CHEM 331
Problem Set #1: Inter-molecular Forces and Vapour Pressure
Submit answers to <u>even numbered questions only</u>. Due Wednesday, Jan. 27th

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	**0.14**	0.77	1.42	**127**
toluene	**5.6**	0.87	1.50	**106**

Solution

a) Vapour Pressures:
Both compounds are apolar and consequently only capable of exhibiting non-specific dispersive intermolecular forces. The higher vapour pressure of methylcyclohexane is a direct result of weaker intermolecular forces in the pure liquid state than those present between toluene molecules in its liquid state. In general, the strength of London (vdW) dispersion forces increases with the size of the molecules involved. However, methylcyclohexane has a larger molar volume ($V_m = MW/\rho$) than toluene suggesting that it should have the <u>lower vapour pressure</u>. Clearly, there is more going on here. All else being equal, size is often used to estimate the *polarizability* of a molecule (*i.e.*, the degree to which a temporary dipole can be induced). However, refractive index is a more direct measure of polarizability and you can see that toluene is, in fact, more polarizable than methylcyclohexane. This is a result of the electrons in the p molecular orbitals that are further away on average from the nuclei and therefore more readily induced to exhibit small temporary distortions responsible for the London (vdW) dispersion forces. Thus, the <u>difference in polarizability of these molecules</u> accounts for the ~2 fold difference in vapour pressure.

b) Water Solubility:
There are only two factors to consider in the water solubility of these apolar compounds, polarizability and size. All else being equal, the more polarizable apolar solute will be more water soluble due to the stronger solute:solvent interactions. As can be seen by the refractive index values, toluene is more polarizable than methylcyclohexane. Molecular size also plays a role in water solubility due the required disruption of the strong water:water H-bonds to form a cavity for the solute. The molar volumes calculated above ($V_m = MW/\rho$) indicate that toluene is smaller than methylcyclohexane and this too favours the dissolution of toluene in water as compared to methylcyclohexane. Thus, the differences in <u>polarizability and molar volume</u> account for the ~40 fold difference in water solubility of these two compounds.

**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	**$CH_3CH_2CH_2CH_2OH$**	**114.7**	**45.1**

Solution

Substance		London dispersion (vdW)	Dipole-Dipole	H-bonding
n-pentane	**apolar**	✔		
diethylether	**monopolar**	✔	✔	
methanol	**bipolar**	✔	✔	✔
ethanol	**bipolar**	✔	✔	✔
1-propanol	**bipolar**	✔	✔	✔
1-butanol	**bipolar**	✔	✔	✔

b) Both *n*-pentane and diethyl ether are similar in size and shape. The close similarity of the ΔH_{vap} and BP values, indicate that the magnitude of the intermolecular forces involved are almost identical. $X_{(l)}$ ==== $X_{(g)}$
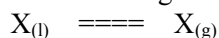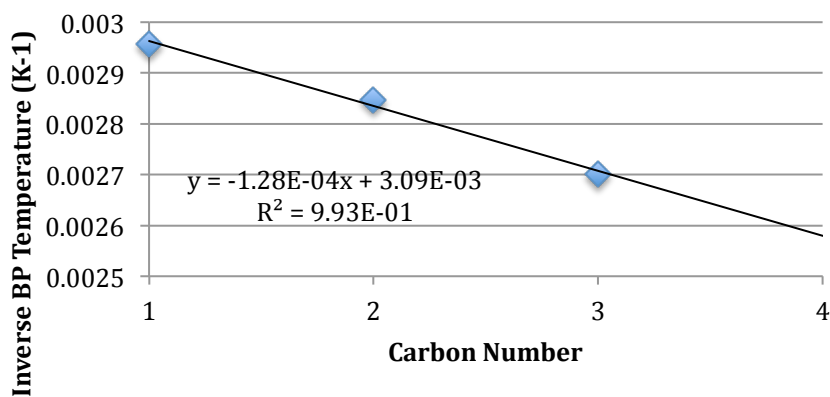
n-pentane is an apolar compound with only vdW dispersion (LDFs). Diethyl ether is slightly polar and has a small dipole – dipole force in addition to the vdW dispersion forces. However, the near identical BPs and ΔH_{vap} values indicate the dispersion forces present in diethyl ether are dominant and significantly larger than the weak dipole – dipole forces, present in this case.

c) Both ethanol and 1-propanol have similar types of intermolecular forces including dispersive vdW and H-bonding. The observed difference in ΔH_{vap} (the enthalpy change in going from a liquid to a gas) must be due the larger size and hence greater polarizability of the larger alcohol.
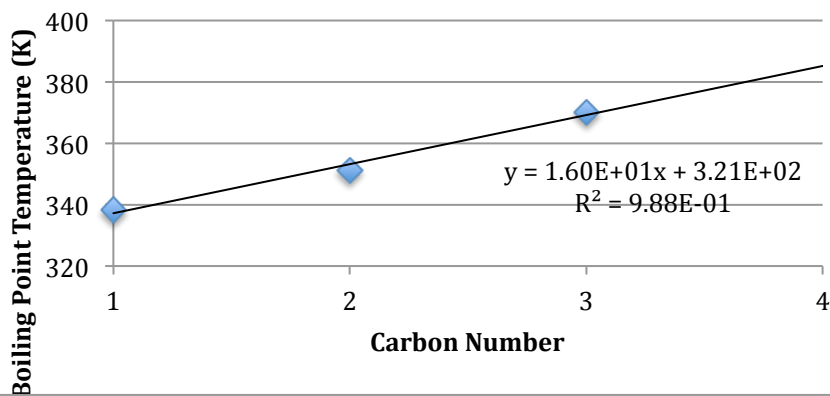
d) The primary alcohols form a homologous series of structurally related compounds differing only by a –CH_2- group in the aliphatic chain. Since they all experience the same type of intermolecular forces, it is therefore reasonable to expect that we could use the properties of methanol, ethanol and 1-propanol to predict those of 1-butanol. See attached plots that predict the values in bold above. These compare well to the literature values of 117 °C and 47.4 kJ/mol.

e) Vapour pressure is inversely related to the strength of the intermolecular forces present in the liquid state. These are reported in the magnitude of the ΔH_{vap} values. Therefore, the vapour pressures from lowest to highest are: 1-butanol < 1-propanol < ethanol < methanol < *n*-pentane ~ diethyl ether
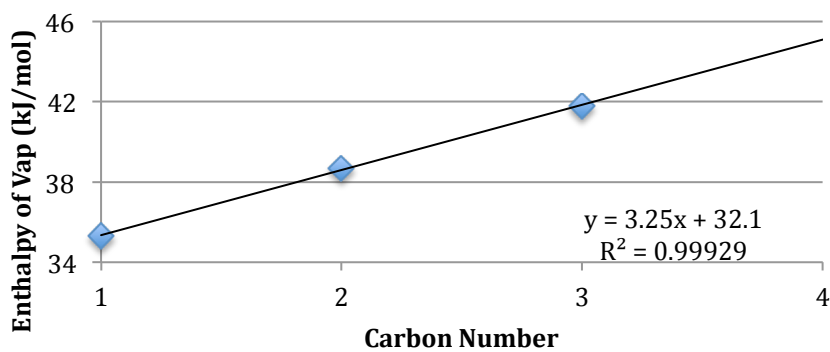
Inverse Boiling Point for 1º Alcohols

Inverse BP Temperature (K-1) vs. Carbon Number

$y = -1.28E-04x + 3.09E-03$
$R^2 = 9.93E-01$

Boiling Point Temperature for 1º Alcohols

Boiling Point Temperature (K) vs. Carbon Number

$y = 1.60E+01x + 3.21E+02$
$R^2 = 9.88E-01$

Enthalpy of Vapourization for 1º Alcohols

Enthalpy of Vap (kJ/mol) vs. Carbon Number

$y = 3.25x + 32.1$
$R^2 = 0.99929$

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?

Solution

An equilibrium partition constant is defined as the relative ratio of the activities of a specific compound in at equilibrium between any two phases. As with any equilibrium constant, it is related to the free energy change (ΔG° = -RT ln K).

a) The molecular factors that determine the magnitude of partitioning between gas phase and the pure liquid are those that affect the strength of the intermolecular forces present in the liquid phase, such as polarizability, polarity and ability to hydrogen bond. For a molecule '*i*' partitioning between liquid and the gas phase, we can write the process as;

$$i_{(l)} \ ==== \ i_{(g)}$$
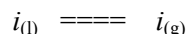
an hence the equilibrium constant is written as;

$$K_{ial} = \frac{\{i_{(g)}\}}{\{i_{(l)}\}}$$

Since the activity of '*i*' in the pure liquid (reference state) is unity, this becomes;

$$K_{ial} = \frac{\{i_{(g)}\}}{1} = P^*_{il}/RT$$

where P^*_{il} is the vapour pressure of the substance *i*.

b) The molecular factors that determine the magnitude of partitioning between two bulk liquid phases relate to those that affect the relative activity in each phase. So if the bulk liquid phases are denoted 1 and 2, respectively, the equilibrium partition constant will be influenced by the magnitude of the *i*:1 and *i*:2 interactions.

$$i_1 \ ==== \ i_2$$
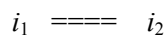
$$K_{i12} = \frac{\{i_2\}}{\{i_1\}}$$

Such is the case in octanol-water partitioning, where the solute *i* is distributed between the two solvents depending largely on it's relative solubility.

$$K_{iow} \cong \frac{C_o^{sat}}{C_w^{sat}}$$

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?

Solution

a) No. Overall, the change in free energy (ΔG_{soln}) for dissolution of hexane in water is positive (unfavourable) and the equilibrium lies heavily on the side of hexane in the pure liquid phase rather than in the aqueous solution. This is the result of the overall process in going from pure hexane (solute) and pure water (solvent) to a solution of solvated hexane molecules. However, on the molecular level, there are no repulsive forces between hexane and water. In fact, there is an attractive dispersive energy (vdW) term (*albeit* a relatively weak one) between water molecules and neighboring hexane molecules (we refer to this as a dipole – induced dipole force).

b) Yes. This all depends on the reference state one chooses. While one must choose some reference point (*i.e.*, state) in chemical thermodynamics, it is an arbitrary choice. In physical organic chemistry, particularly when we are dealing with phase transfer processes, it customary to choose the pure liquid as the reference (ideal) state. In other contexts, it might be convenient to choose an infinitely dilution solution as the reference state (solutes reacting in solution) or the elements in their naturally occurring form as the reference state (reactions describing the formation of compounds). If we choose the infinitely dilute solution as our reference state, an aqueous solution of hexane in water (which is after all, quite dilute), is very close to our reference state. Therefore, the *activity coefficient* (which is the scalar between the actual *activity* of a compound and the *activity* it would have in its reference state) for hexane in water would be expected to be close to unity.

c) It is convenient to choose the pure liquid as the reference state in physical organic chemistry for phase transfer processes as it allows us to express the differences in behavior in terms of the intrinsic properties of different organic molecules. One disadvantage of this choice, is that it may be different from that used in other contexts. For example, the *activity* of inorganic solutes (salts/ions) in aqueous solution are often referenced against how *active* they would be as if they were not influenced by other salts/ions in solution (*i.e.*, as if they were in an infinitely dilution solution). These different choices of reference states can lead to differing interpretations and confusion.

See further pg 77-78 in Schwarzenbach text.

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 all 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.

Solution

a) K$_{ah}$ is a partition constant for compound '*i*' in equilibrium between a hexadecane solvent and the gas phase; $i_{(hexadecane)}$ ==== $i_{(air)}$

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

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; $i_{(water)}$ ==== $i_{(air)}$

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

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 with the vdW dispersive parameter as the solutes become larger.

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*.
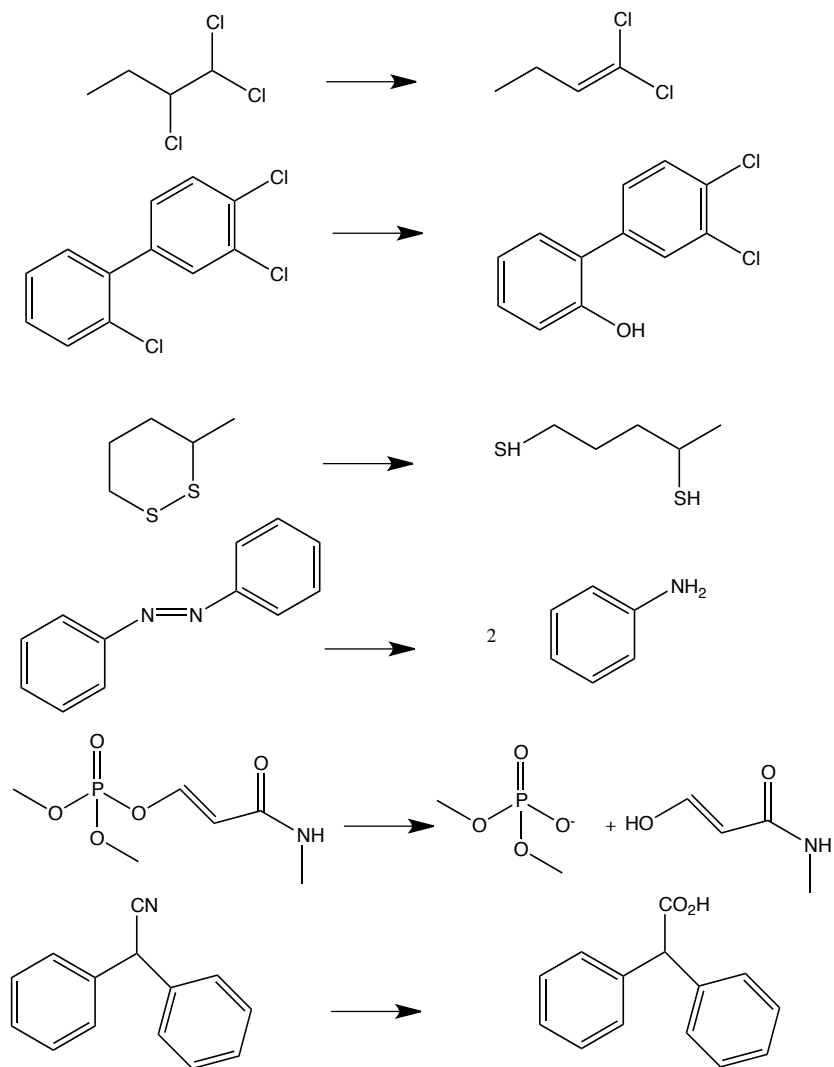
1	elimination	-1 HCl
2	hydrolysis	+1 H$_2$O, - 1 HCl
3	reduction	+2 mols e-, + 2 mols H$^+$
4	reduction	+4 mols e-, + 4 mols H$^+$
5	hydrolysis	+1 H$_2$O, - H$^+$
6	hydrolysis	+ 2 H$_2$O, - 1 NH$_3$

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.

Solution

Recall that

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

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

$$\ln\left(\frac{P_2^o}{P_1^o}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where P_1^o = 132.9 kPa at T_1 = 253.2 K and P_2^o = 292.9 kPa at T_2 = 283.2 K

Therefore, we can write;

$$\Delta H_{vap} = \frac{-\ln\left(\frac{P_2^o}{P_1^o}\right)R}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} = \frac{-(0.7902)(8.314 \text{ J mol}^{-1}\text{K}^{-1})}{(-4.1837\text{x}10^{-4}\text{ K}^{-1})} = 15,700 \text{ J/mol}$$

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**

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 °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).

Solution

There are two parts to solving this problem. They are 1) the determination of the air-water partition constant (K_{aw}) at 5 °C (278 K) and 2) the determination of the amount of benzene present in the bottle headspace and therefore not accounted for in the analysis of water sample after storage.

1) Table 3.4 lists the value of K_{aw} for benzene to be 0.21 (unitless) at 25 °C (298 K). The temperature dependence of any equilibrium constant can be described by;

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where K_1 and K_2 are equilibrium constants at absolute temperatures T_1 nad T_2, respectively.

Since Table 3.4 also lists the enthalpy change (ΔH) associated with benzene partitioning between air and water as 29.7 kJ/mol, we can calculate K_{aw} at 278 K, as follows;

$$\ln K_2 = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln K_1$$

$$\ln K_2 = \frac{-29700\left(\frac{J}{mol}\right)}{8.314\left(\frac{J}{mol\ K}\right)}\left(\frac{1}{278\ K} - \frac{1}{298\ K}\right) + \ln(0.21)$$

Hence, the value of K_{aw} for benzene at 278K is **0.0887** (unitless).

2) Now on to the determination of amount of benzene that was not accounted for in the analysis.

Since all of the benzene in the original 100. mL water sample is conserved within the 1L storage bottle (distributed between being dissolved in the water and in the gaseous headspace above the water), we can use a mass balance approach. In other words, the total mass on benzene in the original 100. mL sample is equal to the equilibrated mass of benzene in the water plus that in the headspace.

Since, $K_{aw} = C_g/C_w$ for the equilibrated sample and we know $K_{aw} = 0.0887$ and $C_w = 100.$ µg/L, we can write;

$C_g = K_{aw} \times C_w = 8.87$ µg/L

Since this is in 0.900L of headspace, the total mass of benzene in the gas phase is given by;

8.87 µg/L x 0.900L = **8.00 µg**

Since all of this benzene was in the original 100. mL sample, we have 10.0 µg + 8.0 µg = 18.0 µg in a 0.100L sample (where the mass of benzene in the equilibrated sample is 100 µg/L x 0.100L = 10.0 µg).

Therefore, the **original concentration was 180 µg/L**.

Alternate solution:

Mass total = mass in water + mass in headspace = $C_w V_w + C_g V_g$

Where C_w and C_g are the mass per volume concentrations in water and gas phase, respectively and V_w and V_g are 100. mL and 900. mL from the information in the question.

We can now write an expression for the fraction of benzene in the gas phase as;

$f_g = C_g V_g/(C_g V_g + C_w V_w)$

and since $K_{aw} = C_g/C_w$, we can write $C_g = K_{aw} C_w$

Substituting this into the expression for f_g yields;

$f_g = K_{aw} V_g/(K_{aw} V_g + V_w)$

Using the value of $K_{aw} = 0.0887$ at 278K, and V_w and V_g provided, we get

$f_g = 0.438$ (i.e., nearly 44% of the benzene in the equilibrated bottle in the headspace)

Since the equilibrated water sample was measured to contain 100. µg/L of benzene after storage and loss of analyte to the headspace, the original sample must have contained more benzene.

In fact, the mass of benzene in 900. mL of headspace came from the original sample. Let's use the conservation of mass to sort this out.

f_g = mass of benzene in gas/(mass of benzene in gas + mass of benzene in water)

Since $f_g = 0.438$ and mass of benzene in water = 100. µg/L x 0.100 L = 10.0 µg.

We can therefore write, that the mass of benzene in headspace that was originally present in the sample = f_g (10 µg)/(1-f_g) = **7.8 µg**

Hence, the original water sample contained 10.0 µg + 7.8 µg = 17.8 µg of benzene.

Since this 17.8 µg was present in a 100. mL sample, the original concentration was

178 µg/L of benzene.

(rounding error accounts for small discrepancy with above)