Addendum to ES/RP 531 Lectures
Overview of Important Chemical Concepts

I. Introduction
  A. Although ES/RP 531 is not a chemistry course per se, there are important chemical concepts (i.e., basic principles and mechanisms) that will be helpful in predicting properties of a compound, its ability to translocate in the environment, its ability to enter cells, its ability to bind with macromolecules, and its reactivity.
  B. Chemical functional groups are also important to being able to predict from a comparative perspective physicochemical properties and reactivities.
  C. I've prepared this set of notes as an overview to chemical structure and recognition of the different kinds of functional groups and some of the properties they impart to a molecule.
  D. Because all of you have had at least general chemistry, I will be making the assumption of some background knowledge; I will review what I believe to be fundamental to understanding certain environmental chemistry or biochemistry principles, but you are expected to review basic concepts that you do not understand.
    1. Toward that end, I suggest that you keep a copy of a general chemistry, organic chemistry, and biochemistry text handy so that you can review fundamental chemical principles as needed.
      a. Also, reacquaint yourself with the Periodic Table;
      b. Reacquaint yourself with the concept of enthalpy and bond energies.
    2. Also, I expect you to understand different expressions for concentration;
      a. You should be able to convert between molar units and ppm, ppb, or ppt

II. Review of Atomic Properties, Bonding, Intermolecular Forces
  A. Table 1 lists the most common atoms found in organic molecules; we will not worry about heavy metals in inorganic molecules at this time, largely because most of the contaminants we will be discussing are organic compounds
  B. You should be familiar with nomenclature of atoms, atomic number, atomic weights, electron shells and orbitals, and valency from general chemistry.
  C. For purposes of this class, however, it is essential that you be familiar with the number of bonds that an atom engages in;
    1. Bonds are formed when electrons between atoms are shared;
      a. **Covalent bonds**, which are the prevalent bonding mechanism of organic molecules and some inorganic molecules, results from the sharing of a pair of electrons, with each electron contributed by the two bonded atoms.
  D. **Polarity**
    1. Some atoms have a greater propensity to attract electrons then others, so the sharing may be somewhat unequal with the electrons found closer to the nucleus of one atom than another;
      a. This unequal sharing causes polarity in the bond;

Table 1. Atomic Mass, Electronic Configuration, and Typical Number of Covalent Bonds of the Most Important Elements Present in Organic Molecules

Name	Symbol	Atomic Number	Atomic Mass	# of Electrons in Shell[a]					Net Charge of Kernel	No. of Covalent Bonds
				1 (K)	2 (L)	3 (M)	4 (N)	5 (O)		
Hydrogen	H	1	1.008	1					1+	1
Helium	**He**	**2**	**4.003**	**2**					**0**	
Carbon	C	6	12.011	2	4				4+	4
Nitrogen	N	7	14.007	2	5				5+	3, (4)[c]
Oxygen	O	8	15.999	2	6				6+	2, (1)[d]
Fluorine	F	9	18.998	2	7				7+	1
Neon	**Ne**	**10**	**20.180**	**2**	**8**				**0**	
Phosphorus	P	15	30.974	2	8	5			5+	3,5
Sulfur	S	16	32.060	2	8	6			6+	2, 4, 6, (1)[c]
Chlorine	Cl	17	35.453	2	8	7			7+	1
Argon	**Ar**	**18**	**39.948**	**2**	**8**	**8**			**0**	
Bromine	Br	35	79.904	2	8	18	7		7+	1
Krypton	**Kr**	**36**	**83.800**	**2**	**8**	**18**	**8**		**0**	
Iodine	I	53	126.905	2	8	18	18	7	7+	1
Xenon	**Xe**	**54**	**131.290**	**2**	**8**	**18**	**18**	**8**	**0**	

[a] letters represent the old system of designating electron shells

[b] noble gases are shown in bold;

[c] number in parentheses indicates positively charged atom;

[d] number in parentheses indicates negatively charged atom

2. The concept of polarity, i.e., which bonds are polar and which are nonpolar is fundamental to understanding many processes in environmental chemistry.
3. The ability of one atom in a bond to attract electrons to itself is termed **electronegativity (EN)**;
    a. Electronegativity increases as one goes from left to right across a row of the periodic table;
    b. EN decreases as one goes down a column of the periodic table
    c. Differences in EN between two atoms determine the polarity of a bond;
    d. When very large differences in EN occur, such as when a row 1 element and a row 7 element combine, the electrons are essentially transferred from the element of lowest electronegativity to the element of highest electronegativity resulting in complete charge separation or the formation of ions
        1. The bonding mechanism is one of electrostatic attraction (rather than sharing of electrons) and the bond is called **ionic.**

Table 2. Electronegativities of Atoms (the greater the number the greater the EN)

Charge of kernel[1]	+1	+4	+5	+6	+7	
	H					Increasing Size of kernel
	2.2					↓
		C	**N**	**O**	**F**	↓
		2.5	3.0	3.5	4.0	
			P	**S**	**Cl**	↓
			2.2	2.5	3.0	
					Br	↓
					2.8	
					I	↓
					2.5	

[1] The kernel refers to the nucleus and the inner filled electron shells

4. The overall polarity of a molecule containing polar bonds is actually determined by the **dipole moment**, which is the vector sum (i.e., there is a magnitude and direction) of the individual polar bonds or dipoles;
    a. Thus, overall polarity depends on both the presence of polar bonds and on the geometry of the molecule (i.e., planar, tetrahedral, etc.--review this concept in a general chemistry text)
        1. ex., CH_3Cl is polar but CO_2 is nonpolar
5. The atoms in a polar bond have partial ionic character, which can be denoted as shown below:

$$\overset{\delta^+}{-C} - \overset{\delta^-}{O} -$$
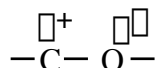
6. When hydrogen is bonded to an electronegative atom like N or O, an opportunity exits for attraction of the electron deficient H (with partial positive charge) to an electron rich atom of another molecule (especially heteroatoms with unbonded electrons) to form a **hydrogen bond**;
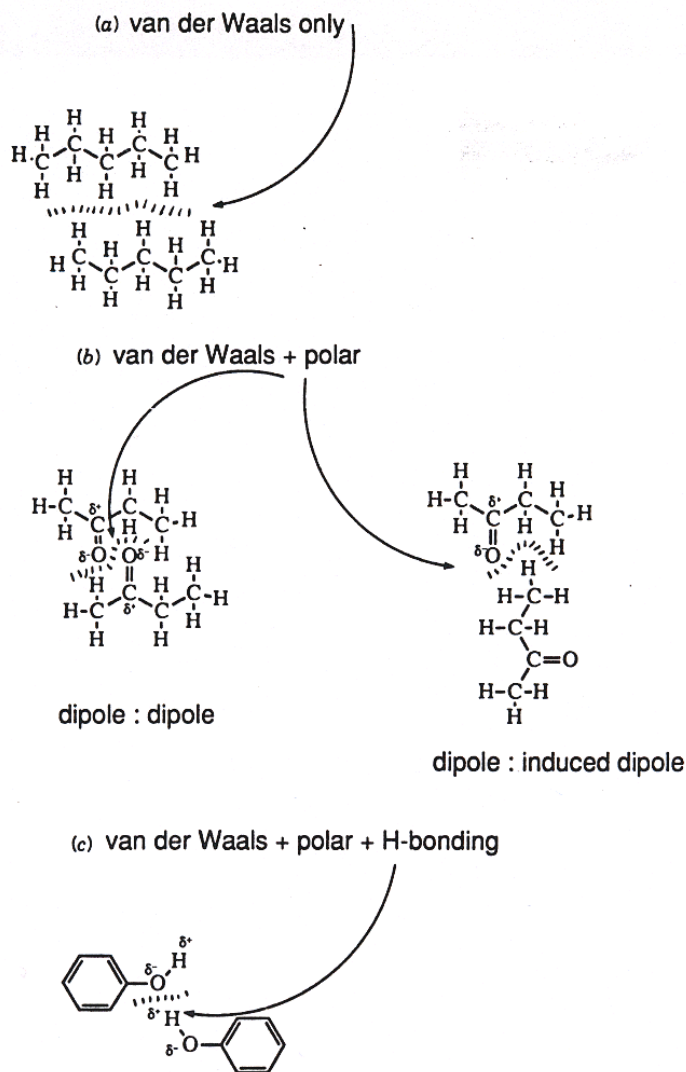
$$\overset{\delta-}{-O}-\overset{\delta+}{H} \quad \text{-----} \quad \overset{\delta-}{:N}-$$
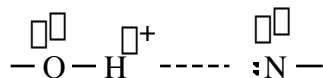
a. Hydrogen bonds are much weaker than covalent bonds (~15-20 kJ compared to >300 kJ), but are important considerations for understanding the magnitude of certain physicochemical properties and phase transfer equilibria (as well as enzyme-substrate interactions)

b. For example, the ability of water to form hydrogen bonds gives it unusually high surface tension (see water solubility discussion below), high boiling point, and explains the lower density of solid ice than of liquid water.

1. Hydrogen bonds are one type of intermolecular force that is important in explaining the magnitude of physicochemical properties.

E. Intermolecular Forces (in addition to hydrogen bonding)

1. These intermolecular forces along with hydrogen bonding are commonly called van der Waal's forces (Brown et al. 1994, *Chemistry: The Central Science*), although van der Waal's forces have also been used strictly for a special type of intermolecular force called London dispersion (see discussion below)..

a. Dipole-dipole forces exists between neutral polar molecules. Polar molecules attract each other when the positive end of one molecule is near the negative end of another. Effective only at very close distances.

1. There are also ion-dipole interactions, which are electrostatic attractions between an ion and the partial charge on the end of a polar molecule

2. Dipole-dipole interactions can explain the differences in boiling point among disparate polar substances; by the same reasoning, hydrogen bonding can also explain these differences

a. For liquids containing molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity.

Substance	Molecular Mass	Dipole Moment μ (D)	Boiling Point K
propane, $CH_3CH_2CH_3$	44	0.1	231
dimethyl ether, CH_3OCH_3	46	1.3	248
methyl chloride, CH_3Cl	50	2.0	249
acetaldehyde, CH_3CHO	44	2.7	294
acetonitrile, CH_3CN	41	3.9	355

b. Intermolecular attractions also exist between nonpolar compounds; these forces of attraction are know as London dispersion forces, and were first hypothesized in 1930;

1. The motion of electrons in an atom or molecule can create an instantaneous dipole moment.

2. The temporary dipole on one atom induces a similar dipole on an adjacent atom, causing the atoms to be attracted to one another; the London dispersion force is only significant when molecules are very close together.
3. Strength of the force increases with molecular size and mass;
   a. Why? Larger molecules have greater polarizability (ease with which charge distribution, i.e., electron distribution, in a molecule is distorted by an external electric field, perhaps an ion or another dipole, because they have greater number of electrons and the electrons are further from the nuclei.
   b. Thus, the boiling point increases from -161 C in methane (1 carbon hydrocarbon) up to 174 C in decane (10 carbon hydrocarbon)
   c. Graphic conceptualization of intermolecular forces (from Schwarzenbach 1993)

(a) van der Waals only

(b) van der Waals + polar

dipole : dipole

dipole : induced dipole

(c) van der Waals + polar + H-bonding

1. Explanation of figure on previous page:
   (a) Nonspecific or Van der Waals attractions occur between all forms of matter, even nonpolar materials like pentane.
   (b) The presence of unevenly distributed electron densities gives rise to bond-size dipoles which are attractive to other dipoles or which induce electron redistribution in neighbor molecules and thereby establish dipole:induced dipole attractions.
   (c) Hydrogen atoms bonded to oxygen or nitrogen are available to be attracted to the nonbonded electrons of other oxygen or nitrogen atoms, establishing hydrogen bonds.

III. Important Functional Groups

A. Functional groups are collections or assemblages of atoms that frequently occur together in a molecule
B. To understand functional groups, it is best to review bonding and valency; Table 1 above lists the number of covalent bonds that the most common atoms found in organic environmental contaminants can engage in.
   1. Inorganic contaminants, characterized by heavy metals, have variable bonding; these will be discussed in the lectures on heavy metals.
C. Common Functional Groups found in organic environmental contaminants
   1. note: non carbon constituents bonded to carbon are conventionally called heteroatoms
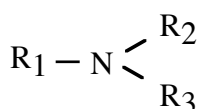
-C-C-C-C-   alkyl (can be denoted by R)

R-OH   hydroxy (alcohol, if phenol then R =)
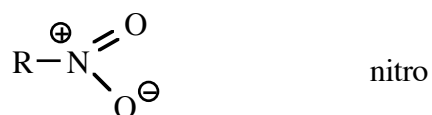
R-SH   mercapto (thiol, mercaptan)

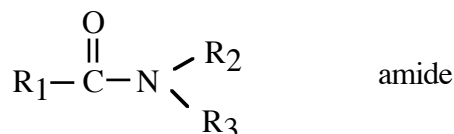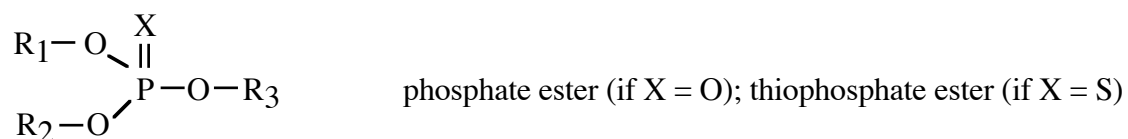R_1-O-R_2 ether

R_1-S-R_2 sulfide (thioether)

$R_1 - N \overset{R_2}{\underset{R_3}{\diagdown}}$ amino (primary amine, R2 = R3 = H
            secondary amine, R3 = H
            tertiary amine, R1, R2, R3 = C

            aniline if R =

$$R_1-\overset{\overset{\textstyle O}{\|}}{C}-R_2 \qquad \text{carbonyl (ketone, aldehyde when } R_2 = H$$

$$R-\overset{\overset{\textstyle O}{\|}}{C}-OH \qquad \text{carboxy (carboxylic acid)}$$

$$R_1-\overset{\overset{\textstyle O}{\|}}{C}-O-R_2 \qquad \text{ester (carboxylic acid ester)}$$

$$R_1-\overset{\overset{\textstyle O}{\|}}{C}-S-R_2 \qquad \text{thioester}$$

$$\begin{array}{c} R_1-O \\ \overset{\overset{\textstyle X}{\|}}{}\ \\ R_2-O \end{array}\!\!P-O-R_3 \qquad \text{phosphate ester (if X = O); thiophosphate ester (if X = S)}$$

$$R_1-\overset{\overset{\textstyle O}{\|}}{C}-N\!\!\begin{array}{c} \diagup R_2 \\ \diagdown R_3 \end{array} \qquad \text{amide}$$

$$R-C\!\equiv\!N \qquad \text{cyano (nitrile)}$$

$$R-\overset{\oplus}{N}\!\!\begin{array}{c} \diagup\!\!\diagup O \\ \diagdown O^{\ominus} \end{array} \qquad \text{nitro}$$

$$R-\overset{\bullet\bullet}{N}\!=\!O \qquad \text{nitroso}$$
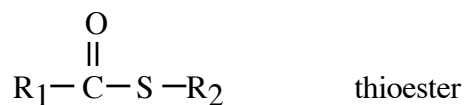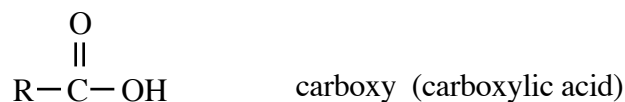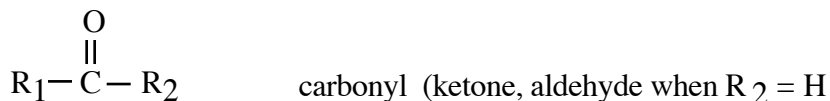
D. Saturation vs. Unsaturation
 1. Saturation refers to single bonds, as in the alkane (hydrocarbon) propane;
      $$H_3C-CH_2-CH_3$$
 2. Unsaturation refers to double bonds as in the alkene hydrocarbon, propene
      $$H_3C-CH_2=CH_3$$
     a. The presence of unsaturation in a molecule imparts a location of comparatively high reactivity
E. Aromatic Rings

1. Aromatic rings are based on the structure of benzene;
   a. Aromatic rings are quite stable because of resonance; a pi electron is delocalized and the ring actually exists in two conformations; this phenomenon is called resonance and results from the "smearing" of pi orbital bonding electrons around the ring

   or
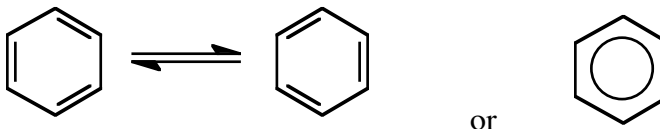
   b. Note that substitutions on the ring are possible, and the position of substitutions confer different properties


   ortho   meta   para
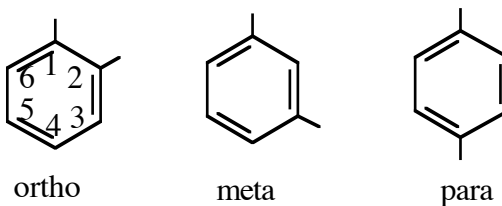
      1. For example, dinitrobenzene melting points differ by isomeric form: ortho = 118 C; meta = 90 C; para = 174 C
   c. Compounds like polycyclic aromatic hydrocarbons, which are products of incomplete combustion and many are known mutagens, have multiple aromatic rings


   anthracene
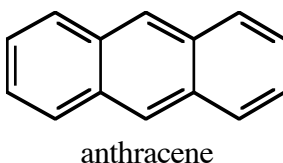
IV. Introduction to Physicochemical Properties
   A. A knowledge of selected physicochemical properties of any chemical can aid prediction of its behavior in the environment, likelihood of cross the surface of an animal and moving into the interior organs and tissues.
   B. Two of the most important physicochemical properties are **vapor pressure** and **water solubility**. Vapor pressure will be discussed more extensively in the lectures on environmental chemodynamics and is a very influential property driving molecules into the gaseous state and thus setting up the potential for s long range transport.
      1. Water solubility influences the potential of molecules to move from surfaces into solution (or the reverse direction). From the viewpoint of toxicokinetics, water solubility can influence the potential of molecules to cross membranes.
   C. Water solubility (WS) can be defined as the amount of a substance that dissolves in a given quantity of water at a given temperature to form a saturated solution.
      1. Note that water solubility is temperature dependent; thus the WS measured at 15 C will be different than that measured at 25 C
      2. Why is WS limited; in other words what limits the total dissolution of a given weight of a substance in a given volume of water?

3. Water molecules form a highly ordered structure as a result of hydrogen bonding; this property also gives water a very high surface tension (i.e., the intermolecular, cohesive attractions between like molecules of a liquid that cause it to minimize its surface area) as well as its higher than predicted boiling point and lower density as ice than as a liquid.
   a. Hydrogen bonding is a type of intermolecular attraction that exists between hydrogen atom in a polar bond (particularly an H-F, H-O, or H-N bond) and an unshared electron pair on a nearby electronegative ion or atom (usually an F, O, or N atom)
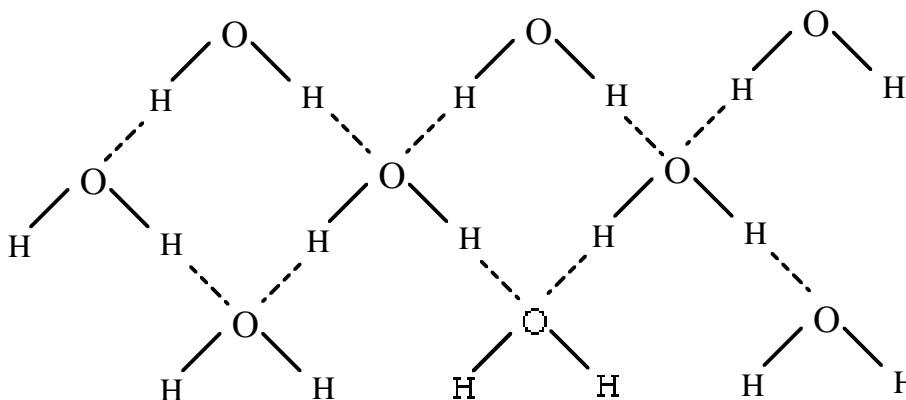
4. Solid lines represent covalent bonds between H and O of same water molecule; dashed lines represent hydrogen bonds between H and O of different water molecules.
5. Now if we represent each H_2O molecule by a circle, and the hydrogen bonding (i.e., intermolecular forces by arrows), then we see an imbalance of forces at the surface (or edge) of the liquid, where the forces are tending to draw the water into the interior, thereby reducing the surface area. (Note that the molecules in the interior are attracted equally in all directions). The inward force at the edges of the liquid also makes the molecules at the surface pack closely together, causing the liquid to behave almost as if it had a skin. A measure of the inward forces that must be overcome to expand the surface area of the liquid is given by its surface tension.
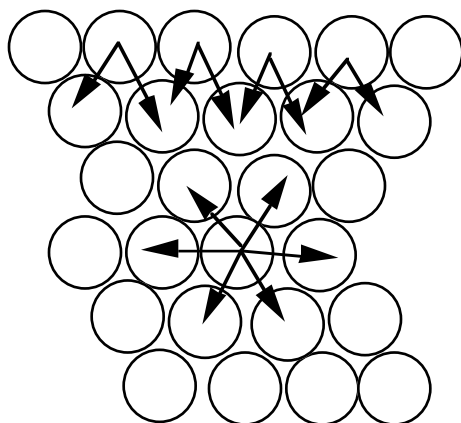
surface tension

6. Now consider what happens if molecules (e.g., a liquid or solid pesticide) other than H_2O are placed in the water. The pesticide molecules essentially disrupt the water structure. Its analogous to punching a hole in the structure.
    a. There are several intermolecular forces at work: the solvent:-solvent attractions; solute-solute attractions; and solvent-solute attractions; maximum solubility occurs when the solvent-solute interactions are stronger than the sum of the solute-solute and solvent-solvent interactions (or energy required to separate like molecules)
    b. If the pesticide molecules have functional groups that can hydrogen bond, then the water structure is disrupted less (by analogy, the hole is not as big) and more of the molecule can dissolve in water (i.e., the greater the tendency for pesticide molecules to disperse or escape from one another and become surrounded by water molecules)
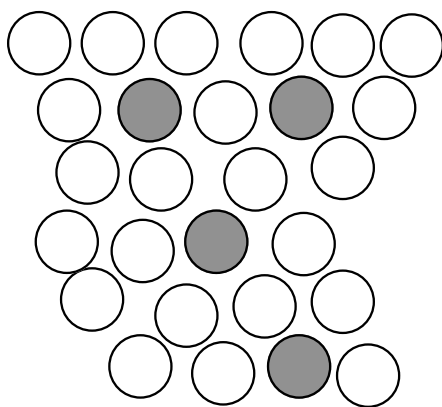
hydrophilic solute

7. If the pesticide molecules lack the ability to hydrogen bond and/or is very hydrophobic ("water fearing"), then the "hole" that is punched is necessarily very large (i.e., larger disruption of the water structure) and comparatively less of the pesticide molecule can be accommodated in the water volume (or in other words fewer pesticide molecules will escape or disperse from one another and become easily surrounded by water molecules); by the same

reasoning, fewer water molecules will separate from one another (i.e., the solvent-solvent interactions are much stronger than the solvent-solute interactions).
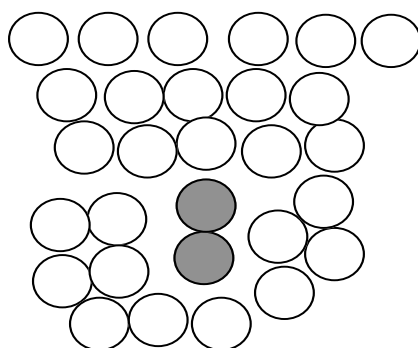
hydrophobic solute

8. Thus the energy costs overcoming solvent-solvent and solute-solute interactions when mixing a nonpolar or hydrophobic pesticides with water are too great to be compensated by the gain in energy from solute-solvent interactions; **rule of thumb "likes dissolve likes"**

V. Introduction to Partitioning Processes (Phase Transfers)
 A. Phase transfer processes can be described as **reversible** partitionings of dilute concentrations of the molecules of a compound between water and air, soil, or an organic phase (lipid material, octanol or other organic solvent or natural organic matter) (i.e., across interfaces, or the boundary where two phases meet and interact with one another).
  1. The equilibrium distribution of a chemical between two phases can be used similarly to the traditional physicochemical properties of pure substances to predict environmental behavior;
   a. The ratio of the concentration of the chemical in the phase of interest (air, soil, organic) to the concentration in water is commonly called a partition coefficient
 B. Absorption and distribution processes in toxicokinetics, can be better understood as a partitioning process. The toxicant is moving across an interface.
  1. For example, all surfaces have a molecular layer of water or are bathed in water (for example, soil particle surfaces, a fish swimming in water, etc.). Thus, partitioning will occur between the water and another phase, solid or liquid.
  2. The extent of the partitioning, i.e., diffusion of the molecules from one phase to another is controlled by the thermodynamic relationships in the system. The magnitude of the physicochemical properties is a function of this relationship, and the extent of partitioning is heavily influenced by the magnitude of the physicochemical properties.
   a. For example, compounds that are highly water soluble (i.e., very polar and hydrophilic compounds) tend not to cross the surface of insects or fish very readily. However, compounds that have very low water solubility (very nonpolar and hydrophobic) do cross the surface readily because thermodynamics favors their diffusion across the hydrophobic interior of the cell membranes.

C. Predicting partitioning in biological matrices (i.e., phases)
1. The potential for crossing cell membranes, and the potential for storage in fat tissue, can be predicted by observation of a partitioning parameter called the octanol:water partition coefficient, designated variously as either P (commonly used by pharmacologists) or Kow (used more often by environmental chemists and toxicologists)
2. Historically, octanol was used for the water-immiscible liquid as a surrogate for an organism; uptake of nonpolar drugs by organisms was found to be proportional to partitioning into octanol
3. Expression of partitioning coefficient: $K_{OW} = C_S/C_W$ (where C_s = concentration of compound in organic solvent and C_w = concentration of compound in water).
    a. The larger the Kow, then the more readily a compound is likely to cross a cell membrane.
        1. Note however that the above statement only applies up to a point. For example, compounds with extremely high Kow's might move into the hydrophobic interior of a cell membrane, but then diffuse very, very slowly through it (remember that "like dissolves like").
        2. Furthermore, the nature of the "skin" surface can slow diffusion down.
            a. Fish and invertebrates generally can "absorb" many toxicants more readily than mammals.
            b. Human skin is fairly impermeable to many compounds (i.e., low efficiency of transfer, but not zero), unless there is a cut or wound.