CHEM 331

Problem Set #2: Water Solubility and Partitioning

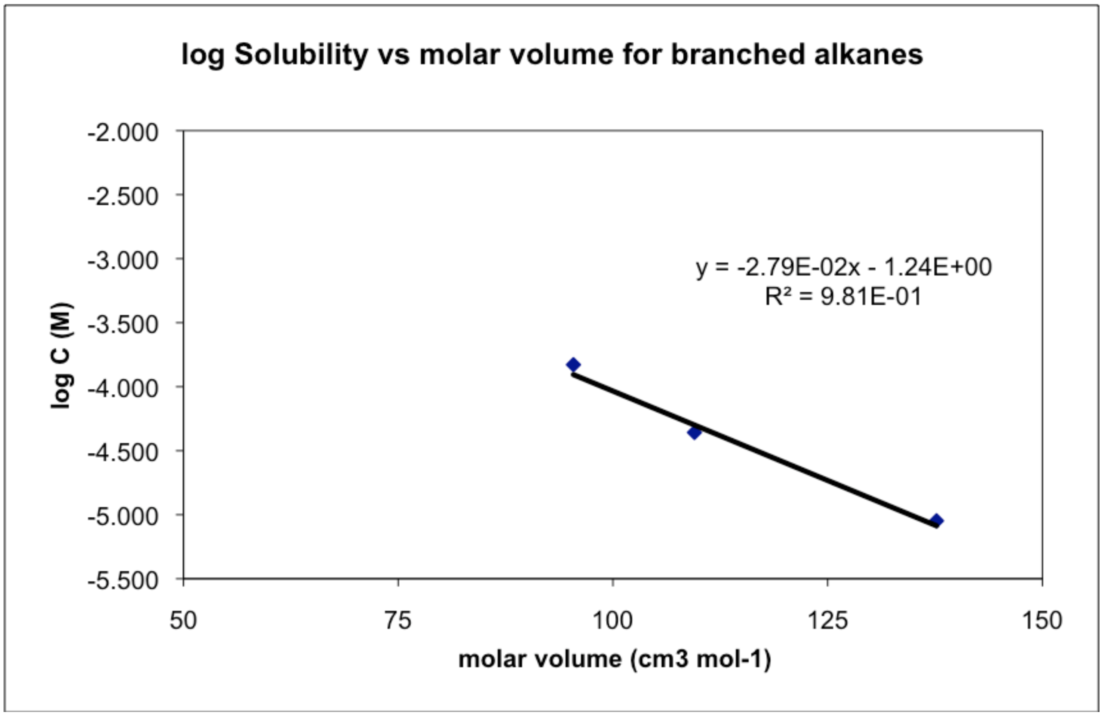
1. Provide the missing information from Appendix C of your textbook and calculate the aqueous activity coefficients, γ_w^{sat} for the following compounds at 25°C (*subcooled/superheated, if necessary)*. Rationalize the magnitude of these values using your understanding of the intermolecular interactions that influence water solubility? Which of these compounds will have the greatest atmospheric concentration in equilibrium with an aqueous solution?

	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**

2. Calculate the activity coefficients for naphthalene in water and in 1-octanol (water-saturated) at 25°C given $C_w^{sat} = 2.5x10^{-4}$ M and $K_{ow} = 2.3x10^3$. Comment on the relative magnitude of these activity coefficients?

3. Use the characteristic 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 Henry's Law constant, K_H (in units of atm M^{-1}) for lindane (hexachlorocyclohexane) and pentachlorophenol.

Branched Alkanes	C (mg/L)	MW	C (M)	log C	#C	#H	#bonds	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**	(using all bran
2,2,4-trimethylpentane	**2.34**	**114.2**	**2.05E-05**	**-4.688**	**8**	**18**	**25**	**123.58**	(using only di a alkanes)

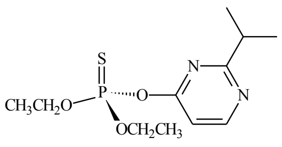


Depending on the choice of alkanes used in generating the correlation, the aqueous solubility of 2,2,4-trimethylpentane is estimated between **18 and 21 uM**. If we limit our choice of alkanes to only those with di- and tri methyl groups (n=4), the correlation is quite good;

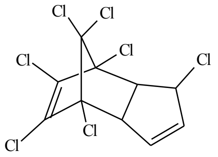
$$\mathbf{\log C\ (M) = -2.8 \times 10^{-2}\ V_m - 1.2\ (R^2 = 0.98)}$$

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.

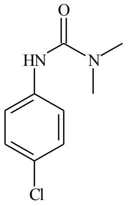
Pesticide	Molar Mass (g.mol^{-1})	Vapour Pressure (mPa)	Solubility (mg.L^{-1})
Diazinon	304	16.0	40.0
Heptachlor	373	22.0	5.60×10^{-3}
Monuron	199	2.30×10^{-2}	2.60×10^{2}



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;

log P^o = 4.73 (Pa), –log C_w^{sat} = 1.01 (mol L^{-1}), -log K_{aw} = 0.66 (unitless)

a) Calculate the concentration of iodomethane in the water and air at equilibrium at 25°C.

b) If the bottle is opened after equilibration and all of the air in the headspace is been flushed out and replaced by fresh air, what will the concentration of iodomethane be in the aqueous solution after equilibrium is re-established?

Solution:

a) The fraction in the gas phase is given by;

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

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

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

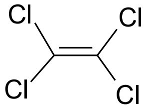
Using the unitless value for K_{aw} = 0.219 and V_g = 0.9 L and V_w = 0.1 L, we obtain **f_g = 0.66**

Hence, the 66% of the original (100. ug/L x 0.1 L = 10.0 ug) is present in the headspace of the sealed container and only 34% of the original 10.0 ug is present in the aqueous solution.

Therefore the concentration of iodomethane in the gas phase is 6.6 ug per 0.90 L = **7.3 ug/L** and **34 ug/L** in the aqueous solution.

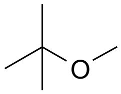
b) After the bottle has been opened and the headspace allowed to escape into the room air, the new aqueous phase concentration is 34 ug/L. This will once again partition into the headspace such that 66% is in the gas phase and 34% in the aqueous phase. Consequently, the new concentration in the aqueous phase solution will be a mere **11.6 ug/L** (down from the original 100. ug/L)!

6. 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?



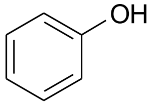
perchloroethene (PCE)

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})

Solution:

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

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

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

$C_g = K_{aw} C_w$

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

So, for PCE 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 %).

To understand the affect of temperature on the air-water partitioning (K_{aw}), we need to examine the affects on both vapour pressure (P^o) and water solubility (C_w^{sat}). vapour pressure (P^o) is very sensitive to temperature and will decrease with decreased temperature for all compounds. The extent of this decrease will depend on ΔH_{vap}, which will depend on the intrinsic properties of the compound. However, the change in water solubility with temperature is a little more subtle and 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 with temperature. Consequently, we should deal with each of these phases separately.

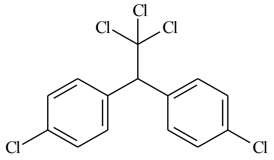
Gases: As the temperature decreases from 25 to 5°C, the C_w^{sat} will increase. Coupled with the decrease in P^o experienced by all cmpds, we see that K_{aw} at 5°C will be considerably less than K_{aw} at 25°C. Therefore, a greater fraction will be present in rainwater at 5°C than at 25°C.

Liquids: As the temperature decreases, the water solubility of organic liquids remains relatively constant. So as P^o 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. Since PCE is a liquid at these temperatures, we expect this affect.

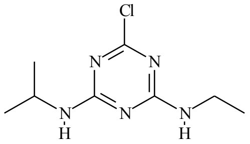
Solids: The water solubility of organic solids generally decreases with decreased temperature. So as both P^o and C_w^{sat} decrease over the range of 25 to 5°C, it can be difficult to assess the extent of the change on K_{aw} without further information. However, since P^o tends to be more sensitive 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. Since 2-methoxyphenol is a solid at these temperatures, we expect this affect.

7. Comment on the distribution of DDT and atrazine between organic rich sediments and the water column from the following information. Explain your reasoning.

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



DDT



Atrazine

Solution:
To answer this question we really need to compare the partition coefficients $K_{om,}$ (water-organic matter) a partition constant used to express partitioning between water and organic matter. This can be further modified using the fraction of organic carbon (f_{oc}) present in a given sediment and expressed as a K_{oc} (organic carbon). Since none of this information is given (or readily available) we might recognize that higher K_{ow} values are generally well correlated with K_{om} and K_{oc} values. These correlations are quite good for a structurally related series of compounds and can be used for predictive purposes. However, for structurally diverse cmpds (such as DDT and Atrazine), higher K_{ow}'s still correlate with higher K_{om} and K_{oc} values.

If we wanted to broaden this question, and consider global environmental distributions, we would need to consider air-water (K_{aw}) and octanol-air (K_{oa}) values of the two compounds. We could estimate K_{aw} from the given information and then determine as $K_{oa} = K_{ow}/K_{aw}$.

$$K_{aw} = \frac{P^o}{C_w^{sat}}\frac{1}{RT} = \frac{10^{-9.87}\,\text{atm}}{10^{-7.85}\,\text{M}}\frac{1}{(0.08206\,\text{L atm mol}^{-1}\text{K}^{-1})(298\text{K})} = 3.9\text{x}10^{-4}$$

	P^o (atm)	**C_w^{sat} (M)**	**K_{ow}**	**K_{aw}** (unitless)	**K_{oa}** (unitless)
DDT	$10^{-9.87}$	$10^{-7.85}$	2.3×10^{6}	3.9×10^{-4}	5.6×10^{9}
Atrazine	$10^{-9.05}$	$10^{-3.81}$	3.6×10^{2}	2.3×10^{-7}	1.6×10^{9}

Both compounds would be characterized as very non-volatile because of their extremely low vapour pressures. The two compounds however differ widely in their water solubility, with atrazine being about four orders of magnitude (10,000x) more water soluble than DDT.

A comparison of the above partition coefficients suggests that DDT will be largely associated with organic particulate phases (aquatic sediments or suspended organic particulates). The high values of K_{ow} and K_{oa} indicate that DDT will distribute out of water and out of air onto organic materials. Also, the relatively large value of K_{aw} indicates than DDT will also partition out of water into air to a much larger extent than Atrazine. All of this suggests that DDT may be distributed globally via atmospheric transport more so than Atrazine, but that it will be largely distributed into the sediment phase (contamination is often local and regional in scale if trapped in sediments with limited exposure to the atmosphere). The lower K_{ow} and K_{aw} values associated with Atrazine will lead to a greater distribution in the aqueous phase, which is generally limited to regional geographic scale.

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 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?

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

$K^{sw} = 0.35$

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

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).

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

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

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

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

K_{aw}(sea) = 29.2 atm/M x 1/((0.08206 L atm mol^{-1} K^{-1}) (298 K)) = **1.2**

Hence, $Q_{aw} < K_{aw}$(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_{aw}(sea) will decrease. This will reduce the driving force for the net flux sea → air and may, in fact, reverse the direction of TCE from air → sea, if $Q_{aw} > K_{aw}$(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^o at 278 K. This could be accomplished using the semi-empirical formula,

$$\ln P^o(L) \approx 19\left(1 - {}^{T_b}\!/\!_{T}\right) + 8.5\left(\ln {}^{T_b}\!/\!_{T}\right)$$

$$\ln P^o(L) \approx 19\left(1 - {}^{347}\!/\!_{278}\right) + 8.5\left(\ln {}^{347}\!/\!_{278}\right) = -4.72 + 1.88 = -2.84$$

$P^o \sim 0.059$ atm

So, K_{aw}(sea) at 5°C ~ 10.4 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.

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

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