat}}$ (M)	$-\log K_{\text{aw}}$	$\log K_{\text{ow}}$
diethyl phthalate	0.66	2.4	4.6	2.4
1,2,3,4-tetrachlorodibenzo- <i>p</i> -dioxin	5.2	8.8	2.8	6.6

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
 $\log K_{\text{ow}} = 1.6$



Dieldrin
 $\log K_{\text{ow}} = 5.5$

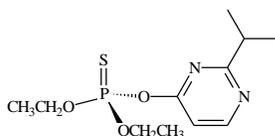
Solution:

a) The tetrachlorodioxin has a larger K_{aw} value despite being less volatile than the phthalate. The dioxin will therefore have a greater tendency to be transported from water to air. Tetrachlorodioxin is considerably less water soluble than the phthalate and is therefore much more hydrophobic (larger activity coefficient). The dioxin will therefore have the larger salting constant and its water solubility will be more sensitive to increased ionic strength of seawater. Bio-accumulate trends with the octanol-water partition coefficient, and here again the dioxin molecule will have the greater tendency.

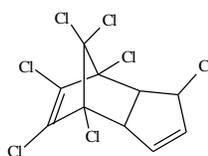
b) K_{ow} is strongly correlated to K_{om} (partitioning onto organic matter) and other partition coefficients related to organic particulate and sediment phase adsorption. Therefore, dieldrin is expected to be more associated with sediments than carbofuran. The molecular structures of the two contaminants suggest that dieldrin which is non-polar and somewhat polarizable, due to the presence of the alkene and chlorine atoms is expected to be very hydrophobic leading to the high K_{ow} value. On the other hand, carbofuran is more polar and capable of participating in hydrogen bonding both as an H-acceptor (lone pairs on **N** and **O**) and as an H-donor (**N-H**). Consequently, carbofuran has a greater water solubility and hence a smaller K_{ow} value. It will be more distributed into the aqueous phase than dieldrin.

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.

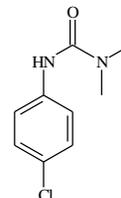
Pesticide	Molar Mass (g.mol ⁻¹)	Vapour Pressure (mPa)	Solubility (mg.L ⁻¹)
Diazinon	304	16.0	40.0
Heptachlor	373	22.0	5.60 x 10 ⁻³
Monuron	199	2.30 x 10 ⁻²	2.60 x 10 ²



Diazinon



Heptachlor



Monuron

Solution:

$$\text{Since, } K_H \gg \frac{P^0}{C_w^{\text{sat}}}$$

We can convert the given vapour pressure and solubility data and determine K_H.

Summarizing,

	P ⁰ (atm)	C _w ^{sat} (M)	K _H (atm M ⁻¹)
<i>Diazinon</i>	1.57 x 10 ⁻⁷	1.32 x 10 ⁻⁴	1.18 x 10⁻³
<i>Heptachlor</i>	2.17 x 10 ⁻⁷	1.50 x 10 ⁻⁸	14.5
<i>Monuron</i>	2.27 x 10 ⁻¹⁰	1.31 x 10 ⁻³	1.73 x 10⁻⁷

Converting to unitless K_{aw} (K_H') values by,

$$K_H' = K_H/RT, \text{ where } R = 0.08302 \text{ L atm mol}^{-1} \text{ K}^{-1} \text{ and } T = 298\text{K}$$

Thus,

$$\begin{aligned} K_{aw}(\text{diazinon}) &= 4.83 \times 10^{-5} \\ K_{aw}(\text{heptachlor}) &= 5.90 \times 10^{-1} \\ K_{aw}(\text{monuron}) &= 7.07 \times 10^{-9} \end{aligned}$$

The fraction in the gas phase is given by,

$$f_g = \frac{C_g V_g}{C_g V_g + C_w V_w}$$

Since C_g = K_{aw} C_w, this becomes;

$$f_g = \frac{K_{aw} V_g}{K_{aw} V_g + V_w} = \frac{K_{aw}}{K_{aw} + 1}$$

when V_g = V_w.

Therefore the fractions in air for equal volumes of air/volume are;

$$\begin{aligned} f_g(\text{diazinon}) &= 5 \times 10^{-5} \\ f_g(\text{heptachlor}) &= 0.37 \\ f_g(\text{monuron}) &= 7 \times 10^{-9} \end{aligned}$$

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 its 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 ?

$$T_m = -30.4^\circ\text{C}; T_b = 74.1^\circ\text{C}; -\log P^\circ = 0.78 \text{ (atm)}; -\log C_w^{\text{sat}} = 2.07 \text{ (mol L}^{-1}\text{)}$$

$$K^{\text{sw}} = 0.35$$

Solution:

We can use the typical concentration values to calculate a unitless reaction quotient Q_{aw} . If we compare this value to the equilibrium constant K_{aw} , we will be able to determine the direction of spontaneous change (ie, shift to reactant or product side of the equilibrium process).

Since $C_g = 0.9 \text{ mg/m}^3$ and the $C_{\text{sw}} = 2.5 \text{ mg/m}^3$, we get $Q_{\text{aw}} = \mathbf{0.36}$

To calculate the value of K_{aw} in seawater, we will need the vapour pressure of TCE (given) and the solubility of TCE in seawater (we will calculate this based on the C_w^{sat} and the salting constant).

$$K_{\text{aw}}(\text{sea}) \cong \frac{P^\circ}{C_{\text{sw}}^{\text{sat}}}$$

$$\text{and } C_{\text{sw}}^{\text{sat}} = C_w^{\text{sat}} 10^{-\{K^{\text{sw}}[\text{salt}]\}}$$

Recall the solubility of organic solutes is decreased in seawater. Using $C_w^{\text{sat}} = 8.5 \times 10^{-3} \text{ M}$, we get $C_{\text{sw}}^{\text{sat}} = \mathbf{5.7 \times 10^{-3} \text{ M}}$.

Thus, given that $P^\circ = 0.166 \text{ atm}$, we calculate a value for $K_{\text{aw}}(\text{sea}) = 29.2 \text{ atm/M}$. Converting this to the unitless yields;

$$K_{\text{aw}}(\text{sea}) = 29.2 \text{ atm/M} \times 1/((0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}) (298 \text{ K})) = \mathbf{1.2}$$

Hence, $Q_{\text{aw}} < K_{\text{aw}}(\text{sea})$ and there is a net flux of TCE to move from **seawater to the atmosphere** under these conditions.

At 5°C , the value of $K_{\text{aw}}(\text{sea})$ will decrease. This will reduce the driving force for the net flux sea \rightarrow air and may in fact reverse the direction of TCE from air \rightarrow sea, if $Q_{\text{aw}} > K_{\text{aw}}(\text{sea})$.

Since TCE is a liquid at room temperature, its water solubility will be invariant with temperature and we could estimate its K_{aw} by calculating its P° at 278 K . This could be accomplished using the semi-empirical formula,

$$\ln P^\circ(\text{L}) \sim 19 (1-T_b/T) + 8.5 (\ln T_b/T) = 19 (1-347/278) + 8.5 (\ln 347/278) = -4.72 + 1.88 = -2.84$$

$$P^\circ \sim 0.059 \text{ atm}$$

So, $K_{\text{aw}}(\text{sea})$ at $5^\circ\text{C} \sim 10.4 \text{ atm/M}$ or 0.45 (unitless), so a greater fraction of TCE will be in the seawater. But since Q_{aw} is still less than K_{aw} (at 5°C), the net flux will still be from seawater to air.

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?

Solution:

There is a lot going on here, so let's start by getting organized. This question is going to have us make two adjustments to the water solubility of naphthalene 1) the reduced solubility in seawater due to the higher salt concentrations (i.e., $[\text{salt}]_{\text{total}} \sim 0.50 \text{ M}$) and 2) the reduced solubility at lower temperature resulting from the fact that naphthalene is a solid solute and there extra energy costs associated with melting before the solute can dissolve. We will need the water solubility of naphthalene as well as some other physical properties, such as the melting point and salting constant.

$$C_w^{\text{sat}, 298} = 10^{-3.60} = 2.51 \times 10^{-4} \text{ M (Appendix C)}$$

$$T_m = 80.2 \text{ °C} = 353.4\text{K (Appendix C)}$$

$$K^s = 0.28 \text{ in seawater (Table 5.7, pg 163)}$$

Water at 298K

$$C_w^{\text{sat}}(\text{s}) = C_w^{\text{sat}}(\text{L}) \times P^{\circ}(\text{s})/P^{\circ}(\text{L})$$

and

$$g_w^{\text{sat}} = \frac{1}{C_w^{\text{sat}}(\text{L}) \bar{V}_w}$$

$$\text{and } P^{\circ}(\text{s})/P^{\circ}(\text{L}) = e^{-\{6.8(T_m/T)-1\}} = e^{-\{(353.4/298)-1\}} = 0.282$$

Therefore,

$$C_w^{\text{sat}}(\text{L}) = (2.51 \times 10^{-4} \text{ M})/0.282 = 8.89 \times 10^{-4} \text{ M (note: the sub-cooled liquid is more soluble than the solid)}$$

And

$$g_w^{\text{sat}} = \frac{1}{C_w^{\text{sat}}(\text{L}) \bar{V}_w} = 6.25 \times 10^4$$

Seawater at 298K

$$\log C_{\text{sw}}^{\text{sat}} = \log C_w^{\text{sat}} - K^s [\text{salt}]_t = -3.60 - (0.28)(0.50) = -3.84$$

$$\text{Hence, } C_{\text{sw}}^{\text{sat}} = 10^{-3.84} = 1.82 \times 10^{-4} \text{ M}$$

We could calculate the activity coefficient for a solid solute as we have before or use

$$\gamma_{\text{sw}} = \gamma_w 10^{K^s [\text{salt}]} \text{ (Eqn 5.28, pg 160)}$$

Thus,

$$\gamma_{\text{sw}} = 6.25 \times 10^4 \times 10^{(0.28)(0.50)} = 8.63 \times 10^4$$

Water at 278K

Here we must adjust for the affect of temperature on solubility. Since the concentration of saturated aqueous solution is essentially the equilibrium constant for the process in which the pure liquid solute dissolves in water (i.e., $C_w^{sat} \sim K_{soln}$), we can use the enthalpy change for the dissolution process to calculate the solubility at any temperature (within the range of temperature that does not result in a phase change, i.e., up to 80 °C for naphthalene).

$$\ln\left(\frac{C_w^{sat,T2}}{C_w^{sat,T1}}\right) = \frac{-\Delta H_{soln}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where $\Delta H_{soln} = -30,000 \text{ J mol}^{-1}$ and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
and T_1 and T_2 are 298K and 278K, respectively.

$$\text{Hence, } C_w^{sat,278} = C_w^{sat,298} \times e^{-\{3608 \text{ K}(2.41 \times 10^{-4} \text{ K}^{-1})\}} = (2.51 \times 10^{-4} \text{ M})(0.419) = 1.05 \times 10^{-4} \text{ M}$$

Since this is the solubility of solid solute, we need to calculate the solubility of the sub-cooled liquid in order to determine the activity co-efficient (as before).

$$g_w^{sat} = \frac{1}{C_w^{sat}(\text{L}) \bar{V}_w}$$

$$\text{and } P^o(\text{s})/P^o(\text{L}) = e^{-\{6.8(\text{Tm}/\text{T})-1\}} = e^{-\{(353.4/278)-1\}} = 0.158$$

$$\text{So } \gamma_w^{sat,278} = 8.3 \times 10^4$$

Summarizing:

The data below, we see that naphthalene is indeed more water soluble and has a greater activity coefficient in seawater at 298K than it does in freshwater at 278K. This may seem a bit counter intuitive at first, but one must consider that extra energy costs associated with dissolving a solid solute. This has a larger influence on the activity coefficient of the sub-cooled liquid at 278 than it does on the activity coefficient in seawater. From a mathematical perspective, it comes down to the magnitude of the $P^o(\text{s})/P^o(\text{L})$ term.

	Water @ 298K	Water @ 278K	Seawater @ 298K
$C_w^{sat}(\text{s}) / \text{M}$	2.5×10^{-4}	1.1×10^{-4}	1.8×10^{-4}
$\gamma^{sat} / \text{unitless}$	63,000	83,000	86,000
$C_w^{sat}(\text{L}) / \text{M}$	8.9×10^{-4}	6.6×10^{-4}	6.4×10^{-4}

At 298K, $P^o(\text{s})/P^o(\text{L}) = 0.282$ whereas at 278K, $P^o(\text{s})/P^o(\text{L}) = 0.158$, so although the activity coefficient is inversely related to the aqueous solubility this is only true for the solubility of the sub-cooled liquid state. See further, the last row in the Table above, which shows that the solubility of the sub-cooled liquid naphthalene in seawater at 298K is actually lower than the corresponding solubility in water at 278K (consistent with the activity coefficient values).

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 $6.56 \text{ cm}^3 \text{ mol}^{-1}$ for each bond no matter whether single, double or triple. Thus, the molar volume for benzene is calculated as $(6)(16.35) + (6)(8.71) - (12)(6.56) = 71.6 \text{ cm}^3 \text{ mol}^{-1}$.

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

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 (°C)	Solubility (25°C) (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