CHEM 331

Problem Set #1: Inter-molecular Forces and Vapour Pressure

Submit answers to <u>even numbered questions only</u>. Due Wednesday, Jan. 29th

1. The vapour pressure of methylcyclohexane and toluene are 4.9 and 2.9 kPa, respectively.
a) Account for this difference in terms of the relative strength of the inter-molecular forces present in the liquid state.
b) Fill in the missing information below and account for the large difference in water solubility.

Substance	C_w^{sat} (mM)	Density at 25°C (g/mL)	Refractive Index n_D	Molar Volume (mL/mol)
methylcyclohexane		0.77	1.42	
toluene		0.87	1.50	

2. Use the information below to answer each of the following.
a) Identify each compound as either apolar, monopolar or bipolar and indicate the type of intermolecular forces present.
b) What does the similarity in the BP of *n*-pentane and diethyl ether imply about the strength of the inter-molecular forces present?
c) Why is the ΔH_{vap} of 1-propanol greater than that for ethanol?
d) Based on the data presented here predict the BP and ΔH_{vap} for 1-butanol. Explain.
e) Rank these compounds from lowest to highest vapour pressure? Explain.

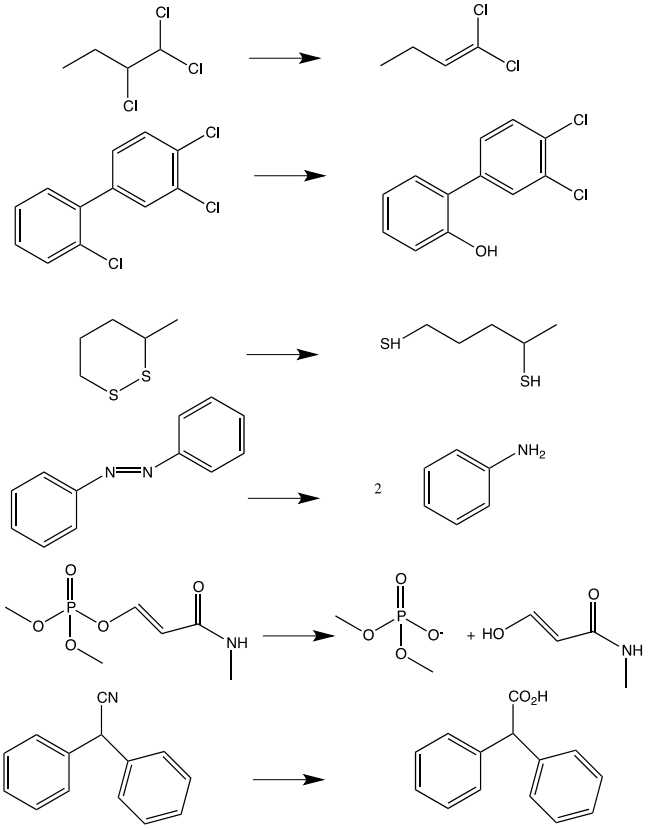
Substance	Molecular formula	BP (°C)	ΔH_{vap} (kJ/mol)
n-pentane	**$CH_3CH_2CH_2CH_2CH_3$**	36	25.8
diethylether	**$CH_3CH_2OCH_2\ CH_3$**	36	26.0
methanol	**CH_3OH**	65	35.3
ethanol	**CH_3CH_2OH**	78	38.7
1-propanol	**$CH_3CH_2CH_2OH$**	97	41.8
1-butanol	**$CH_3CH_2CH_2CH_2OH$**		

3. How is an equilibrium partition constant defined? To which thermodynamic function(s) is the partition constant related, and which molecular factors determine its magnitude, in the case of;
a) Partitioning between the gas phase and a pure liquid?
b) Partitioning between two bulk liquid phases?

4. For each of the following, provide a written explanation;
a) The apolar compound *n*-hexane is considered to be quite *hydrophobic* ('water-hating'). Does this mean that there are repulsive forces between hexane and water molecules?
b) One of your other chemistry professors claims that the activity co-efficient of *n*-hexane in water is close to 1. However, Table 3.2 (Schwarzenbach), indicates a value is 460,000. Could both of these reputable sources be correct?
c) What are the advantages and disadvantages of choosing the pure liquid compound as the reference state?

5. 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 <u>all</u> compounds.
b) What is meant by K_{iaw} and why *ln* K_{iaw} is positively correlated to the dispersive vdW parameter and <u>only</u> within a homologous series of structurally related compounds.

6. 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*.



7. 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.

8. A commercial analysis lab reports the concentration of benzene in a water sample as 100. ug/L. In reviewing the data and lab procedures, you discover that the 100. mL samples were stored in 1L containers at 5 ^{o}C for several days prior to analysis. How much of the benzene originally present in a water sample has partitioned into the headspace of the sampling flask? Assume the benzene has equilibrated between the water and the headspace neglecting adsorption to the walls of the flask itself. The data required to answer this question can be found in Table 3.4 (Schwarzenbach).