CHEM 331

Problem Set #1: Solutions

1. The solubility of several organic compounds are provided in the table below.
a) The solubility of the straight chain aliphatic hydrocarbons decrease dramatically with chain length. With the information provided, show that there is roughly an inverse linear relationship between the molar volume and aqueous solubility for these compounds. Does benzene follow this trend? Why/why not?
b) Complete the table for cyclohexane citing your source/s. How many milligrams of cyclohexane will dissolve in a liter of water? How does this compare to the solubility of benzene in mg/L of water?

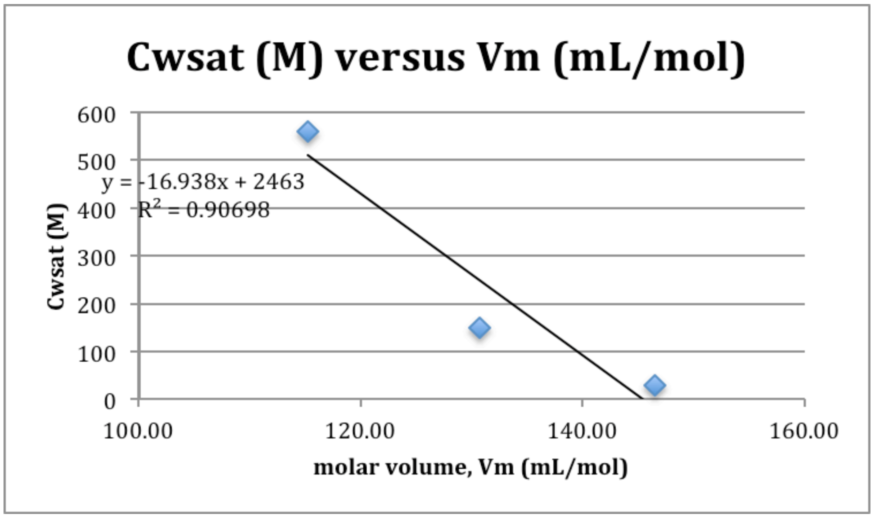
Substance	Molecular formula	C_w^{sat} (µM)	Density (g/mL) at 25°C
n-pentane	$\mathbf{C_5H_{12}}$	560	0.626
n-hexane	$\mathbf{C_6H_{14}}$	150	0.659
n-heptane	$\mathbf{C_7H_{16}}$	30	0.684
Benzene	$\mathbf{C_6H_6}$	22,000	0.874
cyclohexane	$\mathbf{C_6H_{12}}$		

Solution:
a) Using the molar mass and density of the liquids to estimate the molar volume we can summarize the the given below.

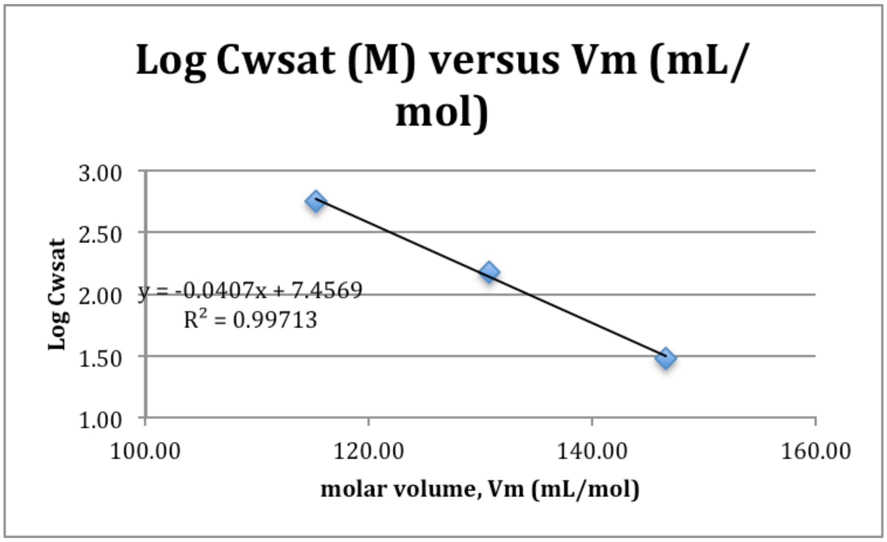
	MW (g/mol)	density (g/mL)	V_m (mL/mol)	C_w^{sat} (uM)	log C_w^{sat}
pentane	72.15	0.626	115.26	560	2.75
hexane	86.18	0.659	130.77	150	2.18
heptane	100.21	0.684	146.51	30	1.48
benzene	78.11	0.874	89.37	22,000	4.34
cyclohexane*	84.16	0.778	108.17	676	2.83

* from Appendix C (p. 1198)

We can try plotting C_w^{sat} vs V_m for the aliphatic compounds only and this yields an $R^2 = 0.91$ (see below).



Whereas a plot of Log C_w^{sat} vs V_m yields R^2=0.99 (see below).



Using the later,
Log C_w^{sat} = -0.0407 V_m + 7.45

Therefore,
Log C_w^{sat} (benzene) = -0.0407 (89.37) + 7.45 = 3.81 ➔ so, C_w^{sat} = 6500 uM (calc) ~ 70% too low

Benzene does NOT follow the size trend established by aliphatic straight chain hydrocarbons. It is not structurally similar and will participate in additional intermolecular interactions, due mainly to it's increased polarizability resulting from the electrons in the π bonds.

b) Appendix C gives –log C_w^{sat} = 3.17 for cyclohexane.
This corresponds to 676 uM or 57 mg/L of water.

Benzene has a –log C_w^{sat} = 1.65, which corresponds to 22,390 uM or 1,750 mg/L of water.

2. Look up and report the vapour pressures of 1- and 2-butanol at 25^{o}C, referencing your source/s. Explain why the vapour pressure of 2-butanol is greater than 1-butanol. Is your answer consistent with the reported boiling points for these compounds?

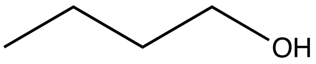
Solution:
Use Wikipedia to get CAS#'s and then a vetted reliable source for physical properties such as http://esc.syrres.com/fatepointer/search.asp
used by US Environmental Protection Agency.

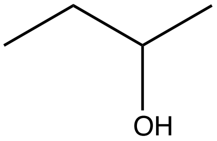
	1-butanol	**2-butanol**
CAS#	71-36-3	78-92-2
T_m (^{o}C)	-89.8	-114.7
T_b (^{o}C)	117.7	99.5
P^{o} (mm Hg) at 20^{o}C	**6.7**	**18.3**
n_D at 20 ^{o}C	1.399	1.398

The vapour pressure of 2-butanol is more than 2x more volatile than 1-butanol at 20 ^{o}C. Since both compounds are liquids at this temperature, a comparison of the vapour pressures is directly related to the sum total strength of the intermolecular forces present in the liquid state. Consequently, we can say the intermolecular forces are stronger in 1-butanol than in 2-butanol. So the next question is why?

Let's examine the nature of the intermolecular forces here. First, all molecules have London dispersion forces (LDF's), which increase with increased polarizability. Polarizability, in turn increases with molecular size or total surface area. Since both molecules are **$C_4H_{10}O$**, they are expected to have similar sizes. Furthermore, the refractive indices are very nearly identical and this too is a measure of polarizability. So, it is very unlikely that the vapour pressure difference is due to differences in the strength of the LDF's.

Also present in these substances are a specific type of dipole-dipole force known as 'hydrogen-bonding'. These arise from the especially large dipole moment within the O-H bond (giving rise to H donor ability) and the close approach to the lone pair electrons on the O of a neighboring molecule. These interaction is essentially electrostatic in character and consequently is dependent of on the magnitude of the dipole moment and inversely related to the distance between adjacent dipoles. Since, we have ruled out differences in LDF's, the vapour pressure difference must be due to weaker 'hydrogen-bonding' in 2-butanol. We can rationalize this by looking at the structure and recognizing that the O-H group in 2-butanol is more crowded and less accessible to neighboring molecules than the O-H group in 1-butanol.





This would be even more obvious if we were to render the structures as space filling models using ChemSketch.

The boiling point of 2-butanol is lower than that of 1-butanol, which is consistent with a lower value of ΔH_{vap} and weaker intermolecular forces.

3. a) Using your textbook as a guide, give an example of an environmentally relevant compound that is (i) apolar, (ii) monopolar and (iii) bipolar compounds. In the case of the monopolar compounds, indicate whether they are H-acceptors or H-donors.
b) Using the recent paper by Richardson (Anal. Chem., **2012**, *84*, 747-778), identify one emerging organic contaminant in each of the following categories; artificial sweetener, perfluroinated compound, brominated flame retardant, dis-infection by-product, sunscreen/uv filter, pesticide transformation product and naphthenic acids. In each case, draw the chemical structure and provide the CAS#.

a) See pg 62, Box 3.1

b) See attached paper.

4. Referring to Figure 3.6 in your text (Schwarzenbach, 2nd Ed), explain;
a) what is meant by K_{iah} and why is *ln* K_{iah} inversely related to the dispersive vdW parameter for all compounds.
b) what is meant by K_{iaw} and why *ln* K_{iaw} is positively correlated to the dispersive vdW parameter and only within a homologous series of structurally related compounds.

a) K_{ah} is a partition constant for compound i in equilibrium between a hexadecane solvent and the gas phase; $X_{(hexadecane)}$ ==== $X_{(air)}$

$$K_{ah} = \frac{C_{air}}{C_{hexadecane}}$$

In the gas phase there are effectively no intermolecular forces, whereas in the hexadecane, the solvent:solvent and the solute:solvent interactions are non-specific dispersive vdW forces for all compounds regardless of the functional groups present on the solute. All cmpds show an inverse relationship, that is the magnitude of ln K_{ah} decreases as the vdW dispersive parameter increases. In other words larger molecules will exhibit a smaller K_{ah}, irrespective of their polarity. This is largely because larger solute molecules will experience a greater attractive dispersive force between solute:solvent.

b) K_{aw} is a partition constant for compound I in equilibrium between a water solvent and the gas phase; $X_{(water)}$ ==== $X_{(air)}$

$$K_{aw} = \frac{C_{air}}{C_{water}}$$

In water the solute:solvent interactions include dispersive vdW as well as dipole and H-bonding for cmpds with appropriate functional groups. In this case, linear relationships exist only with structurally related series of cmpds where the intermolecular forces are similar in nature. Since molecules with a larger vdW dispersion parameter are larger, they are less water soluble due to the greater energy costs associated with cavity formation. Consequently, the magnitude of K_{aw} increases as the solutes become larger.

5. Table 3.6 in your text (Schwarzenbach, 2nd Ed), gives several simple linear free energy relationships (LFERs) for predicting and/or evaluating equilibrium partition constants. Explain in you own words the idea behind these LFERs. What are the advantages and limitations when using these type of LFERs?

Table 3.6 lists several simple one-parameter linear free energy relationships that relate one type of partition constant (K_{12}) as a linear function of another type of partition constant (K_{34}). For example,

$$\log K_{12} = a \log K_{34} + b$$

or

$$\log K_{ow} = m \log k' + c$$

In general, these types of LFERs work best for a series of structurally related compounds when considering two similar systems (e.g., two organic phase/water systems).

Advantages include a useful predictive tool when experimental results are difficult to obtain. They may also be useful in revealing special or unusual behaviour for specific compounds (e.g., intra-molecular interactions) by identifying ‘outliers’. Finally, when considering poorly defined phase systems (e.g., NOM/water, aerosol/air), the slope of the LFER can yield useful insight into these phases.

Disadvantages – these types of LFERs are limited to structurally related series of compounds which exhibit similar types of intermolecular interactions.

See further bottom of pg 89 – 91 (text).

6. The vapour pressure of 1,1,1,2-tetrafluoroethane (HFC-134a) is 132.9 kPa at -20°C and 292.9 kPa at 10°C. Estimate the normal boiling point of HFC-134a.

Solution:

Recall that

$$\ln P^{o} = \frac{-\Delta H_{vap}}{RT} + \text{Constant} \quad \ln P^{o} = \frac{-\Delta H_{vap}}{RT} + \text{Constant}$$

and therefore, at any two temperatures the vapour pressure ratio can be written as;

$$\ln\left(\frac{P^{o}_{2}}{P^{o}_{1}}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where P^{o}_{1} = 132.9 kPa at T_1 = 253.2 K and P^{o}_{2} = 292.9 kPa at T_2 = 283.2 K

Therefore, we can write;

$$\Delta H_{vap} = \frac{-\ln\left(\frac{P^{o}_{2}}{P^{o}_{1}}\right) R}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{-(0.7902)(8.314 \text{ J mol}^{-1}\text{K}^{-1})}{(-4.1837\text{x}10^{-4}\text{ K}^{-1})} = 15{,}700 \text{ J/mol}$$

The normal boiling point is the temperature at which P^{o} = 1.00 atm (or 101,300 kPa).

So, we can write;

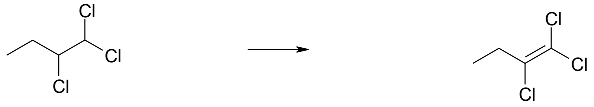
$$\ln\left(\frac{101.3 \text{ kPa}}{132.9 \text{ kPa}}\right) = \frac{-15{,}700 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{T_b} - \frac{1}{253.2 \text{ K}}\right)\left(\frac{1}{T_b} - \frac{1}{253.2 \text{ K}}\right) = 1.4375\text{x}10^{-4}\text{ K}^{-1}$$

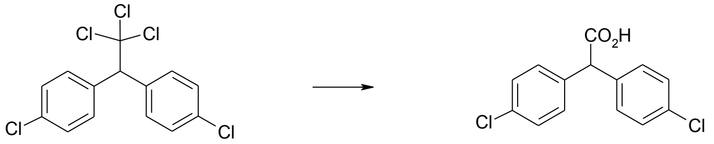
and therefore,

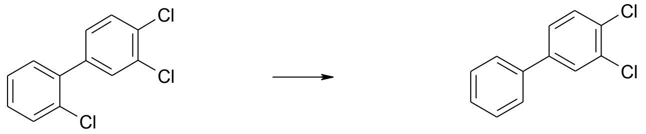
$$\left(\frac{1}{T_b} - \frac{1}{253.2 \text{ K}}\right) = 1.4375\text{x}10^{-4}\text{ K}^{-1}$$

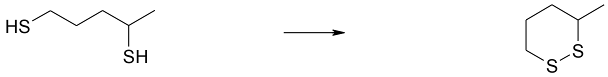
and T_b = 244.3 K or -28.9 °C

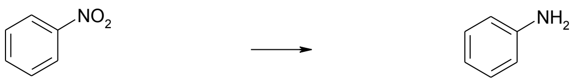
7. Identify the oxidation state changes in the following reactions and indicate the number of moles of electrons transferred in the reaction. If the reaction <u>does not</u> involve an overall change in oxidation state, classify the reaction as one of the following *addition*, *elimination*, *condensation* or *hydrolysis*.

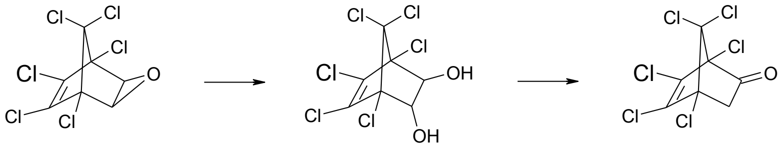


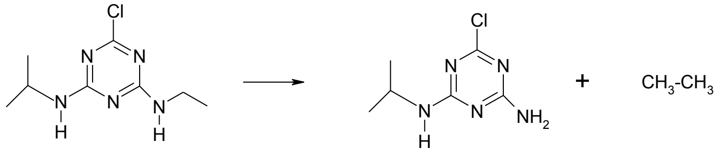


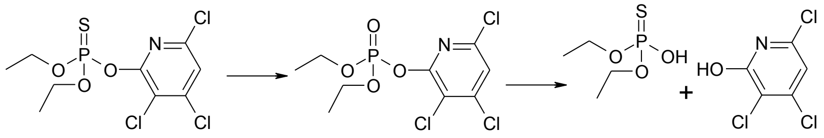












1	oxidation	-2 mols e-
2	hydrolysis	+2 H_2O
3	reduction	+2 mols e-
4	oxidation	-2 mols e-
5	reduction	+6 mols e-
6	hydrolysis/condensation	+H_2O/-H_2O
7	reduction	+2 mols e-
8	hydrolysis/hydrolysis	+H_2O, -H_2S/ +H_2O

8. Pure 1,4-dichlorobenzene (DCB) is still used as a disinfectant and 'air-refresher' in some public urinals. You want to calculate the concentration of DCB in g per m^3 of air at 25 ^oC.

a) Estimate using only melting point (T_m = 53.0 ^oC) and boiling point (T_b = 173.9 ^oC) data.

b) Refine your answer using the vapour pressure data given below.

T (^{o}C)	29.1 s	44.4 s	54.8	84.8	108.4	150.2
P^o (mm Hg)	1	4	10	40	100	400

Solution:

a) Since T_m = 326.2 K and T_b = 447.1 K, DCB is a SOLID at 298 K (or 25 ^oC). We will need the vapour pressure of the solid, $P^o(s)$ at 298 K to solve this problem.

We can use the boiling point to estimate $P^o(L)$ from;

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

and then the melting point to estimate $P^o(s)$ from;

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

Therefore $\ln P^o(L) = -9.506 + 3.448 = -6.058$
and
$P^o(L) = e^{-6.058} = 2.338 \times 10^{-3}$ atm

and

$\ln \{P^o(s)/P^o(L)\} = 6.8\ \{(326.2/298.2)-1\} = -0.6435$

So, $P^o(s) = P^o(L) \times e^{-0.6435} = 1.228 \times 10^{-3}$ atm

The concentration in the gas phase in mol/L is given by;

$$\left(\frac{P^o(s)}{RT}\right) = \frac{1.228\text{x}10^{-3}\ \text{atm}}{(0.08206\ \text{L atm mol}^{-1}\text{K}^{-1})(298\ \text{K})} = 5.024 \times 10^{-5}\text{mol/L}$$

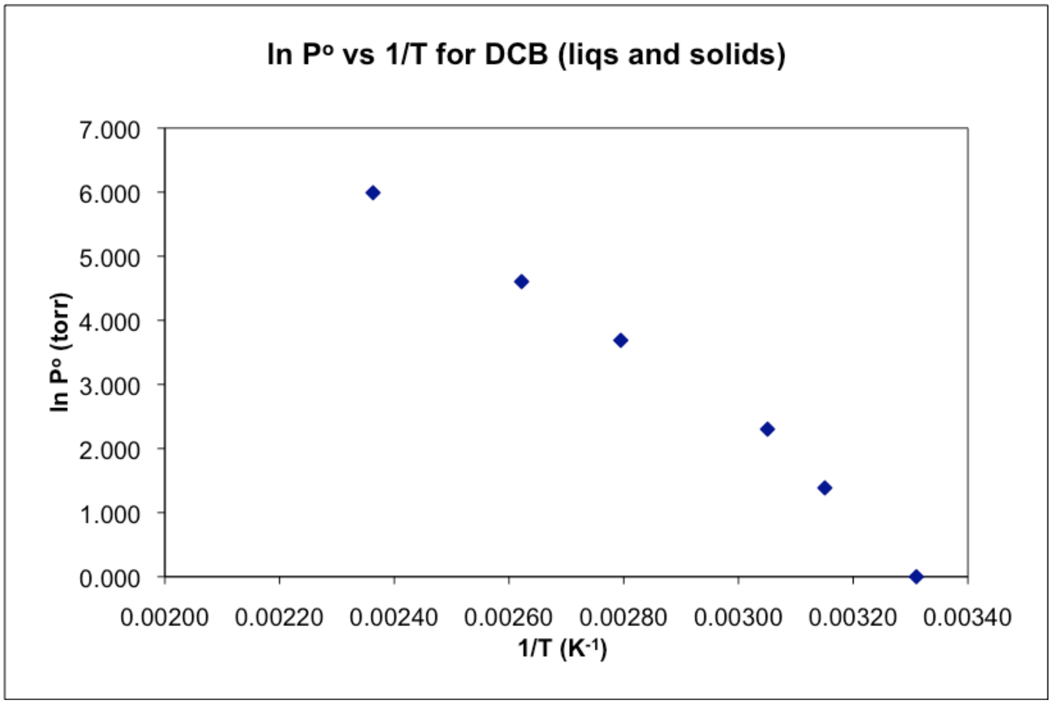
Converting this to g/m^3 yields;

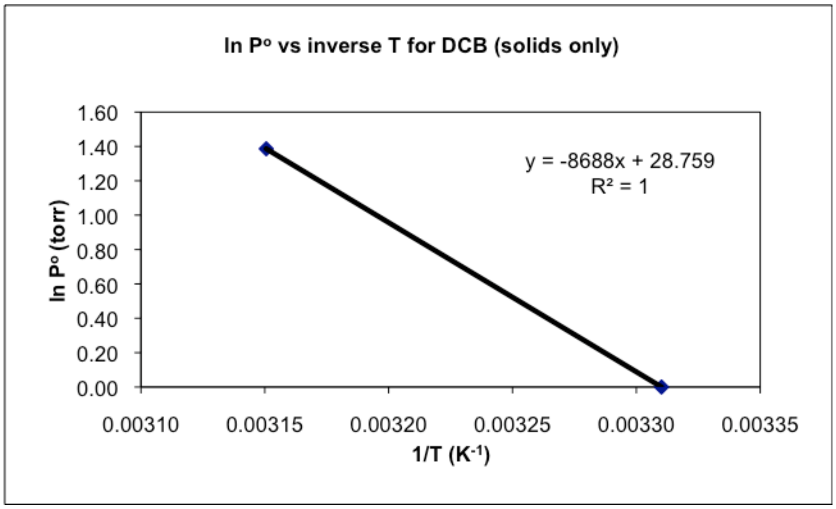
5.024×10^{-5} mol/L x 146.9 g/mol x 10^3 L/m^3 = 7.38 g/m^3

b) Using the data provided, plot *ln* P^o versus inverse Temperature. The slope is equal to $-\Delta H_{vap}/R$ over temperatures where the DCB is a liquid and $-\Delta H_{sub}/R$ over temperatures for which it is a solid.

Data and Plots for Question 8

T(°C)	1/T (K^{-1})	P^o (torr)	ln P^o
29.1	0.00331	1	0.000
44.4	0.00315	4	1.386
54.8	0.00305	10	2.303
84.8	0.00279	40	3.689
108.4	0.00262	100	4.605
150.2	0.00236	400	5.991





Slope = $-\Delta H_{sub}/R = -8688\ K^{-1}$
(or $\Delta H_{sub} = 72232$ J/mol)

Since,

$$\ln\left(\frac{P^o_2}{P^o_1}\right) = \frac{-\Delta H_{sub}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

we can write;

$$\ln\left(\frac{P^o_2}{1\ \text{torr}}\right) = -8688K^{-1}\left(\frac{1}{298.2} - \frac{1}{302.3}\right)$$

and therefore;

$P^o{}_2 = (e^{-0.4147})$ (1 torr) = 0.661 torr

Converting this to g/m^3 yields;

0.661 torr x 1 atm/760 torr x {1/(0.08206 L atm mol^{-1} K^{-1})(298.2 K)} x 146.9 g/mol x 10^3 L/m^3 = 5.22 g/m^3