Lecture 4, Chemical Distribution Between Phases, Solubility and Vapor Pressure and Henry's Law

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Why worry about phases?

- Solid-liquid-gas but solids can be suspended in water or air and liquids can have a partial pressure in air (in the headspace above the aqueous solution). Also chemicals can be soluble to some extent in an aqueous solution, with the remainder in a solid state.

Partitioning between Gases, Liquids and Solids

- Potentially, chemical agents in the environment can become distributed throughout the gas phase (air), liquid phase (aqueous environments and non-aqueous spillages) and solid phase.
- A non-aqueous phase liquid (NAPL) does not mix freely with water and floats on the surface or may be a submerged bolus depending on density.
- The important solid phase components can be taken to include not only macroscopic surfaces, but also particulate matter suspended in air and water. The microscopic solids are often the more significant of the two; especially during clean-up or decontamination operations.
- Even in the subsurface environment it may be necessary to consider partitioning of some contaminants between soil particles, water and trapped air.

Non-miscible Liquids

- If the solubility of some chemical agent under consideration is known in both water ($[S]_{water}$) and the non-aqueous liquid in question ($[S]_X$) then the partition coefficient is given by: $\mathbf{K_X = [S]_X/[S]_{water}}$ and this will not vary by much over the temperature range typically encountered in the environment.
- The partition coefficients for various solutes between 1-octanol and water are of some particular interest (and are widely tabulated) as these have been empirically shown to mimic distributions between water and the fatty tissues of fish!

Vapor Pressure

- In relation to volatile compounds, which tend to become distributed by evaporation, it is useful to define the vapor pressure as: the partial pressure of a compound in the gas phase that is in equilibrium with the pure liquid or solid.
- When necessary (*i.e.* if there is some meaningful control volume) the partial pressure can be converted into the corresponding molar concentration using the ideal gas law: $\boldsymbol{n/V = P/(RT)}$ (since $PV = nRT$);
- *e.g.* Ex. 1-12: n/V = 0.015 atm/[0.082 L•atm/(mol•K)•(21 + 273)K] = 6.2 x 10-4 M.
- Vapor pressures are markedly temperature dependent. The Antoine equation (or a simpler variation) is sometimes used to estimate temperature corrections to vapor pressures: $\mathbf{ln}\ \boldsymbol{(VP) = -B/(T + C) + A}$ where *A*, *B* and *C* are tabulated constants.

Henry’s Law

- Partitioning between the gas phase and liquid phase is usually quantified using Henry’s law constants (*H* or K_H).
- The dimensionless form of K_H is just like a liquid-liquid partition coefficient (but some tabulations involve the gas concentration being expressed in terms of partial pressure) *e.g.* Ex. 1-13:
- K_H = 26 = y (µmol/L) ÷ 100 (µmol/L) $\Rightarrow$ y = 26 x 100 µmol/L = 2.6 mmol/L

Homework

- Page 60 –problems 14 and 15 and page 63 problem 25.
- For next time –conclude Chapter 1.