

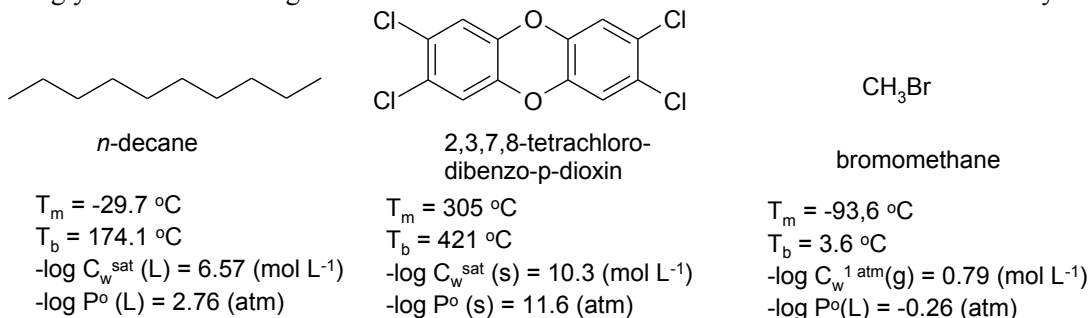
CHEM 331

Problem Set #2: Water Solubility and Partitioning

Hand in all worked solutions in a neat and organized format.

At least four questions will be graded.

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?



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;

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

and hence,

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

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

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

But, for 2,3,7,8-tetrachlorodibenzodioxin, 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 $\gamma_w^{\text{sat}} = 1.86 \times 10^9$.

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

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

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

	<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. Recall, the overall process on a molecular level involves, the separation of solute molecules from another in the pure liquid state (related to $P^\circ(\text{L})$), the separation of solvent molecules to create a cavity for the solute (related to the size of the solute), the interactions between solute and solvent (related to the strength of IMF, which depends on non-specific vdW and dipole-dipole type interactions as well as specific interactions involving H-accepting/donating groups). Factors such as molar volume, polarity and polarizability of the solute 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 coefficient. Although 2,3,7,8-dibenzodioxin is a monopolar molecule (has H-acceptors, $\beta > 0$) and is more polarizable and larger than *n*-decane (by virtue of its π bonding), it also 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 polar molecule accounting for its relatively small activity coefficient.

$$\ln \gamma_w = -\ln P^\circ(\text{L}) + s \left[\bar{V}^{2/3} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \right] + p(\pi) + a(\alpha) + b(\beta) + v\bar{V} + \text{Constant}$$

	<i>n</i> -decane	2,3,7,8-dibenzodioxin	bromomethane
$-\ln P^\circ(\text{L})$	6.35	20.3	-0.599
n_D	1.41	1.66	1.44
π	0		
α	0	0	0
β	0		
$V(\text{cm}^3/\text{mol})^*$	151	182	55

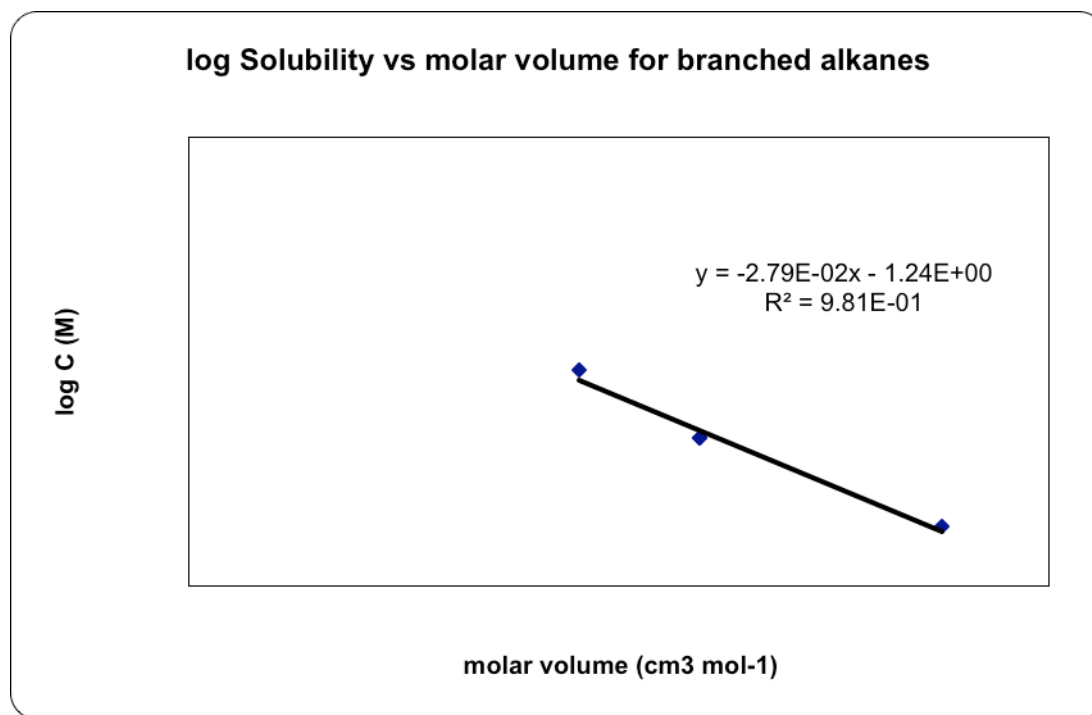
* from atom contributions table provided for Q2

2. Estimate the aqueous solubilities (molar units) of the two gasoline components isooctane (2,2,4-trimethylpentane) and 1-heptene using the experimental data reported (attached table) and the method of characteristic atomic volumes to estimate molar volumes (see attached). Comment on the choice of compounds that you use for your estimates.

Solution:

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 alkane)
(using methyl)



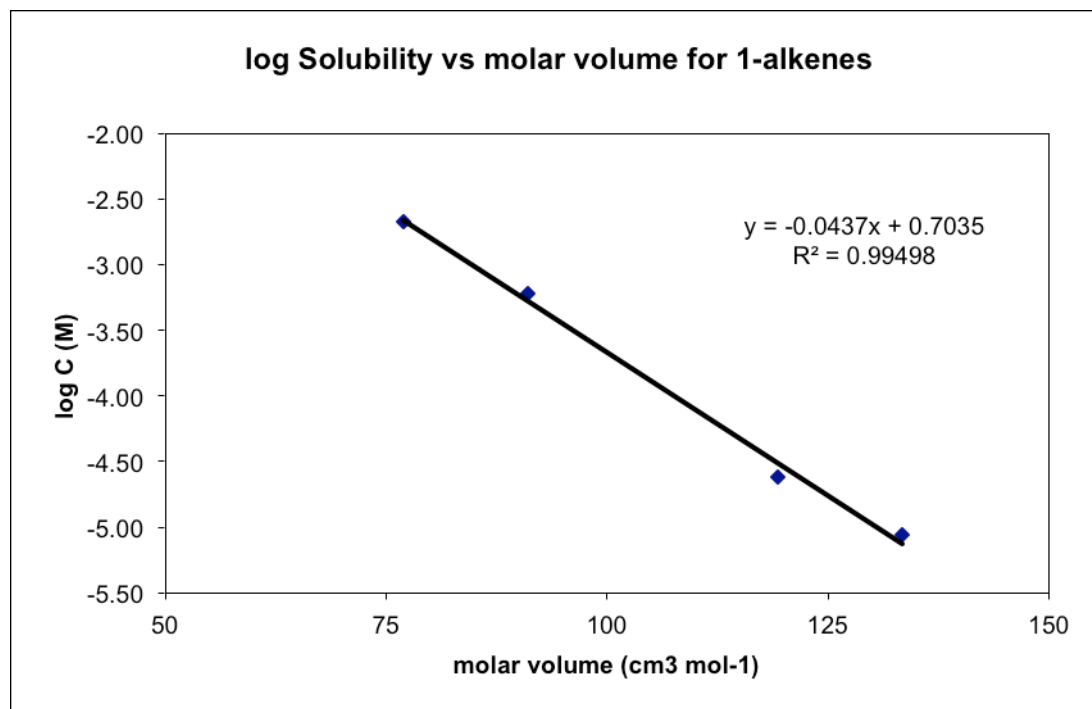
Depending on the choice of alkanes used in generating the correlation, the aqueous solubility of 2,2,4-trimethylpentane is estimated between **18 and 21 μM**. If we limit our choice of alkanes to only those di- and tri methyl groups (n=4), the correlation is quite good;

$$\log C (\text{M}) = -2.8 \times 10^{-2} V_m - 1.24 \quad (R^2 = 0.98)$$

A similar approach for a series of 1-alkenes yields a predicted aqueous solubility of **128 μM** . Using the four alkenes in the table ($n = 4$), yields a strong correlation;

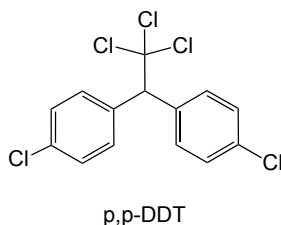
$$\log C (\text{M}) = -4.4 \times 10^{-2} V_m + 0.704 (R^2 = 0.99)$$

1-Alkenes	C (mg/L)	MW	C (M)	log C	#C	#H	#bonds	molar vol
1-pentene	148	70.1	2.11E-03	-2.68	5	10	14	77.01
1-hexene	50	84.2	5.94E-04	-3.23	6	12	17	91.1
1-octene	2.7	112.2	2.41E-05	-4.62	8	16	23	119.28
1-nonene	1.12	128.3	8.73E-06	-5.06	9	18	26	133.37
1-heptene	12.6	98.2	1.28E-04	-3.89	7	14	20	105.19



3. Using the fragment contribution approach of Hine and Mookerjee (attached data table), estimate the Henry's Law constant and report your estimated K_H in units of atm M^{-1} for p,p-DDT (dichlorodiphenyltrichloroethane) and bisphenol-A. How do your estimates compare to literature values?

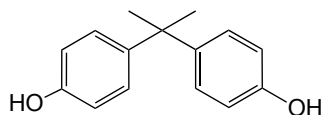
Solution:



	contribution	#	overall contribution
C _{ar} -H	0.15	8	1.2
C _{ar} -Cl	0.02	2	0.04
C _{ar} -C	-0.16	2	-0.32
C-H	0.12	1	0.12
C-C	-0.12	1	-0.12
C _{ar} -C _{ar}	-0.26	12	-3.12
C-Cl	-0.33	3	-0.99
			-3.19
			log K_{aw}

The method of Hine and Mookerjee yields **log K_{aw} (unitless) as -3.19** for p,p-DDT. Schwartzenbach (2nd ed) reports K_{aw} for p,p-DDT as -3.30.

Similarly for bisphenol-A



bisphenol-A

	contribution	#	overall contribution
C _{ar} -H	0.15	8	1.2
C _{ar} -OH	-0.60	2	-1.2
C _{ar} -C	-0.16	2	-0.32
C-H	0.12	6	0.72
C-C	-0.12	2	-0.24
C _{ar} -C _{ar}	-0.26	12	-3.12
O-H	-3.23	2	-6.46
			-9.42
			log K_{aw}

The method of Hine and Mookerjee yields **log K_{aw} (unitless) as -9.45** for bisphenol-A. Converting this to a $K_H = K_{aw} \times RT$ in units of atm/M gives $8.8 \times 10^{-9} \text{ atm/M}$. SRC website reports K_H for bisphenol-A as $1.0 \times 10^{-11} \text{ atm m}^3/\text{mol}$. Converting this to atm/M gives $K_H = 1.0 \times 10^{-8} \text{ atm/M}$.

4. Because of the growing concern over atmospheric contamination by organic pollutants, researchers have focused attention on the composition of rainwater. Calculate the fraction of tetrachloroethene (TCE), methyl-*t*-butyl ether (MTBE) and 2-methoxyphenol (2-MP) present in rainwater at 25°C at equilibrium with the atmosphere. Consider a drop of water (volume = 0.10 mL, pH = 6.0) in a volume of 100. L of air (corresponding to the approximate volume ratio of water aerosols in a cloud). How will your answer change if the temperature is only 5°C?

Solution:

Given $V_w = 1 \times 10^{-4}$ L; $V_g = 100$ L;

And K_{aw} (TCE) = 1.20; K_{aw} (MTBE) = 0.024; K_{aw} (2-MP) = 4.2×10^{-5} (unitless)

Note that at pH = 6.0 all compounds considered here will be present in their neutral (associated form). The pKa of 2-MP is ~ 10, and so at pH 6, it will be 99.99% PhOH.

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

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

$$C_g = K_{aw} C_w$$

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

So, for TCE we calculate that only a trace fraction of 8.3×10^{-7} (or 8.3×10^{-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 %). The K_{aw} value for MTBE is intermediate between these and will have 4.2×10^{-5} (or 0.0042%).

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}). Vapour pressure, P° always decreases with decreased temperature and this will be true for all of the compounds examined here. The extent of this decrease will depend on the magnitude of ΔH_{vap} (i.e., the slope of the $\ln C_w^{\text{sat}}$ vs $1/T$ plot). 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 compounds, 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 TCE 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 → 5 °C range. Hence a greater fraction of 2-methoxyphenol is expected in the rainwater at 5°C.

5. You have carefully prepared 100. mL of a combined aqueous standard containing 100.0 µg/L each of benzene, toluene, ethylbenzene and p-xylene (BTEX). You decide to store this standard solution at room temperature in a well sealed 1.00 L bottle (i.e., 900. mL of air). Using the data in Appendix C of your textbook, calculate the equilibrium concentration (µg/L) of each component in the water at 25°C.

Solution:

Using the following unitless K_{aw} values from Schwarzenbach

$$K_{aw}(\text{benzene}) = 0.224$$

$$K_{aw}(\text{toluene}) = 0.240$$

$$K_{aw}(\text{ethylbenzene}) = 0.339$$

$$K_{aw}(\text{p-xylene}) = 0.288$$

And the fraction in the gas phase;

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

Substituting in $C_g = K_{aw} C_w$ yields;

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

Using the unitless value for K_{aw} benzene and $V_g = 0.900$ L and $V_w = 0.100$ L, we obtain $f_g =$ **0.67**

Hence, the 67% of the original (100.0 µg/L x 0.100 L = 100. µg) is present in the headspace of the sealed container and only 33% of the original 100. µg is present in the aqueous solution. Therefore the concentration of benzene in solution is **33 µg/L** and the concentration in the headspace in the gas phase and **74 µg/L** (67 µg per 0.900 L).

Repeating this calculation for the remaining components of BTEX yields the following results.

	f_g	C_w (µg/L)	C_g (µg/L)
benzene	0.67	33	74
toluene	0.68	32	76
ethylbenzene	0.75	25	83
p-xylene	0.72	28	80

6. 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 ?

$$T_m = -30.4^\circ\text{C}; T_b = 74.1^\circ\text{C}; -\log P^0 = 0.78 \text{ (atm)}; -\log C_w^{\text{sat}} = 2.07 \text{ (mol L}^{-1}\text{)}$$

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

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 (i.e., 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).

$$K_{\text{aw}}(\text{sea}) \cong \frac{P^0}{C_{\text{sw}}^{\text{sat}}} \quad \text{and} \quad C_{\text{sw}}^{\text{sat}} = C_w^{\text{sat}} 10^{-\{K^{\text{sw}}[\text{salt}]\}}$$

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 $P^0 = 0.166 \text{ atm}$, we calculate a value for $K_{\text{aw}}(\text{sea}) = 29.2 \text{ atm/M}$. Converting this to a unitless K_{aw} 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^0 at 278 K . This could be accomplished using the semi-empirical formula,

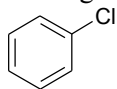
$$\ln P^0(\text{L}) \approx 19 \left(1 - \frac{T_b}{T}\right) + 8.5 \left(\ln \frac{T_b}{T}\right)$$

$$\ln P^0(\text{L}) \approx 19 \left(1 - \frac{347}{278}\right) + 8.5 \left(\ln \frac{347}{278}\right) = -4.72 + 1.88 = -2.84$$

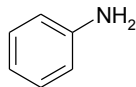
$$P^0 \sim 0.059 \text{ atm}$$

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.

7. Calculate the activity coefficients for chlorobenzene and aniline in water (γ_w^{sat}) and in 1-octanol (water-saturated) γ_o^{sat} at 25°C using the data given below.



$$\begin{aligned} \text{MW} &= 112.6 \text{ g mol}^{-1} \\ T_m &= -45.2 \text{ }^\circ\text{C} \\ C_w^{\text{sat}}(25^\circ\text{C}) &= 4.1 \times 10^{-3} \text{ mol L}^{-1} \\ K_{ow} &= 600 \end{aligned}$$



$$\begin{aligned} \text{MW} &= 93.1 \text{ g mol}^{-1} \\ T_m &= -6.3 \text{ }^\circ\text{C} \\ C_w^{\text{sat}}(25^\circ\text{C}) &= 3.9 \times 10^{-1} \text{ mol L}^{-1} \\ K_{ow} &= 7.9 \end{aligned}$$

Solution:

Since both compounds are liquids at room temperature, we can calculate the activity coefficients directly from the reported solubilities using,

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

Given the molar volume of water of 0.018 L/mol, this yields $\gamma_w^{\text{sat}} = \mathbf{13600}$ for **chlorobenzene** and **142** for **aniline**, respectively.

Since we do not have reported octanol solubilities for either compound, we will need to use some additional information. Since K_{ow} values report the relative solubility in octanol versus water, we can write,

$$K_{ow} = \frac{\gamma_w^{\text{sat}} \bar{V}_w}{\gamma_o^{\text{sat}} \bar{V}_o}$$

Rearranging yields,

$$\gamma_o^{\text{sat}} = \frac{\gamma_w^{\text{sat}} \bar{V}_w}{K_{ow} \bar{V}_o}$$

Using the molar volume of octanol saturated with water (20%) of 0.13 L/mol (0.16 L/mol x 0.80 + 0.018 L/mol x 0.20 = 0.13 L/mol), we get

$$\gamma_o^{\text{sat}} = \mathbf{3.1 \text{ for chlorobenzene}}$$

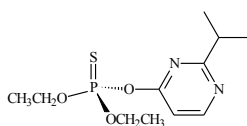
and

$$\gamma_w^{\text{sat}} = \mathbf{2.5 \text{ for aniline}}$$

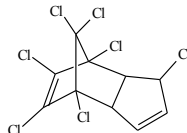
Note that the aqueous activity co-efficients of these two compounds are very different whereas the octanol activity co-efficients are considerably smaller and nearly identical for chlorobenzene and aniline.

8. a) Calculate Henry's Law Constant in units of $\text{Pa m}^3 \text{L}^{-1}$ (at 25°C) for each of the pesticides from the following vapor pressure and water solubility data at 25°C .

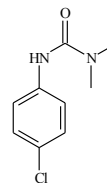
Pesticide	Molar Mass (g mol^{-1})	Vapour Pressure (mPa)	Solubility (mg L^{-1})
Diazinon	304	16.0	40.0
Heptachlor	373	22.0	5.60×10^{-3}
Monuron	199	2.30×10^{-2}	2.60×10^2



Diazinon



Heptachlor



Monuron

Solution:

$$\text{Since, } K_H \approx \frac{P^\circ}{C_w^{\text{sat}}}$$

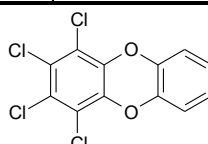
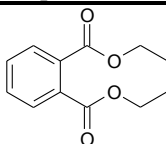
We can convert the given vapour pressure and solubility data and determine K_H .

Summarizing,

	P° (Pa)	C_w^{sat} (M)	K_{aw} ($\text{Pa m}^3 \text{mol}^{-1}$)
<i>Diazinon</i>	1.6×10^{-2}	1.32×10^{-4}	0.120
<i>Heptachlor</i>	2.2×10^{-2}	1.50×10^{-8}	1470
<i>Monuron</i>	2.3×10^{-5}	1.31×10^{-3}	1.75×10^{-5}

b) Using the chemical structure and physio-chemical data below to justify your answer, describe which of these compounds will have a greater tendency to be;

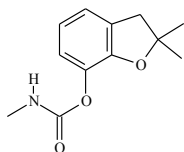
	$-\log P^\circ$ (Pa)	$-\log C_w^{\text{sat}}$ (M)	$-\log K_{\text{aw}}$	$\log K_{\text{ow}}$
diethyl phthalate	0.66	2.4	4.6	2.4
1,2,3,4-tetrachlorodibenzo- <i>p</i> -dioxin	5.2	8.8	2.8	6.6



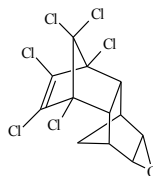
Solution:

- i) 1,2,3,4-tetrachlorodibenzodioxin will have greater tendency to be transported from surface water to the atmosphere since it has the higher K_{aw} value.
- ii) 1,2,3,4-tetrachlorodibenzodioxin will have the greater tendency to be less soluble in seawater than freshwater since it has the lower aqueous solubility (C_w^{sat}) and larger aqueous activity co-efficient.
- iii) 1,2,3,4-tetrachlorodibenzodioxin will have the greater tendency to bio-accumulate in aquatic organisms since it has the higher K_{ow} constant, which is known to be linearly correlated with BCFs.

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



Carbofuran
 $\log K_{ow} = 1.6$



Dieldrin
 $\log K_{ow} = 5.5$

Solution:

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.