



ES/RP 531  
Fundamentals of Environmental Toxicology

Chemistry Review Addendum

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## Overview of Important Chemical Concepts

- Emphasis on valency of atoms and relevance for molecular bonding
- Emphasis on functional groups and the concept of polarity
- Emphasis on physicochemical properties
- Emphasis on phase transfer processes

Periodic Table of Elements

The periodic table shows elements arranged by atomic number. Groups 14, 15, 16, and 17 are highlighted in red. The elements in these groups are: Group 14 (C, Si, Ge, Sn, Pb), Group 15 (N, P, As, Sb, Bi), Group 16 (O, S, Se, Te, Po), and Group 17 (F, Cl, Br, I, At). The noble gases in Group 18 (He, Ne, Ar, Kr, Xe, Rn) are also shown.

Name	Symbol	Atomic Number	Atomic Mass	# of Electrons in Shell <sup>a</sup>					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) <sup>b</sup>
Oxygen	O	8	15.999	2	6				6+	2, (1) <sup>c</sup>
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) <sup>e</sup>
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	

Element (Atomic Symbol)	Atomic Mass	# Electrons in Outer Orbital	# Covalent Bonds
Hydrogen (H)	1	1	1
Carbon (C)	12	4	4
Nitrogen (N)	14	5	3 (4)
Oxygen (O)	16	6	2 (1)
Fluorine (F)	19	7	1
Phosphorus (P)	31	5	3, 5
Sulfur (S)	32	6	2, 4, 6
Chlorine (Cl)	35.4	7	1
Bromine	80	7	1

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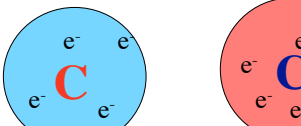
Electronegativity decreases from top to bottom with a column of the periodic table.

H 2.2	Increasing Kernel Size			
C 2.5	N 3.0	O 3.5	F 4.0	↓
	P 2.2	S 2.5	Cl 3.0	
			Br 2.8	
			I 2.5	

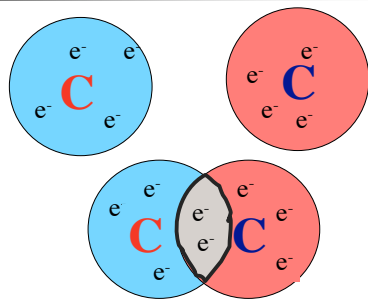
The kernel refers to the electrons in the nucleus and the inner filled electron orbitals

# Covalent Bonds

- Formed between atoms by sharing electrons



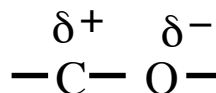
- Formed between atoms by sharing electrons



## Polarity (Polar Bonds)

- Owing to differences in electronegativity, sharing of electrons in the bonding orbitals may be unequal, i.e., toward one atom or the other
- Thus, positive (electron deficient) and negative (electron rich) poles are set up between atoms in a molecule

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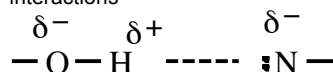


## Ionic Bonding $\text{Na}^+ \text{Cl}^-$

- When atoms of very large differences in EN bond, such as between column 7 and column 1 or 2 elements, then the electrons may be transferred from the atoms of lowest negativity to the atoms of highest negativity
- Thus, the atoms of highest EN would have a "permanent" negative charge
- The atoms of lowest EN would have a "permanent" positive charge

## Hydrogen Bonding

- When hydrogen (H) is bonded to O or N, which are more electronegative, then the relatively positive H can be attracted to an electronegative atom on nearby molecules
  - Especially if the more EN atom has an unbonded pair of electrons
- Forms a hydrogen bond; not as strong as covalent or ionic bond, but it can form stable molecular interactions



## Geometry (Bond Angles)

- Atoms within molecules actually exist in definite geometric spatial relationships to one another that are characteristic of the type of bond
  - For ex., carbon atoms have four valence electrons, each oriented toward the corner of a tetrahedron;

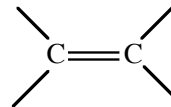
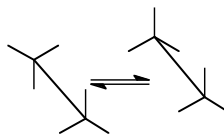


→ Nitrogen often uses three valence electrons (with an unpaired electron available for bonding an electron deficient species like H); its spatial geometry tends to be trigonal



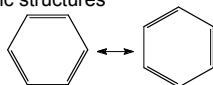
## Geometry (Bond Angles)

- Double bonds will make a molecule more rigid, giving the atoms less degrees of freedom to flop around and rotate about each other



## Geometry (Bond Angles)

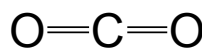
- Aromatic structures (alternating double bonds in ringed systems) tend to be planar (i.e., less free rotation of the carbon atoms)
  - Characterized by delocalized 'pi' electrons that can impart some electronegative character
  - Aromatic structures also are more stable than noncyclic structures



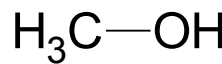
→ Note that double bonds in linear structures also have delocalized 'pi' bonds

## Dipole Moment

- The overall polarity of a molecule depends on both the presence of polar bonds and on the geometry of the molecule
  - Planar, trigonal, tetrahedral
- The determinant of overall polarity is the vector sum of the individual polar bonds, which is called the dipole moment



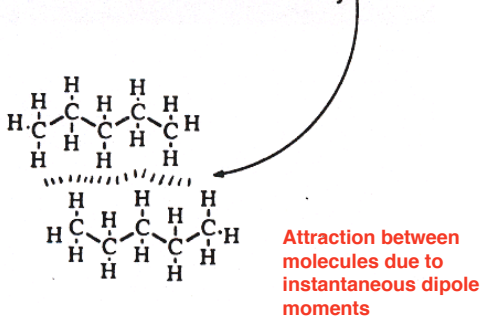
Carbon dioxide



Methanol

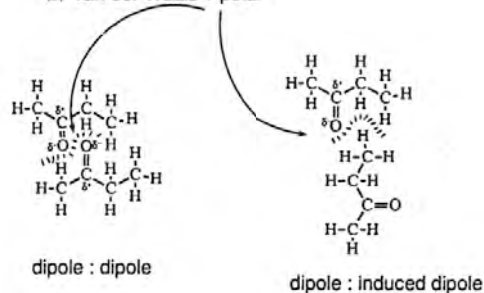
## Intermolecular Forces

(a) van der Waals only



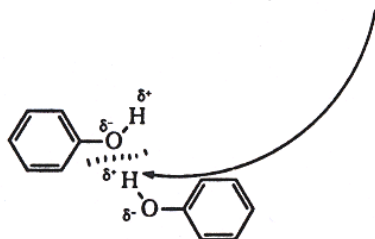
## Intermolecular Forces

(b) van der Waals + polar



## Intermolecular Forces



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



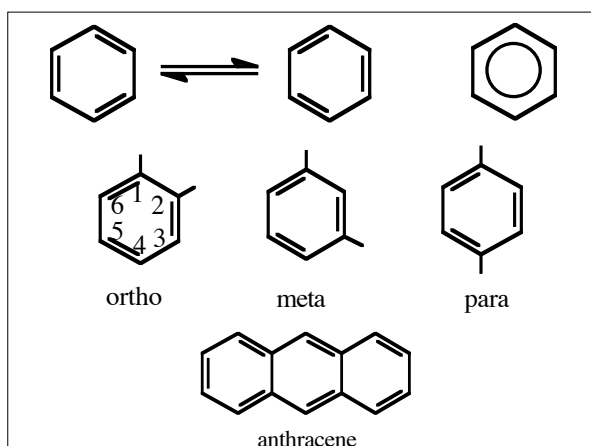
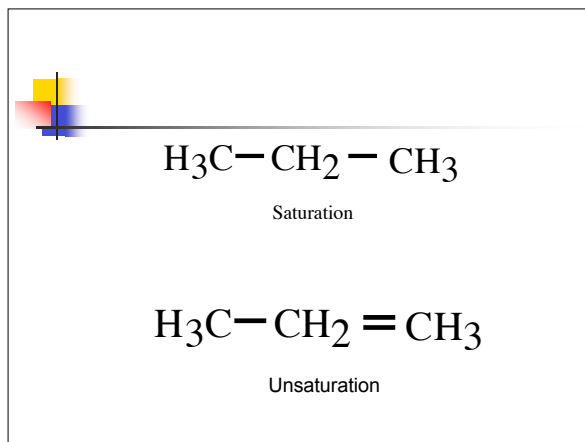
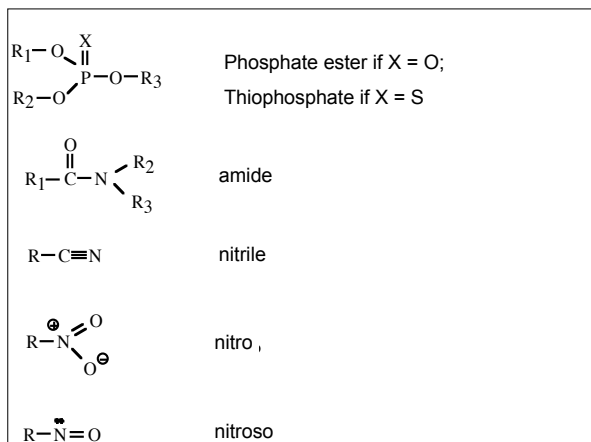
The various intermolecular interactions can explain various physicochemical properties.

Substance	Molecular Mass	Dipole Moment $\mu$ (D)	Boiling Point $^{\circ}\text{K}$
propane, $\text{CH}_3\text{CH}_2\text{CH}_3$	44	0.1	231
dimethyl ether, $\text{CH}_3\text{OCH}_3$	46	1.3	248
methyl chloride, $\text{CH}_3\text{Cl}$	50	2.0	249
acetaldehyde, $\text{CH}_3\text{CHO}$	44	2.7	294
acetonitrile, $\text{CH}_3\text{CN}$	41	3.9	355


Functional Groups impart characteristics upon molecules that are important in intermolecular interactions and reactivity

$-\text{C}-\text{C}-\text{C}-$	alkyl (can be denoted by R)
$\text{R}-\text{OH}$	hydroxy (alcohol, if phenol then $\text{R} = $  )
$\text{R}-\text{SH}$	mercapto (thiol, mercaptan)
$\text{R}_1-\text{O}-\text{R}_2$	ether
$\text{R}_1-\text{S}-\text{R}_2$	sulfide (thioether)
$\text{R}_1-\text{N} \begin{matrix} \nearrow \text{R}_2 \\ \searrow \text{R}_3 \end{matrix}$	amino (primary amine, $\text{R}_2 = \text{R}_3 = \text{H}$ secondary amine, $\text{R}_3 = \text{H}$ tertiary amine, $\text{R}_1, \text{R}_2, \text{R}_3 = \text{C}$ aniline if $\text{R} = $  )

$\text{R}_1-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}_2$	carbonyl (ketone, aldehyde when $\text{R}_2 = \text{H}$ )
$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	carboxy (carboxylic acid)
$\text{R}_1-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}_2$	ester (carboxylic acid ester)
$\text{R}_1-\overset{\text{O}}{\parallel}{\text{C}}-\text{S}-\text{R}_2$	thioester



**Physicochemical Properties**



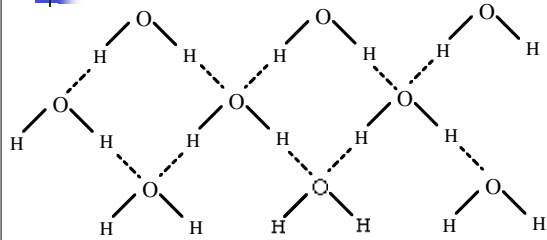
## Water Solubility

- The amount of a substance that dissolves in a given quantity of water at a given temperature to form a saturated solution
- Think of it as the escaping tendency of molecules from one another when placed in water

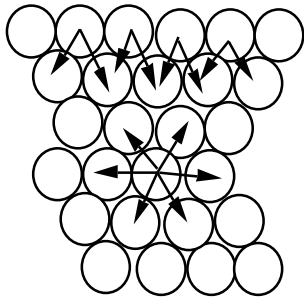
## Limitations to Water Solubility

- Regular, highly ordered structure of water
  - Results from high degree of hydrogen bonding
  - Cause of very high surface tension for such a small molecule
    - Surface tension is the intermolecular, cohesive attraction between like molecules of a liquid that cause it to minimize its surface area
  - Cause the high boiling point of water
- A solute dissolving in water has to disrupt the orderly structure of water (with consequent energy costs)
  - Think of it as punching a hole in the water

## Orderly structure of water due to H-bonding

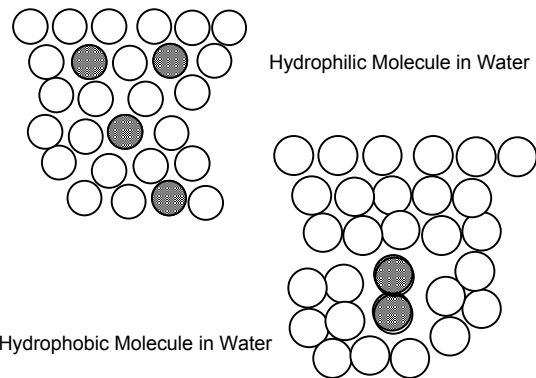


**Intramolecular attractions among water molecules give water its high surface tension; i.e., the amount of energy needed to overcome the molecular attractions**



Hydrophilic Molecule in Water

Hydrophobic Molecule in Water



## Phase Transfer Processes

- Reversible partitionings of dilute concentrations of a compound between two phases
  - Can be thought of as the “escaping” tendency of molecules from one phase into another (a.k.a. fugacity)
- Expressed by the partition coefficient
  - Ratio of the concentration of the chemical in one phase (air, soil, biological tissue, organic solvent) relative to the concentration in water

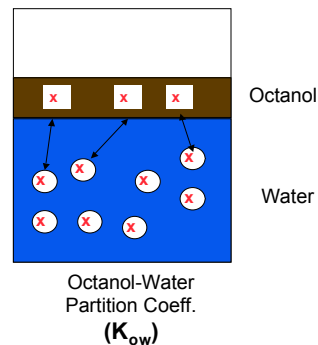
## Organic Solvent-Water Partitioning

- Octanol-Water Partition Coefficient
  - Partitioning behavior is between two immiscible liquids
- Octanol used as the partitioning solvent against water
  - Surrogate for an organism's membranes
- $K_{ow} = C_s/C_w$ , where  $C_s$  is the abundance in the organic solvent phase &  $C_w$  in the water

## Kow

- If place an organic compound in water, and then add octanol, the compound will move from water into octanol until the system is at equilibrium
  - The concentration at equilibrium would represent the lowest energy state
  - The lower the water solubility, the greater the tendency to move into the octanol phase

### Oil:Water







## Biological Significance of Kow

- Kow is often expressed in log form
  - For example, a Kow of 1000 would be express as  $\log Kow = 3$
  - The higher the log Kow, the comparatively greater the hydrophobicity
- Compounds with higher Kow's tend to diffuse across membranes faster compared to those with lower Kow's
  - However, there are some limitations to this generality at very high Kow's