The Air-Water Partition Constant: Using Headspace GC to Determine an Important Physicochemical Parameter

Background:

The transfer of organic contaminants between water and the atmosphere is one of the key processes affecting the transport and distribution of many organic compounds in the environment (*1*). For neutral compounds, at dilute solution concentrations in pure water, the air-water distribution ratio is often referred to as the Henry's Law constant (K_H).

$$X_{(aq)} \quad ==== \quad X_{(g)}$$

K_H is defined as the ratio of a compound's abundance in the gas phase to that in the aqueous phase at equilibrium under conditions of infinite dilution.

$$K_H \cong \frac{C_{air}}{C_{water}} = \frac{P_i}{C_w}$$

where C_{air} and C_{water} are the concentrations in air and water, respectively. Since the partial pressure of a gas can be used to express it's concentration, K_H is often determined as P_i of the chemical in the gas phase and C_w is its molar concentration in water. Henry's law constant can also be estimated from the vapour pressure of the pure liquid (P^o) and the water solubility (C_w^{sat}).

$$K_H \cong \frac{P^o}{C_w^{sat}}$$

There are several unit systems employed in reporting Henry's law constants depending on how the gas phase concentrations are expressed (i.e., atm, Pa, torr etc). If the gas phase concentration is converted to the same units as the aqueous phase concentration, we define the unitless Henry's Law sometimes denoted as K_H' or K_{aw}.

$$K_H' \equiv K_{aw} = \frac{K_H}{RT}$$

A compound with a relatively large value of K_H (K_{aw}) will have a tendency to partition from the aqueous phase and enter the atmosphere. Even molecules with very low vapour pressures such as the pesticide DDT ($P^o \approx 1.3 \times 10^{-5}$ Pa at 25°C) can partition into the atmosphere from water due to their extremely low water solubility ($C_w^{sat} \approx 1.4 \times 10^{-8}$ M at 25°C). Since DDT is relatively unreactive, it can be atmospherically transported large distances accounting for it's detection far from the sites where it was applied ($K_{aw} \approx 4 \times 10^{-4}$ at 25°C).

Table 1: Selected properties and K_{aw} values for some organic compounds (*1*).

	P^o (Pa)	C_w^{sat} (mM)	K_{aw} (calc from P^o/C_w^{sat})	K_{aw} (expt)
cyclohexane	12,600	0.676	0.129	n/a
benzene	12,600	22.4	0.224	0.224
γ-hexachlorocyclohexane	7.08×10^{-3}	2.51×10^{-2}	1.15×10^{-4}	n/a
hexachlorobenzene	2.51×10^{-3}	2.82×10^{-5}	0.0363	0.0288

Traditionally, air-water partition constants are determined using static methods whereby an organic solute is left to equilibrate between an aqueous phase and the atmosphere in the headspace of a closed container (*2-4*). Other dynamic methods using open, flow through systems have also been employed (*5*). Both of these techniques require that the concentration of the compound be quantified by conventional analytical techniques. A convenient variation on the static method has been proposed by Lincoff (*6*). It does not require the determination of absolute chemical concentrations and is therefore less time consuming. This approach will be employed in this lab and is based on a mass balance of the organic compound between two phases in a closed system, Figure 1 (*7*). The total amount of organic compound in the bottle must be equal to the sum of the amounts in each phase. Hence, we can write

$$\text{total \#mol added} = C_wV_w + C_gV_g$$

where C_w and C_g are the molar concentrations in the aqueous and gas phases and V_w and V_g are the volumes of each phase. If the same mass of compound is introduced into two closed containers containing different volumes of pure water, a mass balance expression can be written for each system. Equating these two expressions and introducing Henry's law to substitute for the aqueous phase concentrations yields an equation relating K_{aw} to the headspace concentrations and known volumes.

$$K_{aw} = \frac{(C_{g1}/C_{g2})V_{w1} - V_{w2}}{V_{g2} - (C_{g1}/C_{g2})V_{g1}}$$

where C_{g1} and C_{g2} are the concentrations in the headspace of bottle one and two, respectively and V_{w1} and V_{w2} are the volumes of the aqueous phases in the two bottles. Thus, the only experimental information needed to determine K_{aw} is the ratio of the gas-phase concentrations (C_{g1}/C_{g2}) and the volumes. In this treatment, absolute concentrations are not necessary and any proportional measure of concentration (such as GC peak areas) will suffice (*7*).
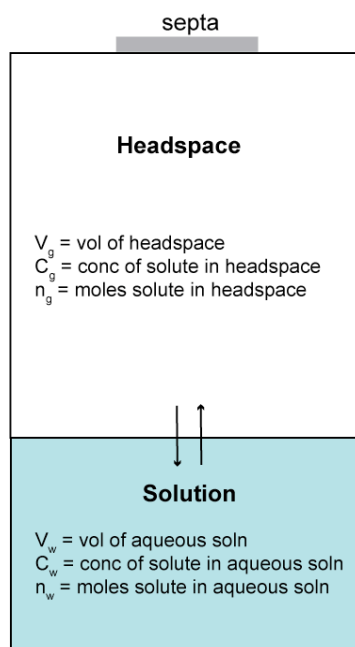

Figure 1: Sample bottle with aqueous solution and headspace.

<u>EXPERIMENTAL</u>

Objectives:
- Obtain Henry's law constants K_{aw} (K_H) values for a series of volatile and semi-volatile organic compounds from the peak areas using headspace GC-FID.

- Measure the temperature dependence of K_{aw} (K_H) for *trans*-1,2-dichloroethene.

- Discuss structural features that relate to trends in observed Henry's law constants.

Procedures:

Solution Preparations

Saturated aqueous stock solutions have been prepared by adding excess organic compound to 250. mL of deionized water and stirring at 25 ^{o}C for 10 days. Each of each of the following compounds will be supplied as saturated aqueous solutions in water; *trans*-1,2-dichloroethene, *n*-hexane, *n*-heptane, methylcyclohexane, *n*-octane, tetrachloromethane, trichloromethane, 1,1,1-trichloroethane and 1,3,5-trimethylbenzene.

Each group will be responsible for carrying out the K_H determination on three compounds. Two of these will be done only at room temperature. Each compound will require four equilibrated solutions prepared at least 24 hours in advance of the headspace analysis. A third compound will be carried out at three temperatures. This will require a total of six equilibrated solutions prepared at least 24 hours in advance of the headspace analysis.

Compound #1: Obtain four clean dry 250 mL amber glass bottles with Teflon backed sealed septa caps. Choose one relatively insoluble compound from the list (C_w^{sat} < 5 mM) and prepare four aqueous solutions as follows. Pipet 20 mL of deionized water into a 250 mL bottle followed by 20 mL of the saturated aqueous stock solution. (Be careful NOT to pipet from the bottom of the saturated aqueous stock solution bottles). Prepare a second bottle, this time pipetting 200 mL of deionized water into a 250 mL bottle followed by 20 mL of the same aqueous stock solution. This set of samples form a pair and can be used to generate a value for C_{g1}/C_{g2} from the relative peak areas. Prepare a duplicate set of samples in the same manner as above for a total of four samples. Cap all solutions immediately, shake well and label each bottle. Stir the sealed containers at constant temperature for at least 24 hrs before analyzing the headspace. ALL TRANSFER VOLUMES SHOULD BE ACCURATELY AND PRECISELY MEASURED AS WELL AS THE TOTAL INTERNAL VOLUME OF THE BOTTLES.

Compound #2: Obtain four clean dry 250 mL amber glass bottles with Teflon backed sealed septa caps. Choose one relatively soluble compound from the list (C_w^{sat} > 5 mM) and prepare four aqueous solutions as follows. Pipet 20 mL of deionized water into a 250 mL bottle followed by 2 mL of the saturated aqueous stock solution. (Be careful NOT to pipet from the bottom of the saturated aqueous stock solution bottles). Prepare a second bottle, this time pipetting 200 mL of deionized water into a 250 mL bottle followed by 2 mL of the same aqueous stock solution. This set of samples form a pair and can be used to generate a value for C_{g1}/C_{g2} from the relative peak areas. Prepare a duplicate set of samples in the same manner as above for a total of four samples. Cap all solutions immediately, shake well and label each bottle. Stir the sealed containers at constant temperature for at least 24 hrs before analyzing the

headspace. ALL TRANSFER VOLUMES SHOULD BE ACCURATELY AND PRECISELY MEASURED AS WELL AS THE TOTAL INTERNAL VOLUME OF THE BOTTLES.

Compound #3: *trans*-1,2-dichloroethene
Obtain six clean dry 250 mL amber glass bottles with Teflon backed sealed septa caps. Pipet 20 mL of deionized water to three of these and 200 mL of deionized water to the remaining three. Pipet 1 mL of a saturated aqueous solution of *trans*-1,2-dichloroethene. Cap all solutions immediately and label each bottle. You will now have three pairs of solutions. Each pair will be equilibrated at a different temperature between 20 and 45 ^{o}C. Stir the sealed containers at constant temperature for at least 24 hrs before analyzing the headspace.

Gas Chromatography
Flush a gas-tight GC syringe ~ five times with the headspace being careful not to draw up any aqueous solution (see Figure 2). Inject 100. µL of the headspace of each sample into the GC injection port (Figure 3) and record the gas chromatogram of the headspace for all temperature equilibrated sample bottles. It is important that all injections volumes for a given compound are identical. Run multiple injections of the headspace of each sample through the GC in order to estimate the sample-to-sample variance in injection volume (compounds elute in 1-5 mins and multiple injections can be made on the same chromatogram). Record the peak areas and use them to calculate the K_{aw} according to the expression given in the background section.

Record GC conditions and injection volumes.

Table 2: Selected properties of organic compounds in order of decreasing water solubility (*1*)

Compound	CAS#	MW (g mol^{-1})	ρ (g mL^{-1})	C_w^{sat} (mM)	P^o (Pa)	K_H (Pa m^3 mol^{-1})	K_{aw}
trichloromethane	67-66-3	119.4	1.48	71.2	25100		
E-1,2-dichloroethene	156-60-5	96.95	1.27	64.6	40700		
1,1,1-trichloroethane	71-55-6	133.4	1.34	9.75	16600		
tetrachloromethane	56-23-5	153.8	1.59	5.38	14500		
bromobenzene	108-86-1	157.0	1.50	2.83	557		
1,3,5-trimethylbenzene	108-67-8	120.2	0.88	0.416	331		
methylcyclohexane	108-87-2	98.19	0.77	0.163	6170		
n-hexane	110-54-3	86.18	0.66	0.151	19900		
n-heptane	142-82-5	100.2	0.68	0.0299	6170		
n-octane	111-65-9	114.2	0.70	0.00876	1820		

Note about units;
There are a number of units used to report these partitioning values, which can get confusing. For the purpose of this course, it will be useful to be familiar with the dimensionless K_{aw} values. Other units may also be convenient, particularly when comparing data from different sources. For this purpose, it will be useful to have K_H values in SI units of Pascals per mole per cubic meter (Pa m^3/mol) or Pascals per mole per liter (Pa L/mol).

$$K_H = RT K_{aw}$$

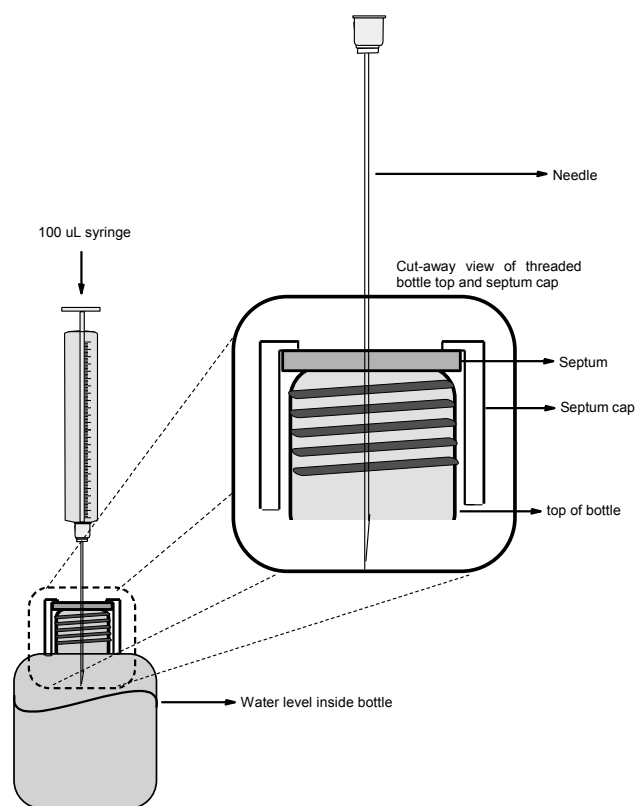making sure that the appropriate units are used for R – the universal gas constant.

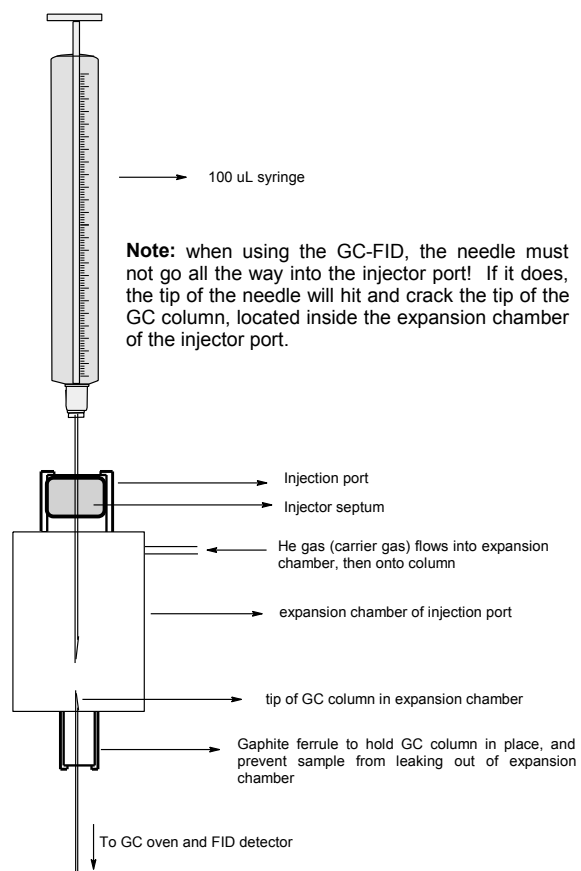**Figure 2**: Withdrawing headspace from sample bottle with gas-tight syringe.

Figure 3: Injecting sample into GC – injection port

Calculations:

For each of the two compounds studied only at room temperature, you should have a total of four GC runs and corresponding peak areas. This will give you four pairs of peaks to generate a total of four independent K_{aw} determinations. Report the mean and standard deviation for compound #1 and #2. Share your results with others.

For *trans*-1,2-dichloroethene, you will have one pair of GCs at each of three temperatures. Calculate the K_{aw} at each temperature and share your results with others to obtain mean values and standard deviations.

Convert all values to K_H in units of Pa m^3 mol^{-1} for comparison to literature values.

Plot ln K_H versus 1/T for *trans*-1,2-dichloroethene and obtain the slope.

Questions:

Derive the expression for K_{aw} used in this lab.

Compare your experimentally determined K_H values to i) accepted literature values, ii) values calculated from P^o and C_w^{sat} and iii) those estimated by the bond fragment contribution method (*8*) as outlined in Table 6.4 of Schwarzenbach (*1*).

How can the K_H values of the different compounds investigated be understood in terms of their chemical structure and the inter-molecular forces present (*1*).

Interpret the slope of the ln K_H versus 1/T plot (*7, 9-10*).

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