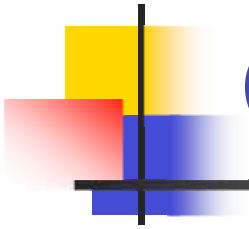
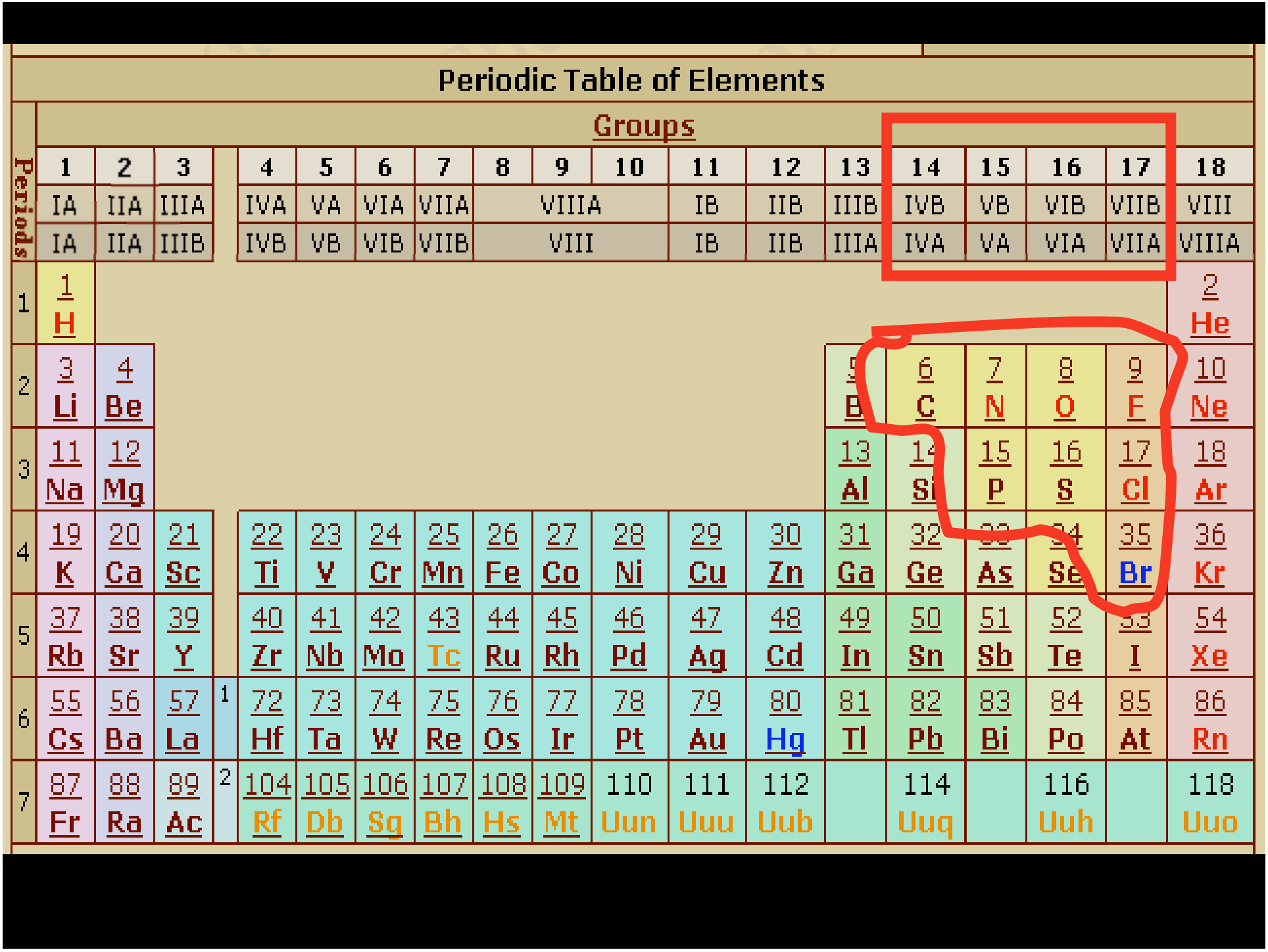
ES/RP 531
Fundamentals of Environmental Toxicology

Chemistry Review Addendum

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
Groups
Periods
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
IA IIA IIIA IVA VA VIA VIIA VIIIA IB IIB IIIB IVB VB VIB VIIB VIII
IA IIA IIIB IVB VB VIB VIIB VIII IB IIB IIIA IVA VA VIA VIIA VIIIA
1 1 H 2 He
2 3 Li 4 Be 5 B 6 C 7 N 8 O 9 F 10 Ne
3 11 Na 12 Mg 13 Al 14 Si 15 P 16 S 17 Cl 18 Ar
4 19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr
5 37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe
6 55 Cs 56 Ba 57 La 1 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn
7 87 Fr 88 Ra 89 Ac 2 104 Rf 105 Db 106 Sg 107 Bh 108 Hs 109 Mt 110 Uun 111 Uuu 112 Uub 114 Uuq 116 Uuh 118 Uuo

				# of Electrons in Shell[a]						
Name	Symbol	Atomic Number	Atomic Mass	1 (K)	2 (L)	3 (M)	4 (N)	5 (O)	Net Charge of Kernel	No. of Covalent Bonds
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**	

Number of Covalent Bonds that Elements Can Have Helps Understand Molecular Structure

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

Electronegativity increases from left to right across the rows of the periodic table.

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

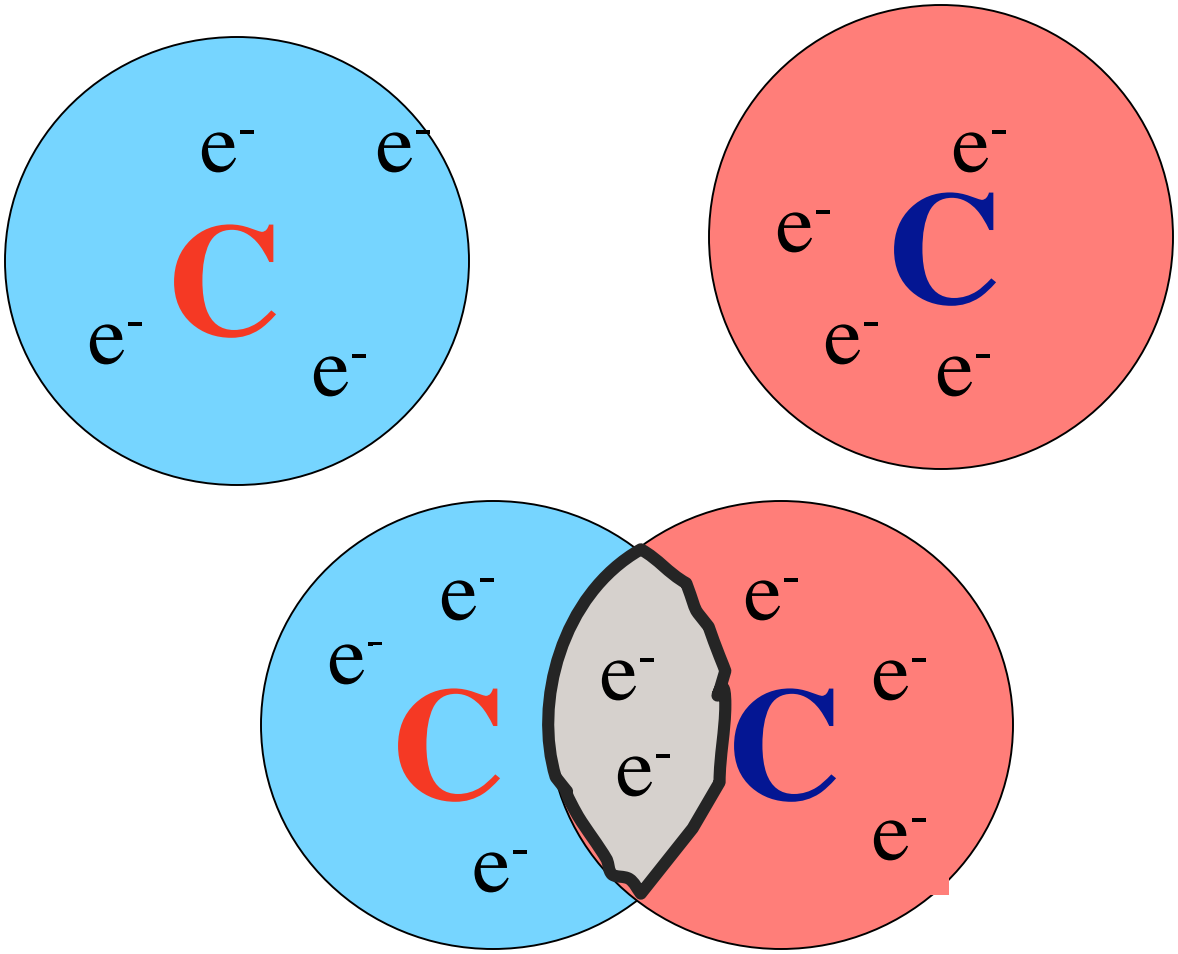
		H 2.2					
		C 2.5	**N** 3.0	**O** 3.5	**F** 4.0		
			P 2.2	**S** 2.5	**Cl** 3.0		
					Br 2.8		
					I 2.5		

Increasing Kernel Size

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

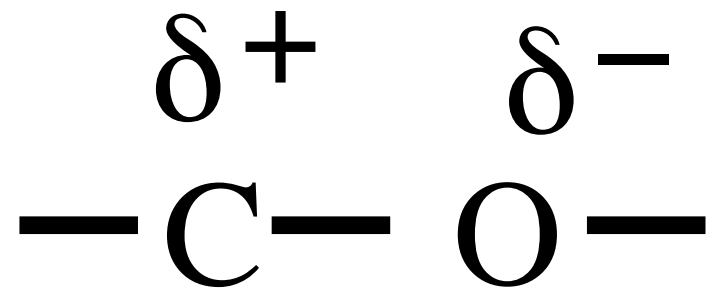
Covalent Bonds

- 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

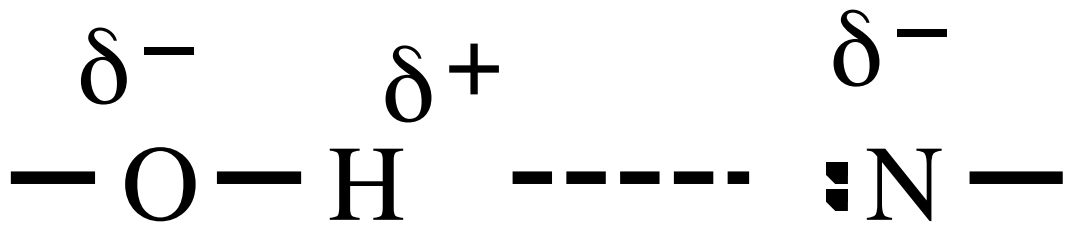


Ionic Bonding $Na^+ Cl^-$

- 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 too 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

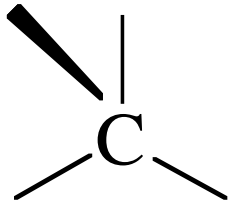
Hydrogen Bonding

- 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 as an unbonded pair of electrons
- Forms a hydrogen bond; not as strong as covalent or ionic bond, but it can form stable molecular interactions

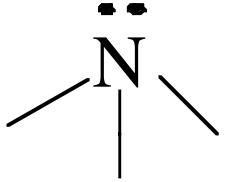


Geometry (Bond Angles)

- 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;

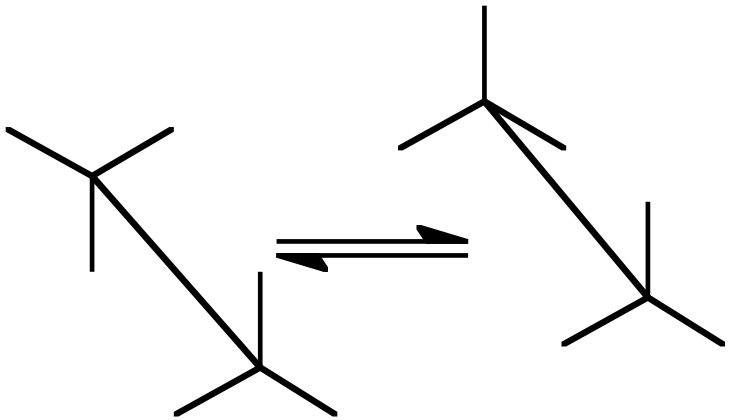


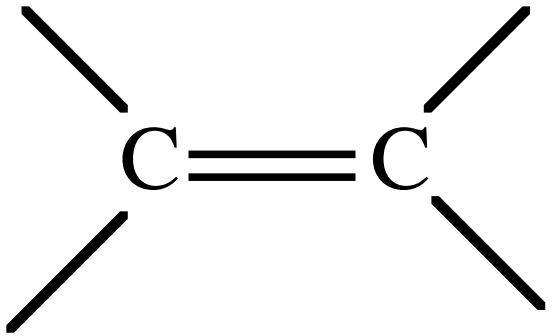
➢Nitrogen often uses three valence electrons (with an unpaired electron available for bonding an electron deficient species like H); its spatial geometry tends to by trigonal



Geometry (Bond Angles)

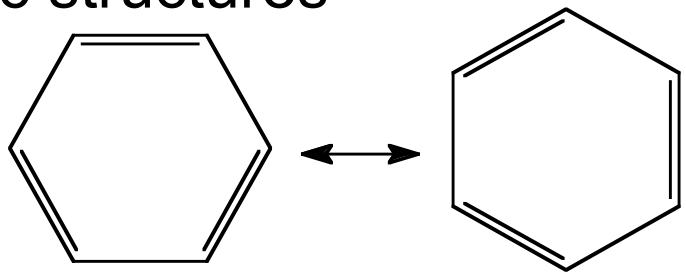
- Double bonds will make a molecule more rigid, giving the atoms less degrees of freedom to flop around and rotate about each other





Geometry (Bond Angles)

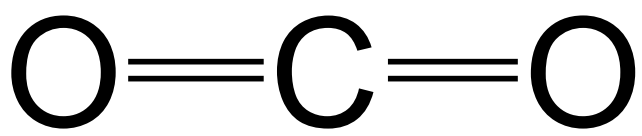
- Aromatic structures (alternating double bonds in ringed systems) tend to be planar (i.e., less free rotation of the carbon atoms)
  - Characterized by delocalized ‘pi’ electrons that can impart some electronegative character
  - Aromatic structures also are more stable than noncyclic structures



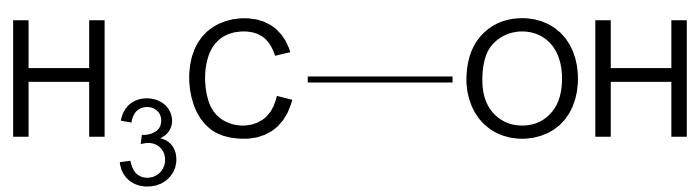
➢Note that double bonds in linear structures also have delocalized ‘pi’ bonds

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 the determinant of overall polarity is the vector sum of the individual polar bonds, which is called the dipole moment

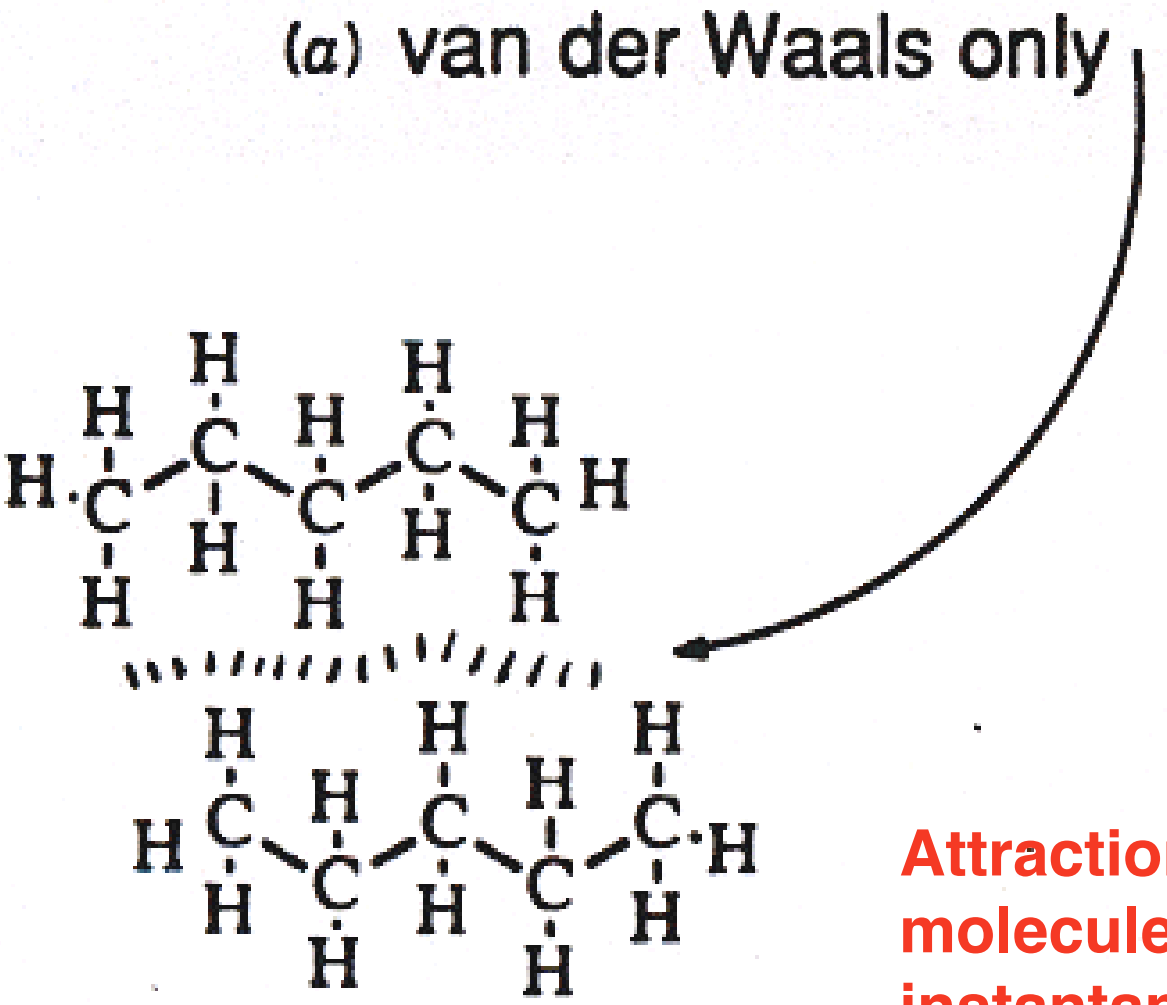


Carbon dioxide



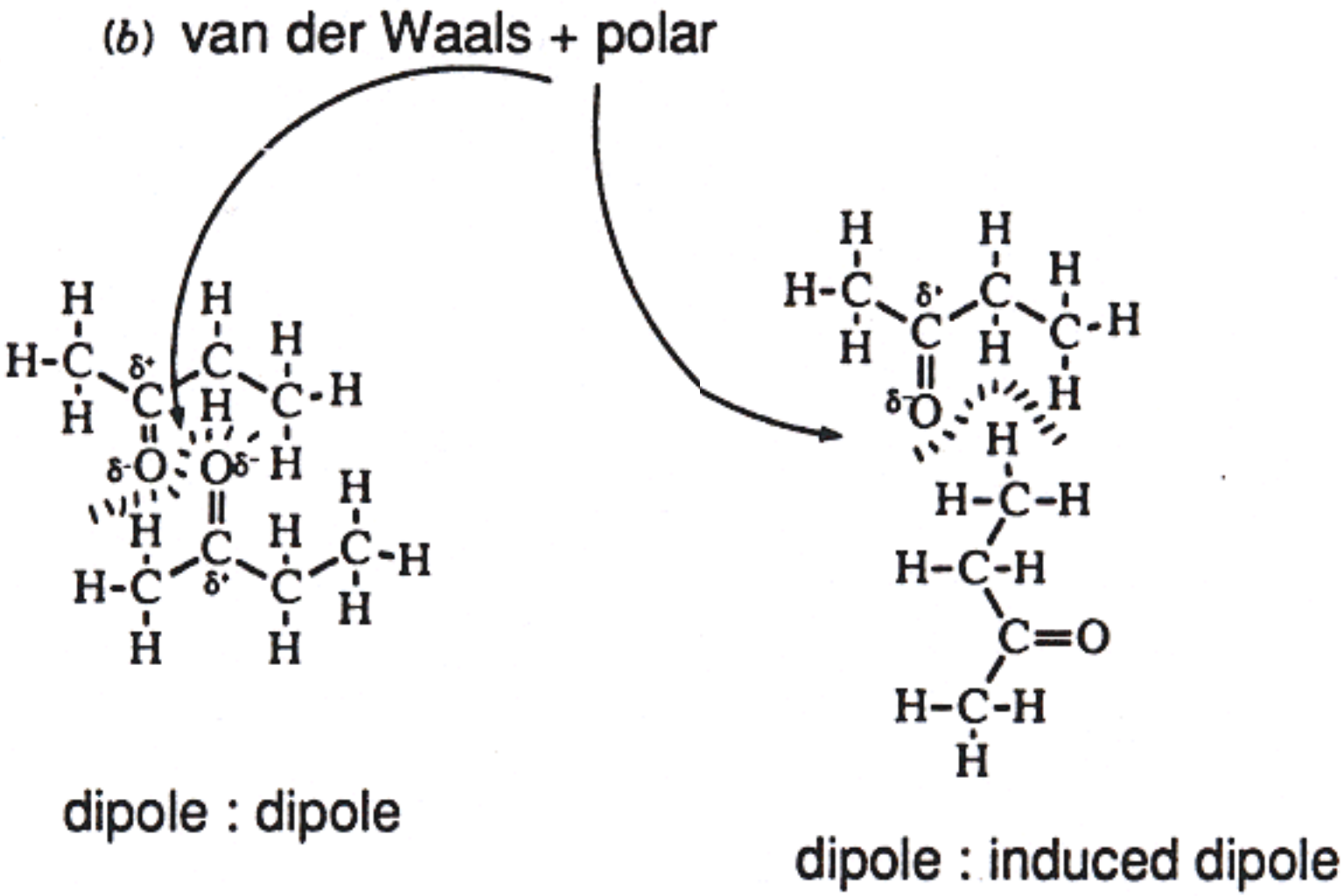
Methanol

Intermolecular Forces



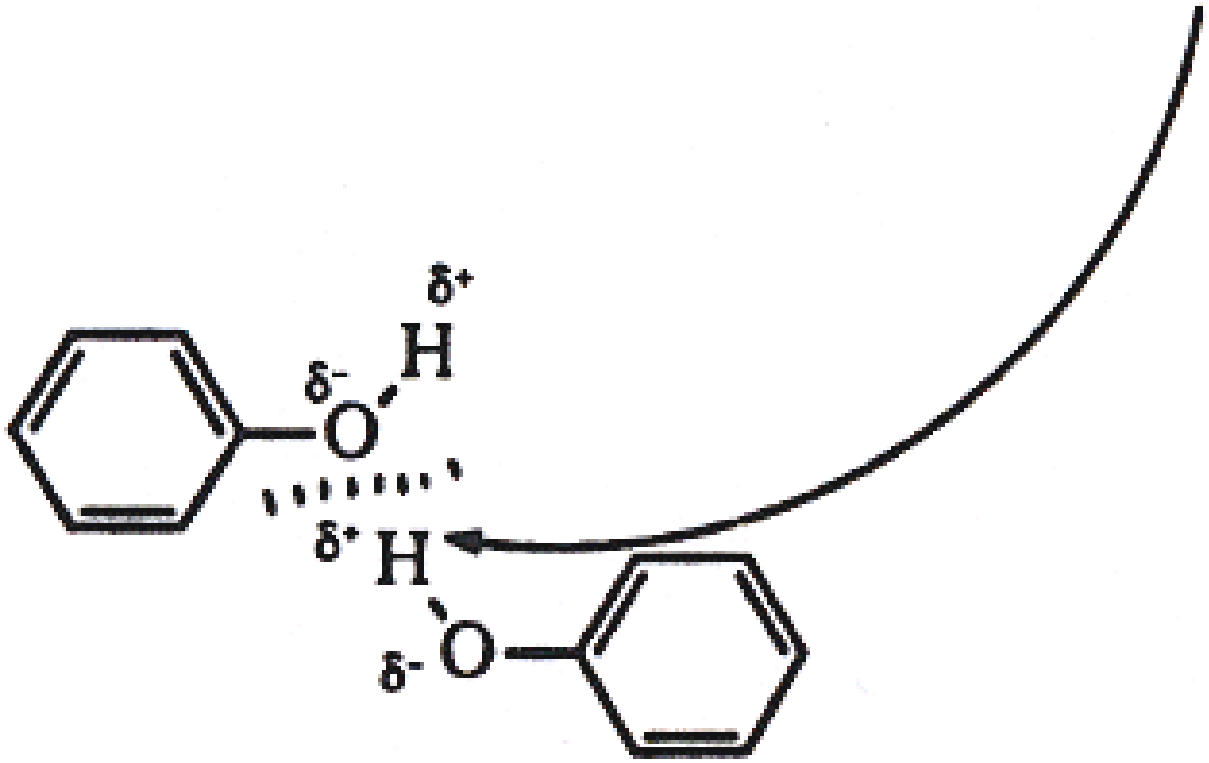
Attraction between molecules due to instantaneous dipole moments

Intermolecular Forces



Intermolecular Forces

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



The various intermolecular interactions can explain various physicochemical properties.

Substance	Molecular Mass	Dipole Moment μ (D)	B oiling 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

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

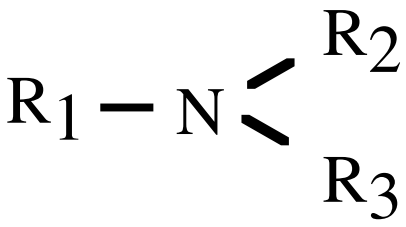
-C-C-C-C- alkyl (can be denoted by R)

R-OH hydroxy (alcohol, if phenol then R = )

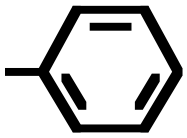
R-SH mercapto (thiol, mercaptan)

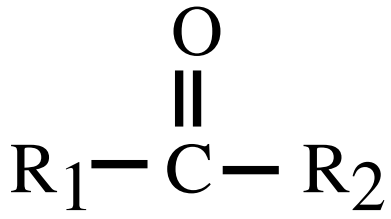
R_1-O-R_2 ether

R_1-S-R_2 sulfide (thioether)

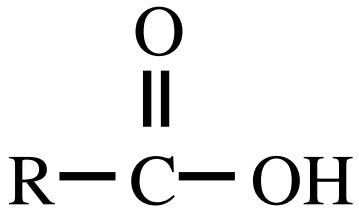


amino (primary amine, R2 = R3 = H
secondary amine, R3 = H
tertiary amine, R1, R2, R3 = C

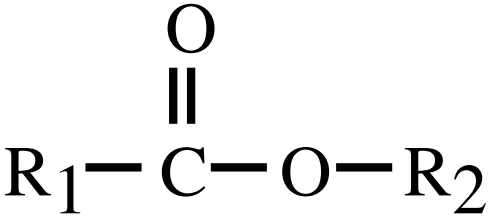
aniline if R = 



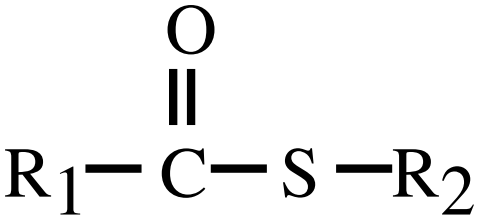
carbonyl (ketone, aldehyde when $R_2 = H$



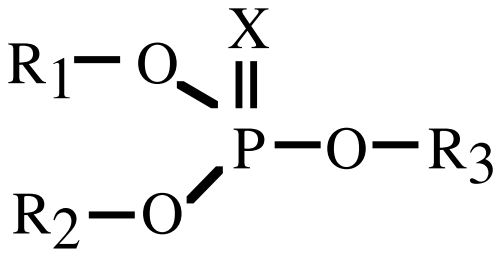
carboxy (carboxylic acid)



ester (carboxylic acid ester)

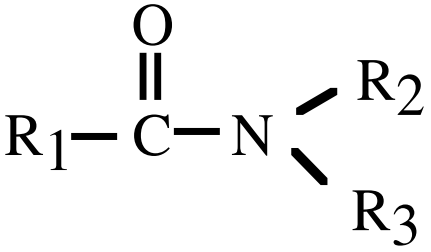


thioester



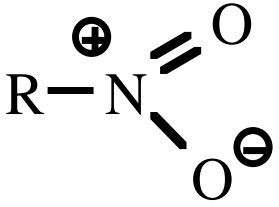
Phosphate ester if X = O;

Thiophosphate if X = S

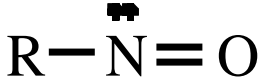


amide

nitrile



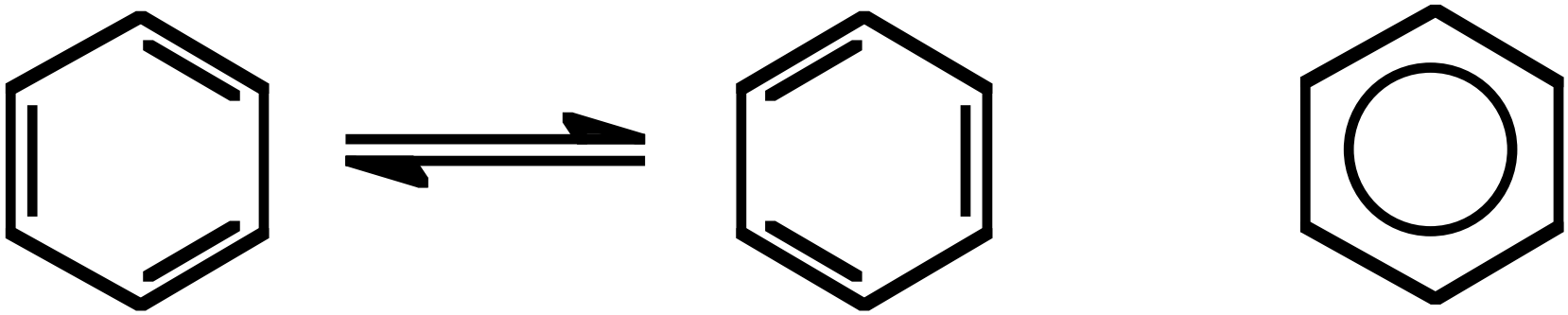
nitro ,

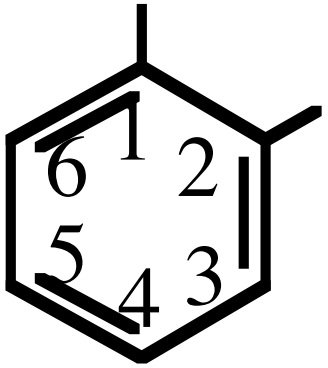


nitroso

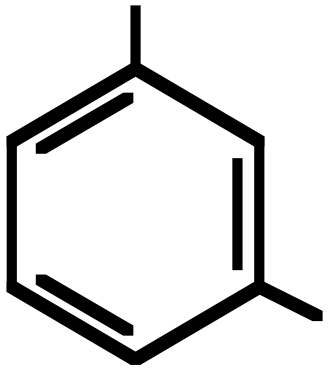
Saturation

Unsaturation

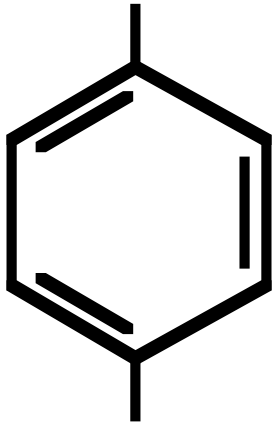




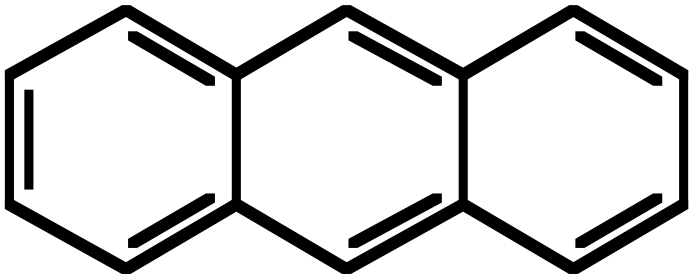
ortho



meta



para



anthracene

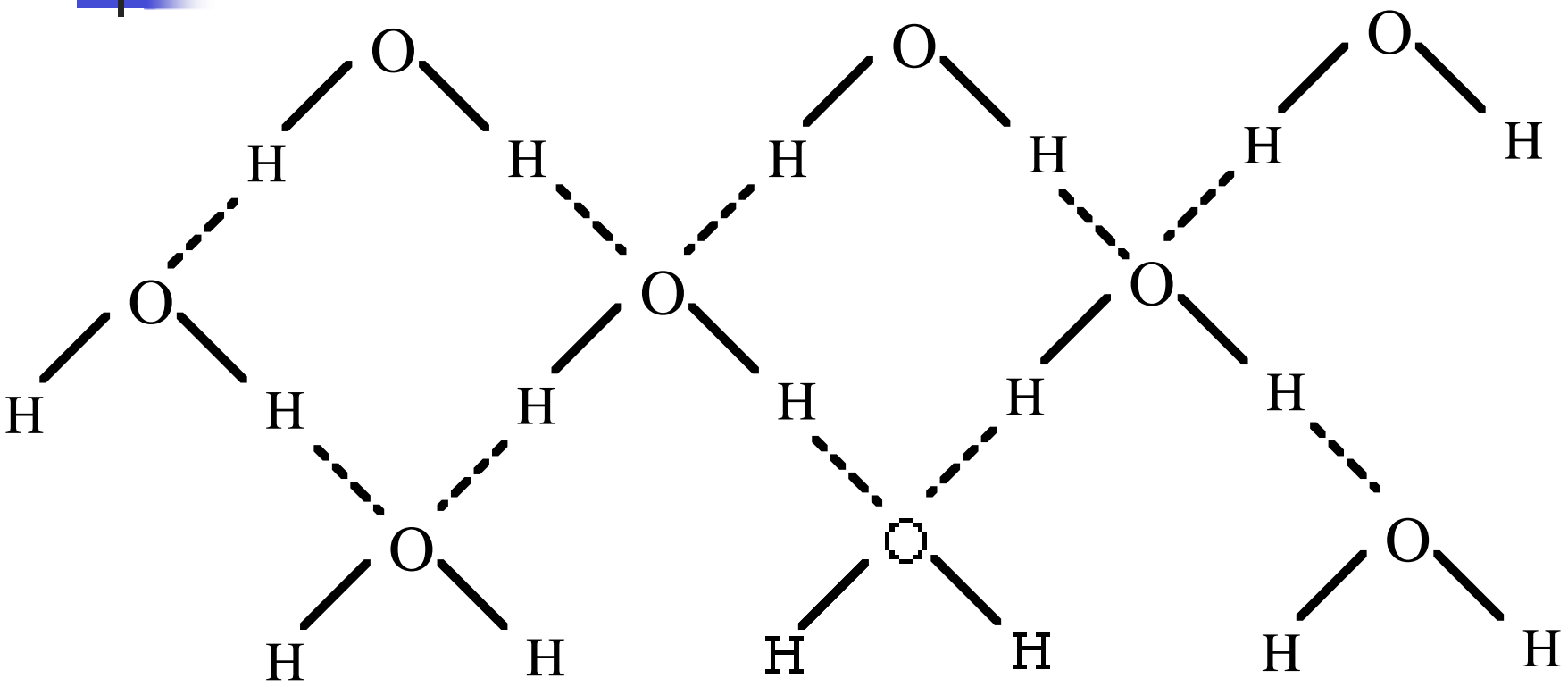
Water Solubility

- 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

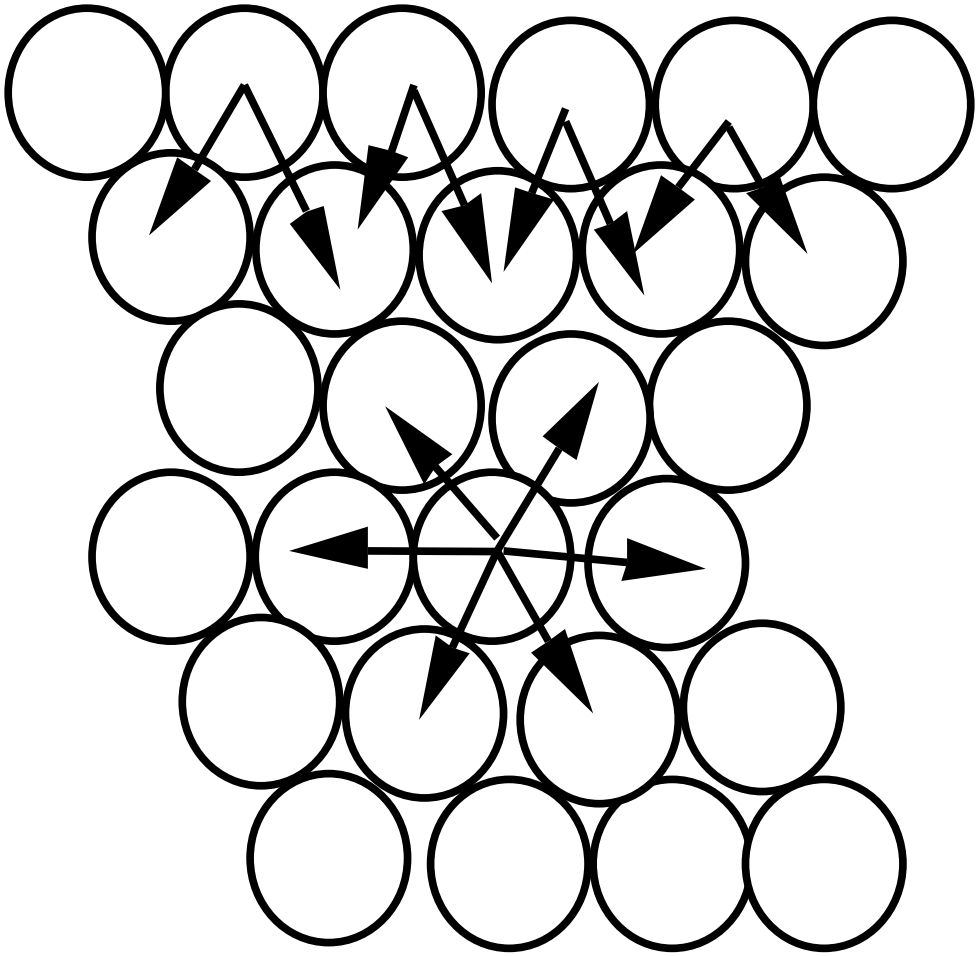
Limitations to Water Solubility

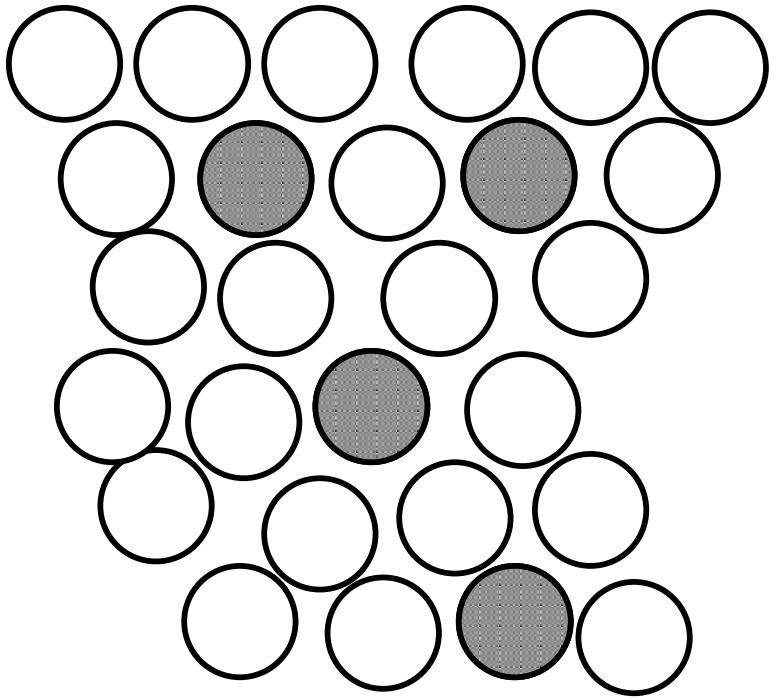
- Regular, highly ordered structure of water
  - Results from high degree of hydrogen bonding
  - Cause of very high surface tension for such a small molecule
    - Surface tension is the intermolecular, cohesive attraction between like molecules of a liquid that cause it to minimize its surface area
  - 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

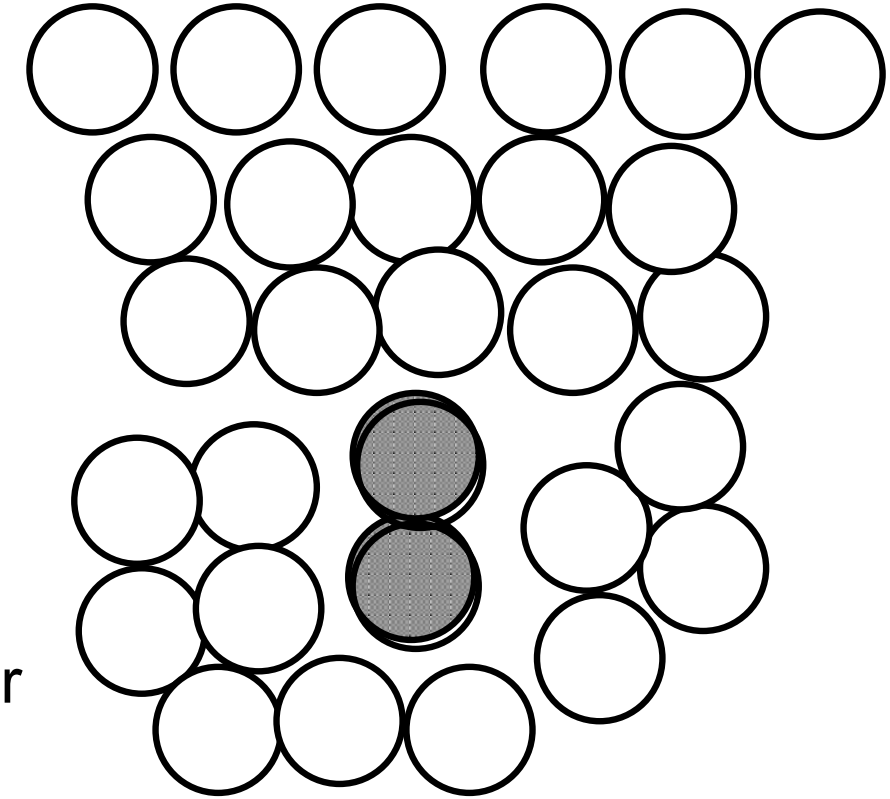


Intramolecular attractions among water molecules give water its high surface tension; i.e., the amount of energy needed to overcome the molecular attractions





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

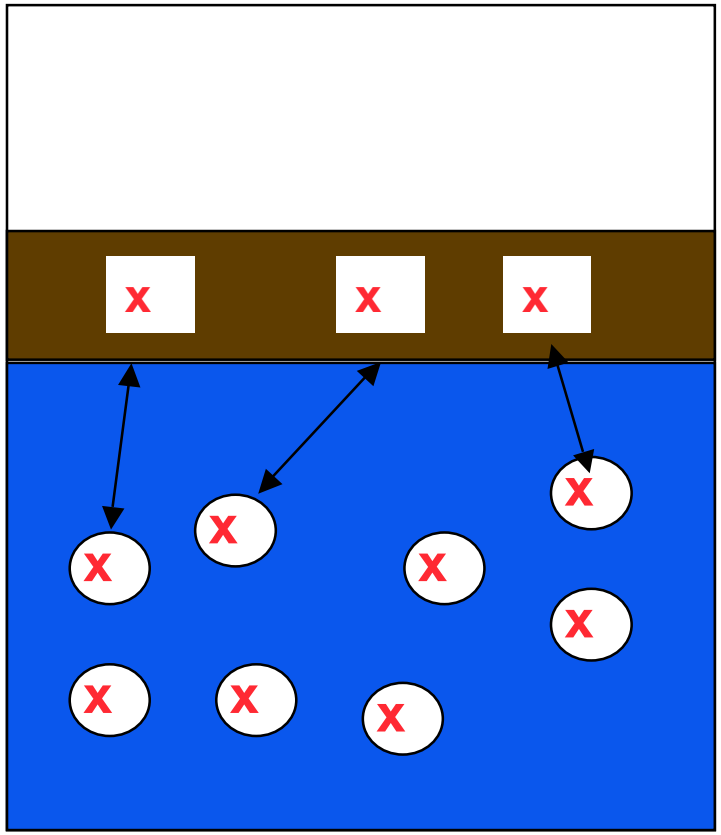
Organic Solvent-Water Partitioning

- 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 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



Octanol-Water
Partition Coeff.
(K_{ow})

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