

Oh Henry! (a constant)

by Blayne Hartman

[Editor's Note: This is the first in a series of articles that review some of the physical/chemical properties that are commonly used in environmental assessment and remediation.]

Okay, here's a question that, when I ask it, over 75 percent of the people answer incorrectly. See how you do.

Suppose I fill a closed container with water until there are equal amounts of air and water. Then I spike 100 molecules of benzene into the container, and shake it until the benzene distributes itself between the air and water. Where will the benzene end up?

- (a) Mostly in the water.
- (b) Mostly in the air.
- (c) Equal amounts in the air and water.
- (d) It sinks to the bottom as a DNAPL.

Got the answer?

Well you know it's not (d), because benzene is lighter than water and would float as a free product. (DNAPL refers to dense non-aqueous-phase liquid—a liquid heavier than water.) It's not (c), because there is a preferred phase for all compounds, including benzene. So, do you choose (a) or (b)?

Some hints:

- Benzene has a relatively high vapor pressure and is considered to be a volatile compound.
- Although benzene is considered the most soluble of the aromatics, the solubility of all of the aromatics in water is relatively quite low.
- Very few regulatory agencies (in fact, none that I know of) consider benzene data from water samples that contain air bubbles valid, because of concerns about the loss of the benzene to the bubbles.

Do these hints convince you that (b) (mostly in the air) is correct? If so,

you're wrong. The correct answer is (a). The benzene prefers to stay in the water! Surprised? Well, welcome to the 75 percent club.

The distribution, or partitioning, of a compound between air and water is given by the Henry's law constant and is defined as

$$H = C_{\text{air}} / C_{\text{water}}$$

where C_{air} and C_{water} are concentrations of a compound in the air and water phases, respectively. The units for the air and water concentrations are the same (i.e., $\mu\text{g}/\text{L}$).

Dimensional vs. Dimensionless

Henry's law constants are derived empirically (i.e., by measurement in the laboratory) and are commonly tabulated in two forms: dimensional and dimensionless. While both forms are useful, the dimensionless form is the easiest form to work with for the inexperienced user.

The dimensionless form can be thought of as the number of molecules or mass of a compound that exists in the air versus the number of molecules or mass that dissolves into the water. If the dimensionless Henry's constant for a compound is greater than one ($C_{\text{air}} > C_{\text{water}}$), then the compound prefers to be in the air phase. In contrast, if the Henry's constant is less than one ($C_{\text{air}} < C_{\text{water}}$), then the compound prefers to be dissolved in the water. This partitioning ratio will hold until a compound has reached saturation in either the air or water.

The dimensional form of the Henry's constant is typically given in units of $\text{atm}\cdot\text{m}^3/\text{mole}$ and can be computed from the dimensionless constant using the ideal gas law by multiplying by the universal gas constant times temperature (0.082 times the temperature in degrees Kelvin, which is equal to 22.4 at 0°C, and 24 at 20°C).

Day-to-Day Applications

So, how do you apply Henry's constant to day-to-day LUST situations? Well, for one thing, you can use the it to predict the likelihood that a compound exists in the soil vapor or headspace. For example, consider the alkane and aromatic hydrocarbons. For the lower alkanes (methane through hexane), the dimensionless Henry's constant ranges from 30 to 70 (let's use 50 as an average). For a system at equilibrium with equal volumes of soil vapor and water, 50 molecules of these alkanes will exist in the air for every 1 that dissolves into the water.

In contrast, the Henry's constant for the four common aromatics (benzene, toluene, ethyl-benzene, and xylene) is approximately 0.25. At equilibrium, 1 molecule will exist in the air for every 4 that dissolve into the water. Thus, the alkanes will partition into the air approximately 200 times more than the aromatics (50/0.25).

When measuring air samples for fuel-related hydrocarbons (e.g., soil vapor surveys, screening soils and waters using a head-space technique, exhaust from a vapor extract system), sample analysis with a flame ionization detector (FID) instrument has a far greater chance of detecting the contamination than one with a photo ionization detector (PID), because FIDs detect all alkanes whereas PIDs are relatively insensitive to alkanes.

You can use Henry's constants to compute the equilibrium concentration of a compound in the air or water from the other phase. Rearranging the expression for the Henry's constant gives:

$$C_{\text{air}} = H * C_{\text{water}}$$

For example, if the groundwater concentration was 10 $\mu\text{g}/\text{L}$ for both

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methane and benzene, the equilibrium soil vapor concentration above the water would be:

For methane ($H = 30$):

$$C_{sg} = 30 * 10\mu\text{g/L} = 300 \mu\text{g/L}$$

For benzene ($H = 0.25$):

$$C_{sg} = 0.25 * 10\mu\text{g/L} = 2.5 \mu\text{g/L}$$

It is very important to remember that Henry's constants assume that equilibrium exists between the air and water phases and that the compound's solubility in the air or water has not been reached (i.e., below saturation). These conditions are often not met in the real environment, so values computed from these constants are approximations that can be used for predictive purposes, but should be used cautiously for quantitative conclusions.

Now Back to the Original Question...

Benzene has a Henry's constant of approximately 0.25, meaning that for every 1 molecule of benzene that partitions into the air, 4 molecules partition into the water. So, the correct answer is (a). Remember, our example assumed equal volumes of air and water in the container. If the air/water volumes are not equal, then the actual distribution also depends upon the ratio of air to water. In other words, in a water sample where air bubbles make up 10 percent of the total container volume, the distribution of benzene would be roughly 1 molecule in the air bubble for every 40 molecules in the water (only 2.5 percent of the total). The startling conclusion here is that a few bubbles in a water sample don't significantly change the water concentration, depending upon the compound's Henry's constant. Oh Henry!

Got it? Now go ask the question to your co-workers. (P.S., I get 10 percent of any winnings). ■

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