

## Rubric

### Problem 1 (20 pts)

Correct Answer	1 pt each
Formula	3 pts each
Discussion	3 pts
Bet or not	1 pt

### Problem 4 (40 pts)

- Each compound 10 pts

Answer 1	1 pt
Method 1	3 pts
Answer 2	1 pt
Method 2	3 pt
Comparison w/ reported	1 pt
Comparison w/ estimated answer	1 pt

**Carnegie Mellon University**  
**Department of Civil and Environmental Engineering**

**12-725: Fate, Transport, and Physicochemical Processes of Organic Contaminants  
in Aquatic Systems and their Measurement in Environmental Samples**

**Problem Set #4 Spring 2020-SOLUTIONS**  
**Due February 13 by 5pm**

1. P9.6 in EOC

1. Here, you need to adjust solubility of a solid for temperature and salinity, then compare the values.

$$\Delta_{ws}H_i = \frac{30\text{kJ}}{\text{mol}}$$

This value can be directly used in Van't Hoff equation (because this is the  $\Delta H$  from solid to gas).

We also know  $C_{i,w}(298K) = 2.5E - 4 \text{ mol/l}$ ,  $T_m = 351K$ ,  $\tau = 0$ ,  $\sigma = 4$

$$\ln(C_{iw}^{sat}, 278K / C_{iw}^{sat}, 298K) = -\frac{\Delta_{ws}H_i}{R} * \left( \frac{1}{278K} - \frac{1}{298K} \right)$$

$$C_{iw}^{sat}(278K) = 1.1E - 4 \text{ mol/l}$$

$$\ln(P_{is}^*/P_{iL}^*) = -\left( (6.8 + 1.1\tau - 2.3\log\sigma) \left( \frac{T_m}{T} - 1 \right) \right)$$

Plug in values, at 278K,  $(P_{is}^*/P_{iL}^*) = 0.24$ ; at 298K,  $(P_{is}^*/P_{iL}^*) = 0.38$

$$x_{i,w}^{sat} = \frac{1}{\gamma_{i,w}^{sat}} \left( \frac{P_{is}}{P_{iL}} \right)$$

$$\gamma_{iw}^{sat}(278K) = 1.3 \times 10^5 \text{ (in DI water)}$$

$$\gamma_{iw}^{sat}(298K) = 8.4 \times 10^4 \text{ (in DI water)}$$

$$35\% \approx 0.5M \text{ salt}[tot], K_{is}=0.28$$

$$\text{At } 298K, \gamma_{iseawater}^{sat}(298K) = \gamma_{iw}^{sat}(298K) * 10^{K_{is}*Stot} = 1.2 \times 10^5$$

$$S_{iseawater}^{sat}(298K) = 1.8 \times 10^{-4} \text{ mol/l}$$

	C (mol/l)	$\gamma$
<b>5 °C, DI Water</b>	$1.1 \times 10^{-4} \text{ mol/l}$	$1.3 \times 10^5$
<b>25 °C, DI Water</b>	$2.5 \times 10^{-4} \text{ mol/l}$	$8.4 \times 10^4$
<b>25 °C, Seawater</b>	$1.8 \times 10^{-4} \text{ mol/l}$	$1.2 \times 10^5$

The solubility and activity of naphthalene in seawater at 25 °C are NOT both higher than in DI water at 5 °C (but they are almost). There are two effects to consider. One is the effect of salt on the solubility. The other is the effect of temperature on the solubility.

For  $H_{ws}=30$  kJ/mol, you expect a 53% decrease in solubility for a 10 °C decrease in temperature (see Table 3.5). So for a 20 °C decrease in temperature you would anticipate a ~75% decrease in solubility. The salt will decrease solubility at a rate of 10<sup>0.28</sup> per molar concentration of salt. So for seawater (0.5M salt) we anticipate 10<sup>0.14</sup> decrease (or 30%). So, here the effect of temperature on solubility is more significant thus you would expect a lower solubility in DI water at 5 °C compared to 25 °C. The activity coefficient of a solid is affected by both the solubility of the compound and the fusion/melting process (reflected by  $P_{is}^*/P_{il}^*$ ). This ratio is reduced by ~30% changing from 298k to 273k. Given you also anticipated ~75% decrease in solubility in DI water at 5 °C and you anticipated only ~30% decrease in solubility in seawater at 25 °C, it is expected that the activity coefficient in DI water at 5 °C is higher than the activity coefficient in seawater at 25 °C.

## 2. P9.9 in EOC

The system is 0.1ml water (pH=6), 100L air. T=278K and 298K, respectively

$$F_w^{-1} = 1 + K_{iaw} \frac{V_a}{V_w}$$

Methyl bromide,  $K_{iaw}$  (298K)= 0.447

Atrazine  $K_{iaw}=1.2 \times 10^{-7}$

2,4-dinitro-6-methylphenol= $3.0 \times 10^{-5}$

For 2,4-dinitro-6-methylphenol, we also need to consider dissociation ( $PK_a=4.31$ ), and we should use  $Diaw$  to replace  $K_{iaw}$ .  $Diaw=K_{iaw} \times \alpha_{ia}$ .

$$\alpha_{ia} = \frac{1}{1 + 10^{pH - pK_{ia}}}$$

This  $\alpha_{ia} = 1/(1+10^{1.79})=0.01$

$Diaw=K_{iaw} \times \alpha_{ia}=3.0 \times 10^{-7}$

$F_w$  Methyl bromide, 298K=  $2.2 \times 10^{-6}$

$F_w$  Atrazine at 298K= 0.89

$F_w$  2,4-dinitro-6-methylphenol at 298K= 0.77

To correct for the effect of temperature, we need to know the  $\Delta H$ .

Here,  $\Delta H_{vap} \approx \Delta H_{iaw}$

Use  $\Delta_{vap}H_i$  (kJ mol<sup>-1</sup>) =  $-8.79(\pm 0.07) \log p_{il}^*$  (Pa) +  $70.0(\pm 0.2)$  to estimate  $\Delta H$

$\Delta H_{vap}$  for Methyl bromide is 23KJ/mol

For Atrazine it is 109KJ/mol, for 2,4-dinitro-6-methylphenol it is 80KJ/mol

You can use the correlation between  $\ln K$  and  $1/T$  to do the calculation, or you can directly use Table D.1 in appendix D in your book.

For a 20K temperature difference,

For Methyl bromide,  $K_{iaw}(278K) \approx 0.56 * K_{iaw}(298K) = 0.25$

For Atrazine,  $K_{iaw}(278K) \approx 0.04 * K_{iaw}(298K) = 5 * 10^{-9}$

For 2,4-dinitro-6-methylphenol,  $K_{iaw}(278K) \approx 0.1 * K_{iaw}(298K) = 3 * 10^{-6}$

Assuming the change of pKa is minimal,  $D_{iaw}(278K) \approx 3 * 10^{-8}$

$F_w$  Methyl bromide,  $298K = 4 * 10^{-6}$

$F_w$  Atrazine,  $298K = 0.99$

$F_w$  2,4-dinitro-6-methylphenol,  $298K = 0.97$

By lowering the temperature, both vapor pressure and solubility of the compounds would be affected, but vapor pressure is more sensitive to temperature changes, thus we assumed the  $\Delta H_{iaw}$  is appropriately  $\Delta H_{vap}$ . By decreasing the temperature, we would decrease vapor pressure. Thus we end up having more in the water phase.

It should be noted that pKa is also affected by temperature, but we assumed that this influence is small relative to the influence on vapor pressure.

### 3. Q9.8 in EOC

Dissolved organic salts in water tend to decrease the aqueous solubility of most organic compounds. This is because the salts compete with the organics for water to hydrate them. With lots of water molecules coordinating with salt ions, less is available for solubilizing the organic compounds.

The effect of salt of the solubility is not linear. It is log linear (exponential) with respect to salt concentration.

The magnitude of the effect depends on the salt concentration. However, for seawater, the magnitude of the effect of salt on the activity coefficient is a factor of 2 or less. The magnitude of the effect on Henry's constant is the same because it does not affect the molecular interactions in the gas phase or the inherent volatility of the compounds.

4. Atoms and functional groups on a molecule lead to the intermolecular forces between molecules that lead to behaviors like air-water partitioning. Fortunately, the effects of, e.g. a C-H bond or a C-O bond are similar in different molecules. One exception is that C atoms in aromatic rings behave differently than C atoms in olefins, which behave differently than C atoms in aliphatics. One can predict the air-water partition coefficient,  $K_{iaw} (C_{ia}/C_{iw})$  by summing up all of the contributions from bonds and/or functional groups in a molecule according to equation 9-19 and Table 9-4. Use this approach to estimate  $K_{iaw}$  for the following compounds at 25 °C: a) PFOS, b) trinitrotoluene c) carbon tetrachloride, and d) 1,2-dichlorophenol. Compare this estimate to the value that you find in the literature (Appendix C in your book is one resource for this), and to one other estimation method of your choosing.

Using the bond contribution approach:

- a) PFOS-cannot use this approach because there are no bond contributions for the sulfonate group.

Estimate based on vapor pressure and water solubility =  $4.1 \times 10^{-4}$  atm-m<sup>3</sup>/mol

Measurements by 3M (manufacturer)=  $4.34 \times 10^{-7}$  atm-m<sup>3</sup>/mol

The estimate and measured values are off by 3 orders of magnitude. However, both values are very low, which is consistent with expectations since PFOS is an ionic species in water.

b) Trinitrotoluene

Bonds	Value	# of bonds
Car-Car (Intra)	-0.2638	6
Car-H	0.1543	3
Car-N	-0.7304	3
N=O	-1.0956	6
Log Kiaw	-9.88	
Published value	-6.22	
Error (calculated after converting logkiaw to kiaw)	457,000%	
Source	Appendix C	

A second estimate can come from the vapor pressure ( $8.02 \times 10^{-6}$  mmHg) and water solubility ( $4.2 \times 10^{-4}$  M). Both of these values come from PubChem (<https://pubchem.ncbi.nlm.nih.gov/compound/8376#section=Vapor-Pressure>)

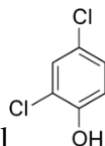
$K_{iH} = 8.02 \times 10^{-6} \text{ mmHg} / 760 \text{ mmHg/atm} / (4.2 \times 10^{-4} \text{ M}) = 2.5 \times 10^{-5} \text{ atm-L/mol}$ .

$K_{iaw} = 1 \times 10^{-6}$ . So it is quite low also and pretty close to the published value (factor of 1.6)

c) Carbon tetrachloride:

f <sub>k</sub>	n <sub>k</sub>	value	total
C-Cl	4	-0.335	-1.34
Log K <sub>iaw</sub>	-1.34	Kiaw,1 (Cia/Ciw)	0.05
Vapor pressure	Solubility		
11.9kpa	0.005M	Kiaw,2 (Cia/Ciw)	0.96

Appendix C value is reported at  $10^{-0.04} = 0.91$ . This is about 17 times higher than 0.05 estimate from the bond contribution approach, and about 5% different than the second estimate.



d) 1) 2,4 dichlorophenol

Bonds	Value	# of bonds
Car-Car (Intra)	-0.2638	6
Car-H	0.1543	3

Car-OH	-0.5967	1
Car-Cl	0.0241	2
O-H	-3.2318	1
Log Kiaw	-4.9	
Published value	-3.61	
Error (calculated after converting logkiaw to kiaw)	~300% error	
Source	Appendix C	

A second estimate can come from the vapor pressure (0.09mmHg) and water solubility (0.03M).

$$K_{iH} = 0.09 \text{ mmHg} / 760 \text{ mmHg/atm} / (0.03\text{M}) = 0.004 \text{ atm-L/mol.}$$

$K_{iaw} = 1.6 \times 10^{-4}$ . This is about 53% difference compared to the published value.

- Using your knowledge of the molecular scale factors influencing intermolecular interactions, explain the trends for benzene and n-butylbenzene and for decane and eicosane in Table 8.2. Consider  $T_m$ ,  $\Delta H_{fus}$  and  $\Delta S_{fus}$  in your discussion.

From Table 8.2

Compound	$T_m$ (°C)	$\Delta H_{fus}$ (kJ/mol)	$\Delta S_{fus}$ (J/mol K)
Benzene	5.5	10	35.8
n-butylbenzene	-88.0	11.2	69.1
Decane	-29.7	28.8	115.1
eicosane	36.8	69.9	207.1

### **Benzene vs. n-butylbenzene**

The  $\Delta H_{fus}$  (kJ/mol) of both benzene and n-butylbenzene are similar. They are close to the same size and both are only H-acceptors, and only undergo VdW interactions. The n-butylbenzene is slightly higher due to its higher size.

The  $\Delta S_{fus}$  of n-butylbenzene is significantly larger than that of benzene. This is because n-butylbenzene has less symmetry, and therefore gains much more energy in moving from a solid to a liquid than does benzene. This extra energy gain upon melting allows n-butylbenzene to melt at a significantly lower temperature than benzene.

### **Decane (10 carbons) vs. eicosane (20 carbons)**

Decane has a lower  $\Delta H_{fus}$  (kJ/mol) than eicosane. Since both only undergo VdW (London Dispersive Forces), this is simply a difference in size, with eicosane having much higher VdW forces due to its larger size. The  $\Delta S_{fus}$  of eicosane is higher due to its higher number of conformations that it can have in space (higher tau) compared to decane.

While eicosane benefits from greater entropic gains upon melting compared to decane, the significantly higher  $\Delta H_{fus}$  (kJ/mol) offsets these gains, resulting in a higher  $T_m$  for eicosane compared to decane.

