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	-45.2	230.0	109
log P^o / Pa	3.20	-2.60	-4.70
-log C_w^{sat} / M	2.39	7.55	7.80
-log K_{aw}	0.80	1.44	3.30
logK_{ow}	2.78	5.80	6.36

Solution:

Chlorobenzene is a <u>liquid</u> at 25 °C, therefore we can use,

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

and the activity co-efficient for chlorobenzene in water is given by,

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w \ C_w^{sat}(l)} = \frac{1}{(0.01802\text{L/mol})(10^{-2.39}\text{mol/L})} = 1.36\text{x}10^4 \ (unitless)$$

Hexachlorobenzene is a <u>solid</u> at 25 °C, therefore we first use the following relation to determine the water solubility of the sub-cooled liquid state.

$$C_w^{sat}(s) = C_w^{sat}(L) \ \text{x} \ \frac{P^o(s)}{P^o(L)}$$

$$\therefore C_w^{sat}(L) = \frac{C_w^{sat}(s)}{P^o(s)/P^o(L)} \cong \frac{10^{-7.55} \ \text{mol/L}}{e^{-6.8(503/298-1)}} = \frac{2.82 \ \text{x} \ 10^{-8}}{9.30 \ \text{x} \ 10^{-3}} = 3.0x10^{-6} \ \text{mol/L}$$

where we are using the semi-empirical relation below in the denominator

$$\ln\left(\frac{P^o(s)}{P^o(L)}\right) = -6.8\left[\frac{T_m}{T} - 1\right]$$

Therefore, the activity co-efficient for hexachlorobenzene in water is given by,

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w \ C_w^{sat}(L)} = \frac{1}{(0.01802\text{L/mol})(3.0x10^{-6} \ \text{mol/L})} = 1.8\text{x}10^7 \ (unitless)$$

DDT is also a <u>solid</u> at 25 °C, therefore we can again use

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w\, C_w^{sat}(L)} = \frac{1}{\overline{V}_w \left\{\dfrac{C_w^{sat}(s)}{P^o(s)\Big/P^o(L)}\right\}} \cong \frac{e^{-6.8\left(T_m/T - 1\right)}}{V_w\, C_w^{sat}(s)}$$

$$= \frac{0.147}{(0.01802\ \text{L/mol})(10^{-7.80}\ \text{mol/L})} = 5.1 \times 10^8\,(unitless)$$

Summarizing the aqueous activity co-efficients

Compound	Aqueous activity co-efficient
Chlorobenzene	1.4×10^4
Hexachlorobenzene	1.4×10^7
DDT	2.4×10^{10}

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 $P°(L)$), 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. Remember, any term that contributes a All of these compounds are apolar, with α and β terms equal to zero. The vapour pressure terms in the table below are for the liquid or sub-cooled liquid states. In the case of the latter, they are estimated from $P°(s)$ and the T_m values given in Appendix C and reported in units of bar (1 bar = 100,000 Pa). We expect chlorobenzene to be less polarizable then hexachlorobenzene and DDT. Although we might compare the refractive indicies, these are difficult to come by for solids. The molar volumes can be estimated from the characteristic atomic volumes and are included in the table below. As we can see, the major differences in contributing to the activity coefficients and hence the water solubility are $P°(L)$ and size (i.e., molar volume, V). Note, that molar volume is embedded in three terms in the equation below ($P°(L)$, vdW dispersive energy term and of course the independent molar volume term).

$$\ln \gamma_w = -\ln P°(L) \text{ (bar)} + -0.572 \left[\overline{V}^{-2/3} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \right] - 5.78\ (\pi)\ -\ 8.77\ (\alpha) - 11.1\ (\beta) + 0.04722\ \overline{V} + 9.49$$

	chlorobenzene	hexachlorobenzene	p,p'-DDT
-ln P°(L) (bar)	4.2	11.8*	20.4*
n_D			
π	0.65**	> 0.65	> 0.65
α	0	0	0
β	0	0	0
V (cm^3/mol)***	83.9	145.1	221.8

* from P°(s) and T_m values in Appendix C
** from Table 5.5 (p.152)

The K_{ao} partition constants can be determined from the K_{ow} and K_{aw} as follows,

$$K_{ao} = \frac{K_{aw}}{K_{ow}}$$

Summarizing the air-octanol partition constants

Compound	Air-octanol co-efficient
Chlorobenzene	$10^{-3.58} = 2.6 \times 10^{-4}$
Hexachlorobenzene	$10^{-7.24} = 5.8 \times 10^{-8}$
DDT	$10^{-9.66} = 2.2 \times 10^{-10}$

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?

Solution:

Trichloroethene is a liquid at room temperature, therefore it's activity coefficient is directly related to its water solubility through

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w \, C_w^{sat}(l)} = \frac{1}{(0.01802 \text{L/mol})(8.32 x 10^{-3} \text{mol/L})} = 6.67 \times 10^3 (unitless)$$

To calculate the activity co-efficient in octanol, we use

$$K_{ow} = \frac{C_o^{sat}}{C_w^{sat}} = \frac{\gamma_w^{sat} \overline{V}_w}{\gamma_o^{sat} \overline{V}_o}$$

Rearranging and using 0.13 L/mol for the molar volume of water saturated octanol (pg. 215), we can write

$$\gamma_o^{sat} = \frac{\gamma_w^{sat} \overline{V}_w}{K_{ow} \overline{V}_o} = \frac{(6.67 \times 10^3)(0.018 \text{ L/mol})}{(2.63 \times 10^2)(0.13 \text{ L/mol})} = 3.5$$

The magnitude of the activity co-efficient of trichloroethene is <u>significantly larger</u> in water than it is in octanol. Remember, the activity co-efficient is a measure of the degree of dissimilarity between the solute and solvent. Trichloroethene is much more similar to octanol than it is to water. This is a general result for organic solutes, with aqueous activity coefficients varying for different solutes by over ten orders of magnitude. Octanol activity coefficients vary by roughly one order of magnitude.

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?

Solution:

a) Molar volume estimates

   di-*n*-butylphthalate: 16(Carbon) + 4(Oxygen) + 22(Hydrogen) – 42(6.56) = 16(16.35) + 4(12.43) + 22(8.71) – 42(6.56) = **234.4 cm^3 mol^{-1}**

   2,4,6-trichlorophenol: 6(Carbon) + 1(Oxygen) + 3(Hydrogen) + 3(Chlorine) – 13(6.56) = 6(16.35) + 12.43 + 3(8.71) + 3(20.95) = **114.2 cm^3 mol^{-1}**

b) K_H estimates

   di-*n*-butylphthalate:
   log $K_H' = 6(C_{ar}-C_{ar}) + 2(C_{ar}-CO) + 2(CO-O) + 2(C-O) + 4(C_{ar}-H) + 18(C-H) = 6(-0.264) + 2(-1.24) + 2(-0.071) + 2(-1.09) + 4(0.154) + 18(0.120) =$ **-3.61** (unitless)

   Therefore $K_H' = 10^{-3.61} =$ **2.45 x 10^{-4}**
   Converting to K_H (atm M^{-1}),
   K_H = RT K_H' = (0.08206 L atm mol^{-1} K^{-1}) (298 K) (2.45 x 10^{-4}) = **6.00 x 10^{-3} atm M^{-1}**

   2,4,6-trichlorophenol:
   log $K_H' = 6(C_{ar}-C_{ar}) + 1(C_{ar}-OH) + 3(C_{ar}-Cl) + 2(C_{ar}-H) + 1(O-H) = 6(-0.264) + (-0.597) + 3(0.0241) + 2(0.154) + (-3.23) =$ **-5.03** (unitless)

   Therefore $K_H' = 10^{-1.80} =$ **9.33 x 10^{-6}**
   Converting these to K_H (atm M^{-1}),
   K_H = RT K_H' = (0.08206 L atm mol^{-1} K^{-1}) (298 K) (9.33 x 10^{-6}) = **2.28 x 10^{-4} atm M^{-1}**

c) Comparison of estimated and experimental K_H values

$$K_H \sim P^o/C_w^{sat}$$

Summarizing the air-water partition constants

| Compound	Estimated K_H Using Hine & Mookerjee (atm M^{-1})	P^o at 25 °C (atm) converted from Pa	C_w^{sat} (M)	Calculated K_H from P^o and C_w^{sat} reported in Schwarzenbach (atm M^{-1})
di-*n*-butylphthalate	6.00 x 10^{-3}	5.18 x 10^{-8}	4.37 x 10^{-5}	1.18 x 10^{-3}
2,4,6-trichlorophenol	2.28 x 10^{-4}	2.31 x 10^{-5}	4.27 x 10^{-3}	5.41 x 10^{-3}

The bond fragment approach can provide reasonable estimates of air-water partition constants and are generally good for 'order of magnitude' estimates. They tend to work better for smaller molecules that are not encumbered by intramolecular interactions and/or steric effects. On the other hand, air-water partition constants can be calculated quite well if both vapour pressures and water solubilities are known with some certainty. Note that you do not need to correct for the solute being a solid, liquid or gas in this case as both the vapour pressure and the water solubility are for the solute in the same physical state and the energy of fusion or vapourization is incorporated in both.

In the case of di-*n*-butylphthalate and 2,4,6-trichlorophenol, the ortho substitution creates some challenges for the bond fragment approach due to steric interactions and the level of agreement is worse than in the cases illustrated in the text (Example 6.4, pg 207).

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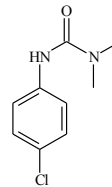
Pesticide	Molar Mass (g.mol^{-1})	Vapour Pressure (mPa)	Solubility (mg.L^{-1})
Diazinon	304	16.0	40.0
Heptachlor	373	22.0	5.60×10^{-3}
Monuron	199	2.30×10^{-2}	2.60×10^{2}
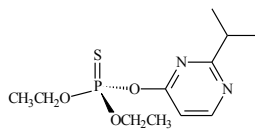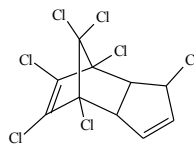
Diazinon   Heptachlor   Monuron

Solution:

Convert vapour pressure from mPa to atm as follows;
$$P^{o} (atm) = P^{o} (mPa) \times 1\ Pa/10^{3}\ mPa \times 1\ atm/101,300\ Pa$$

Convert water solubility from mg L^{-1} to molarity as follows;
$$C_{w}^{sat} (M) = S\ (mg\ L^{-1}) \times 1\ g/10^{3}\ mg \times 1/MM\ (g\ mol^{-1})$$

Calculate the Henry's Law constant using,
$$K_{H} \sim P^{o}/C_{w}^{sat}$$

Summarizing the air-octanol partition constants

Compound	P^{o} (atm)	C_{w}^{sat} (M)	K_{H} (atm M^{-1})
Diazinon	1.58×10^{-7}	1.32×10^{-4}	1.20×10^{-3}
Heptachlor	2.17×10^{-7}	1.50×10^{-8}	14.5
Monuron	2.27×10^{-10}	1.31×10^{-3}	1.74×10^{-7}

We can use a mass balance approach to calculate the fraction of each compound in the air of an air – water system as follows;
$$f_{air} = \frac{C_{air}V_{air}}{C_{air}V_{air} + C_{water}V_{water}}$$

Since the volume of air and water are equal in this case, the expression simplifies to;
$$f_{air} = \frac{C_{air}}{C_{air} + C_{water}}$$

Using the definition $K_{aw} = C_{air}/C_{water}$, we can rearrange for the $C_{water} = C_{air}/K_{aw}$ and substitute into the fractional abundance expression above to yield,
$$f_{air} = \frac{C_{air}}{C_{air} + \frac{C_{air}}{K_{aw}}} = \frac{1}{1 + \frac{1}{K_{aw}}} = \frac{K_{aw}}{K_{aw} + 1}$$

Note that this approach requires that we use the unitless Henry's law constant (K_{H}' or K_{aw}).

Converting using $K_{H}' = K_{H}/RT$ yields the following;

Compound	K_{H} (atm M^{-1})	K_{aw}	f_{air}
Diazinon	1.20×10^{-3}	4.91×10^{-5}	**~5 x 10^{-5}**
Heptachlor	14.5	0.593	**0.37**
Monuron	1.74×10^{-7}	7.12×10^{-9}	**~7 x 10^{-9}**

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?

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 $C_g = K_{aw} C_w$ and cancelling common terms yields,

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

Using the unitless value for $K_{aw} = 0.219$ and $V_g = 0.900$ L and $V_w = 0.100$ L, we obtain $f_g = 0.67$

$$K_{aw} = \frac{K_H}{RT} = \frac{542 \text{ Pa m}^3 \text{ mol}^{-1}}{(8.314\text{J mol}^{-1}\text{K}^{-1})(298\text{K})} = 0.219$$

$$f_g = \frac{0.219(0.900L)}{0.219(0.900L) + (0.100L)} = 0.67$$

Hence, 67% of the iodomethane present in the original sample is present in the headspace of the sealed container and only 33% is present in the aqueous solution. Since the original sample contained 0.100 L at 100 ug/L, there was a total of 10.0 ug of iodomethane present initially. Therefore, the concentration of iodomethane in the gas phase is 6.7 ug per 0.900 L = 7.4 ug/L. The remaining 3.3 ug is present in the 0.100 L water sample for a concentration of **33 ug/L**.

b) After the bottle has been opened and the headspace allowed to escape into the room air, the new aqueous phase concentration is 33 ug/L. Once the bottle is re-sealed, the system will again equilibrate with 67% of the iodomethane partitioning into the headspace. Consequently, the new concentration in the aqueous phase solution will be a mere **11 ug/L** (down from the original 100. ug/L).

c) The fraction in the aqueous phase for an air-water system can be written as follows,

$$f_w = 1 - f_g = 1 - \left(\frac{K_{aw} V_g}{K_{aw} V_g + V_w} \right)$$

Substituting in the $V_g = 100.$ L and $V_w = 1.0 \times 10^{-4}$ L yields;

$$f_w \sim 5 \times 10^{-6} \quad \text{(i.e., > 99.999\% remains in the gas phase and is not rained out of the atmosphere).}$$

At lower temperatures, the value of K_{aw} is expected to decrease. This will increase the fraction of iodomethane in the aqueous phase. However, even if the value of Kaw drops by ten times in going from 25 °C to 5 °C, the vast majority of the iodomethane remains in the gas phase in the gas phase in an atmosphere with water aerosol droplets.

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)	$\log K_{ow}$	K_H (atm M^{-1})
DDT	9.87	7.85	6.36	9.5×10^{-3}
Carbofuran*	**9.13**	**2.81**	1.60	4.8×10^{-7}
Atrazine	9.05	3.81	2.56	5.8×10^{-6}
Dieldrin**	**8.11**	**6.27**	5.50	1.5×10^{-2}

DDT

Atrazine

Carbofuran
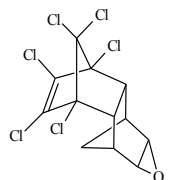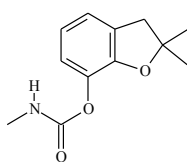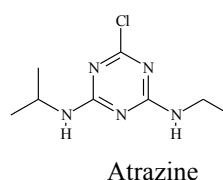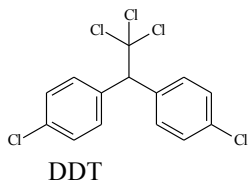
Dieldrin

* values for Carbofuran from Appendix C
** values for Dieldrin from Handbook of Groundwater Chemicals

Solution:
i) All of these compounds are expected to be solids based on the chemical structures. The most hydrophobic will be **DDT**, since it is considerably less water soluble than the rest and the aqueous activity coefficient for solids is given by

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w \, C_w^{sat}(L)} = \frac{1}{\overline{V}_w \left\{ \dfrac{C_w^{sat}(s)}{P^o(s)\big/P^o(L)} \right\}} \cong \frac{e^{-6.8\left(T_m/T -1\right)}}{V_w \, C_w^{sat}(s)}$$

ii) The K_H values have been calculated using P^o/C_w^{sat}. **Dieldrin** is the most likely to partition from surface water to the atmosphere since it has the largest K_H in the Table above.

iii) Reduction in water solubility from fresh to seawater conditions will scale with the salting constant (K^s) which varies with each solute. The greatest salting constants are associated with the most hydrophobic solutes. In this case, we would expect this to be for **DDT**, which we have identified as the solute with the greatest activity co-efficient in water.

iv) K_{ow} is a good predictor of tendency to bio-accumulate in aquatic organisms, hence we expect this to be greatest for **DDT**.

v) K_{ow} is a good predictor of partitioning onto organic rich sediments in the water column, hence the compound with the lowest K_{ow} is expected to have the highest aqueous concentration (**Carbofuran**, in this case).

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 chlorobenzenes 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.

Solution:

The air-octanol partition co-efficient is governed by the vapour pressure relative to the solubility in **octanol**. For a series of apolar compounds, their solubility in octanol is expected to be quite high and relatively invariant with molecular size (i.e., the variation in the octanol activity coefficients between chlorobenzene and hexachlorobenzene will be small). However, the vapour pressure of these molecules will vary considerably as the larger molecules will have greater dispersive vdW energy terms reducing their vapour pressures. As a consequence, we expect the values of K_{aw} to vary considerably due to variations in the vapour pressures across a series of apolar molecules.

On the other hand, the air-water partition co-efficient is governed by the vapour pressure relative to the solubility in **water**. For a series of apolar compounds, their solubility in water is expected to decrease considerably with molecular size due largely to the energy costs of cavity formation (i.e., the aqueous activity coefficient of hexachlorobenzene will be considerably smaller than that of chlorobenzene). Since the vapour pressure also decreases with molecule size, these two effects have a compensating influence on each other and the ratio of vapour pressure to water solubility does not vary dramatically across the series.

$$K_{aw} \sim P^o / C_w^{sat} \sim P^o \, V_w \, \gamma_w^{sat} \text{ (for liquids)}$$

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 $\rightarrow$ sea or sea $\rightarrow$ 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?

$T_m = -30.4°C$; $T_b = 74.1 °C$; $-\log P° = 0.78$ (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).

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

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

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 $P° = 0.166$ 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 $\times 1/((0.08206$ 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 $\rightarrow$ air and may, in fact, reverse the direction of TCE from air $\rightarrow$ 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 $P°$ at 278 K. This could be accomplished using the semi-empirical formula,

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

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

$P° \sim 0.059$ atm
So, **$K_{aw}(sea)$ at 5°C $\sim$ 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

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)