Lecture 5, Chemical Partitioning to Solids and Fugacity

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Partitioning to Solids

- Relevant <u>sorption</u> can be from air to solid, or from water to solid. Such processes can involve either surface <u>adsorption</u>, or <u>absorption</u> into the bulk solid. **Adsorption** is the attachment of a chemical to the two-dimensional surface of a solid, while **Absorption** is the diffusion of a chemical into a three dimensional solid.

- Solids vary enormously in terms of composition, surface characteristics and porosity, resulting in much more complicated phase partitioning than in the case of gas-liquid and liquid-liquid examples. **Sorptive solid phases** are called **<u>sorbents.</u>**

Partitioning to Solids

- Solids capable of sorbing chemicals are **sorbates.**

- **Sorbates can include minerals and metal oxide particles, organic material-even living tissue and plastics.**

- Mechanisms of sorption:

1. Absorption into natural organic matter.

2. Adsorption to mineral surfaces via intermolecular forces.

3. Adsorption through electrostatic attractions to oppositely charged sections of the solid.

4. Adsorption through covalent bonding to surface groups on the solid.

Partitioning to Solids

- Typically, the relationship between the concentration of an aqueous chemical agent and its sorbed concentration is non-linear and may sometimes be quantitated by a <u>sorption isotherm</u>: $C_{\text{sorbed}} = K_f(C_{\text{water}})^n$ where K_f is the <u>Freundlich</u> constant and *n* reflects the non- linearity (a simple partition coefficient is described by n = 1 and this indicates linearity). C_{sorbed} is the *C of sorbed chemical [M/M]*, C_{water} is the C of dissolved chemical in water [M/L^3].

- If n is < 1 than as the dissolved chemical concentration increases, the additional molecules sorb in smaller proportion-conversely if n is > 1 than as dissolved concentration increases more sorption occurs. (Figure 1-10, page 51)

Partitioning to Solids

■ – For sorption of inorganic species, the partition coefficient (or distribution coefficient, K_p, or K_d) which depends on pH, solid type and ionic strength, cannot even be applied to the same compound interacting with the same solid under different conditions. K_d must often be determined in the laboratory.

■ -Neutral (uncharged) organic molecules of limited water solubility, tend to be absorbed by natural organic matter as the primary sorption mechanism.

• This is because they are non-polar, where polarity is the extent to which a charge is unevenly distributed within a molecule.

• **Non-polar compounds** are **well balanced charge wise**, they are **hydrophobic** and tend to be absorbed in natural organic matter-especially fats-so they are **lipophylic**.(go over figure 1-11, page 52 polar and non-polar compounds-water is very polar and dissolves readily other polar chemicals (**hydrophilic**)).

Partitioning to Solids

- In fact the more non-polar a compound is the more lipophylic it is and it will have a higher octanol-water partition coefficient-K_{ow}.

- K_{ow} is inversely correlated with the polarity of a compound-nonpolar compounds having relatively high K_{ow}.

- K_{ow} was developed for use by the pharmaceutical industry and is a useful index of whether or not a chemical will sorb to solids in the body or stay in aqueous solution.

- Large molecules that are non-polar have high K_{ow} , which means that they will more likely partition into body fat than water. This is the basis of bioaccumulation of persistent organic pollutants, such as DDT and PCB's in aquatic systems (mainly fish fats) and in mammalian body fats.

Example 1-14, page 53

- $K_H = [\text{toluene}_{air}]/[\text{toluene}_{water}] = 0.28;$ $K_{ow} = [\text{toluene}_{oct}]/[\text{toluene}_{water}] = 490$

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- Toluene in swim bladder $= 0.03(V_{fish})(K_H \bullet C_w) = B_f$
- Toluene in fatty tissue $= 0.05(V_{fish})(K_{ow} \bullet C_w) = F_f$
- Toluene in fish body water $= 0.85(V_{fish})C_w = W_f$

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- Fraction of toluene in the fatty tissue is: $F_f/(F_f + B_f + W_f)$
- $= 0.05 \bullet K_{ow}/(0.05 \bullet K_{ow} + 0.03 \bullet K_H + 0.85) = 0.97 \ (97\%)$

Equilibrium partitioning simultaneously between all phases is formulated in terms of the <u>fugacity</u>

☐ ● Fugacity- meaning "run away" — like King Arthur's knights in the face of severe French taunting{only Peterson could coin this phrase}.

☐ ● Fugacity (f) has units of pressure and is related to concentration by a <u>fugacity</u> <u>capacity</u> <u>constant</u> (Z) [T^2/L^2]. For any species in phase i: $C_i = Z_i \cdot f$.

Equilibrium partitioning simultaneously between all phases is formulated in terms of the <u>fugacity</u>

- At equilibrium, the fugacity for the system is: $f = n/\sum_i(Z_i \bullet V_i)$ where n is the total number of moles of the compound in question present in the system and V_i is the volume of phase i. If $f = P$, then $f = (n/V)RT \Rightarrow Z_{air} = 1/(RT)$ since $C = n/V$ $Z_{water} = 1/K_H$; $Z_{sediment} = (\rho_s\text{-}K_d)/K_H$; $Z_{fish} = (\rho_f\text{-}K_f)/K_H$ where ρ_s and ρ_f are the relevant densities and K_d, K_f the relevant partition constants.

Equilibrium partitioning simultaneously between all phases is formulated in terms of the <u>fugacity</u>

- ▢ •   Once the fugacity capacity for each phase is known, then the moles of compound in each phase are given by: $n_i = fV_iZ_i$.

- This formalism does not provide any new information to that available by stepwise application of the partition coefficients, but it can be useful in some situations, such as when the concentration of a contaminant in one or more phases is of less interest than its distribution between them;

Ex. 1-15:

- $Z_{air} = 40.9$ mol/(atm•m^3) $\bm{Z_{air} = 1/(RT)}$
- $Z_{water} = 333$ mol/(atm•m^3) $\bm{Z_{water} = 1/K_H}$
- $Z_{fish} = 1.5$ mol/(atm•m^3) $\bm{Z_{fish} = (\rho_f\text{-}K_f)/K_H}$

$f = 118/(40.9\bullet10^{10} + 333\bullet[7 \times 10^6] + 1.5\bullet3.5) = 2.9 \times 10^{-10}$ atm

$n_{air} = 2.9 \times 10^{-10} \times 10^{10} \times 40.9 = 117$ mol

$n_{water} = 2.9 \times 10^{-10} \times 7 \times 10^6 \times 333 = 0.7$ mol

$n_{fish} = 2.9 \times 10^{-10} \times 3.5 \times 1.5 = 1.5 \times 10^{-9}$ mol

$C_{air} = 117/10^{10} = 1.2 \times 10^{-10}$ mol/m^3

$C_{water} = 0.7/(7 \times 10^6) = 1.0 \times 10^{-7}$ mol/m^3

$C_{fish} = (1.5 \times 10^{-9})/3.5 = 4.3 \times 10^{-10}$ mol/m^3