Chemistry Review: Reactivity, Bonds, Reactions, Enzymes, Water

Lecture 2

Objectives

Understand/know/focus on/note

- what the subatomic particles of the atom are
- terms associated with atoms & chemistry: element, atomic number, mass number, isotope
- hydrogen and its isotopes
- recognition of elements that are metals and nonmetals
- meaning of valence shell
- electronegativity as an indicator of atom's strong (or weak) need for electrons
- what a chemical reaction is and mass & charge should be balanced

Objectives 2 of 2

Understand/know/focus on/note

- what a chemical reaction is and mass & charge should be balanced
- there is a spectrum of bonding related to electronegativity:
  covalent <--> polar covalent <--> ionic
- other types of bonding or interaction between atoms and molecules: hydrogen, van der Waals, hydrophobic interaction
- structure of water and usefulness of its properties
- what catalysis means

Quick Drive Through Chemistry

- Atom: structure/properties
- Interacting ("bonded") atoms: molecules and such
- Electrons: orbitals atomic and molecular
- Quantum nature of chemistry lightly discussed
- Relationship of Periodic Table to biological science

The Atom

- Atoms are made of three subatomic particles
  1. Protons

     which actually give the element its identity
  2. Electrons

     chemistry is really about electrons, because it is electrons that allow atoms to bond to each other
  3. Neutrons

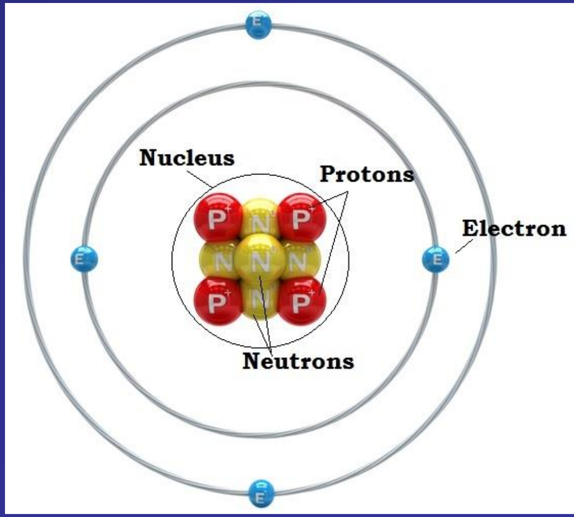
     it takes about 1800 electrons to equal mass of a proton, and the neutron is slightly bigger than the proton by 0.15%.

Because neutrons have a mass that is slightly higher than sum of a proton & electron, and because neutrons have been shown to decay to a proton, electron, and some other particles in physics, speculation is that a neutron is special gluing of a proton and electron.

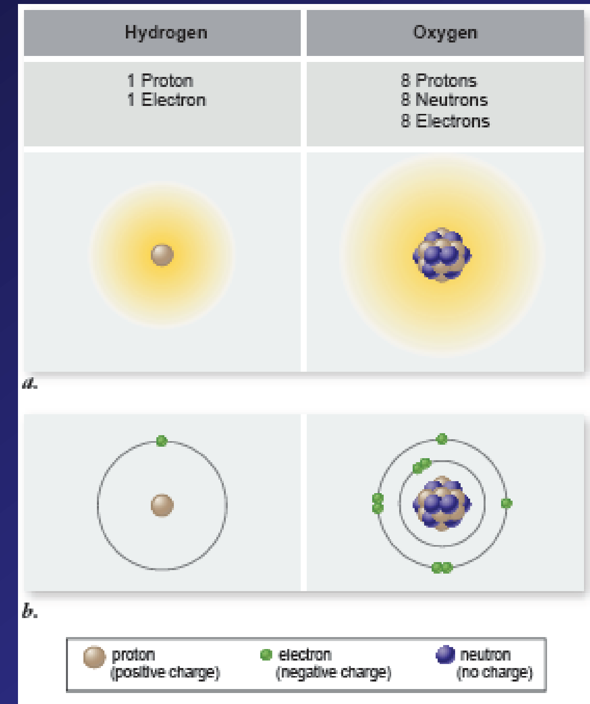
Nucleus & Orbitals

- Protons and neutrons organized in the nucleus
- Electrons spatially located outside of the nucleus
- Electrons "orbit" the nucleus in orbitals but not like planets revolving around the sun
- Their position/location is determined by probabilities calculated by complex mathematical expressions
- Each orbital pairs two electrons of opposite spin

  Yes, electrons have a spin just as the Earth rotates on an axis, and this spin generates a magnetic field



Elements

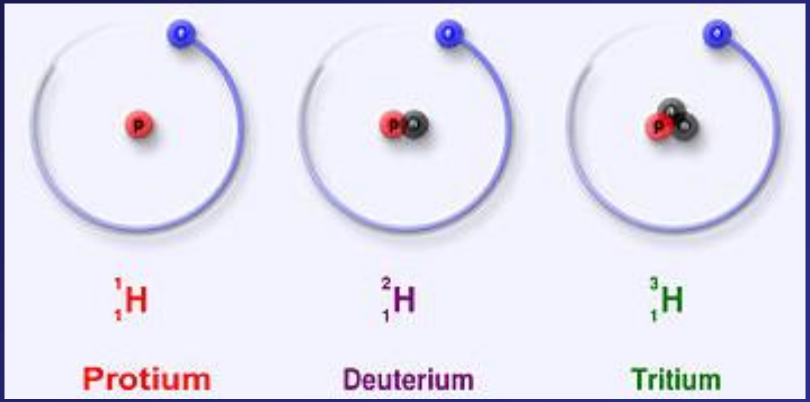


- Elements all have the same number of protons
- But elements can have different number of neutrons
- An element with different numbers of neutrons is an isotope of the element
- When referring to an isotope of an element, use this ${}^{Z}_{A}X$

Where

- *X* is element symbol (e.g, hydrogen = H)
- *A* is atomic number, = # protons (A = 1 for H)
- *Z* is mass number, = #protons + #neutrons

Hydrogen

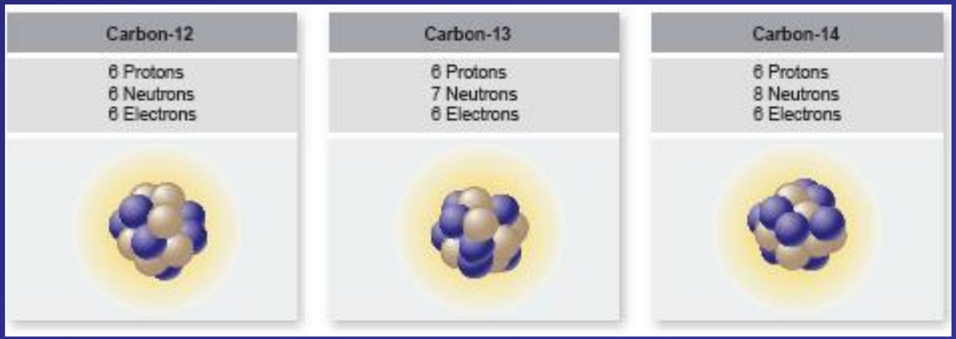


Hydrogen has three isotopes:

1. Protium ($^1{}_1H$)
   - 1 proton, 0 neutrons
   - usually just called "hydrogen"
   - 99.9885% of all hydrogen isotopes in nature is this isotope
2. Deuterium ($^2{}_1H$)
   - 1 proton, 1 neutron
   - It is a stable isotope
   - 0.0115% of hydrogen isotopes is deuterium in nature
3. Tritium ($^3{}_1H$)
   - 1 proton, 2 neutrons
   - It is an unstable isotope, meaning it is radioactive
   - Probably less than 0.0000001% in natural abundance

Carbon

- Organic chemistry *is* the chemistry of carbon
- Total of 6 electrons in two shells (n =1 and n = 2)
- Will use 4 electrons in its valence shell to bond with other atoms
- Other atoms it bonds with in biological organisms:
  - H, N, O, and other C atoms mostly
  - S, P atoms also



Periodic Table of Elements

Biologists should know what elements are (1) metals and (2) nonmetals generally

Main groups — Main groups — Transition metal groups

Period	1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12	3A 13	4A 14	5A 15	6A 16	7A 17	8A 18
1	1 H 1.00794																	2 He 4.00260
2	3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
3	11 Na 22.98977	12 Mg 24.305											13 Al 26.98154	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.9045	54 Xe 131.29
6	55 Cs 132.9054	56 Ba 137.33	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.0254	89 †Ac 227.0278	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Ds (271)	111 Rg (272)	112 (285)	113 (284)	114 (289)	115 (288)	116 (292)		118 (294)

Lanthanides	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.965	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
Actinides	90 Th 232.0381	91 Pa 231.0399	92 U 238.0289	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Metals — Metalloids — Nonmetals

The periodic table of the elements. Each element is identified by a one- or two-letter symbol and is characterized by an *atomic number*. The table begins with hydrogen (H, atomic number 1) in the upper left-hand corner and continues to the yet unnamed element with atomic number 118. The 14 elements following lanthanum (La, atomic number 57) and the 14 elements following actinium (Ac, atomic number 89) are pulled out and shown below the others.
Elements are organized into 18 vertical columns, or *groups*, and 7 horizontal rows, or *periods*. The two groups on the left and the six on the right are the *main groups*; the ten in the middle are the *transition metal groups*. The 14 elements following lanthanum are the *lanthanides*, and the 14 elements following actinium are the *actinides*; together these are known as the *inner transition metals*. Two systems for numbering the groups are explained in the text. Those elements (except hydrogen) on the left-hand side of the zigzag line running from boron (B) to astatine (At) are *metals*, those elements to the right of the line are *nonmetals*, and most elements abutting the line are *metalloids*.

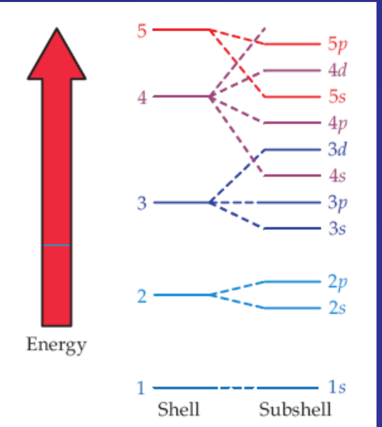
McMurry et al, *Fundamentals of General, Organic and Biological Chemistry*, 6 Ed, p 58

Shells of Electrons & Periodic Table

- Each period (row) of the Periodic Table corresponds to a "shell" of electrons
- Shells are designated by the principal quantum number *n* by chemists: *n* = 1, 2, 3, …

  letters *K, L, M, N, O,* … by physicists
  - Within the shells are subshells: *s, p, d, f*
  - In quantum chemistry/physics, each electron is described by a set of four quantum numbers: $\{n, \ell, m_\ell, m_s\}$
- There is a correspondence between a shell's energy and its shell number/letter (distance from nucleus): higher shell number relates to higher energy of the electron
- The maximum number of electrons in each shell (period) is 2, 8, 8, 18, 18, 32, 32, ..

Shell name	Subshell name	Subshell max electrons	Shell max electrons
K	1s	2	**2**
L	2s	2	2 + 6 = **8**
	2p	6	
M	3s	2	2 + 6 + 10 = **18**
	3p	6	
	3d	10	
N	4s	2	2 + 6 + 10 + 14 = **32**
	4p	6	
	4d	10	
	4f	14	



▲ **FIGURE 3.6 Order of orbital energy levels.** Above the 3*p* level, there is some crossover of energies among orbitals in different shells.

The Valence Shell

- The outermost shell of electrons is where all the chemistry happens
- Atoms want to have "complete" shells
  - This means shedding or giving up electrons if there are too few
  - Grabbing electrons from other atoms if they need only a few
  - Giving up electrons means acquiring a positive + charge
  - Grabbing electrons means acquiring a negative – charge
- In forming molecules or crystals, atoms form complete stable shells by having the complete set of electrons in their valence shell, whether or not they share them with other atoms

Electronegativity

- The affinity of an atom for one or more electrons
- The factors affecting electronegativity are
  - atom's need to acquire electrons to complete shell
  - size of atom: smaller atoms more electronegative
- atoms are given a value that indicates their electronegativity: the higher the value, the higher the affinity (the more the atom wants electrons)
- decreasing order of electronegativity: F, O, Cl, N, Br, I, C, S, Se, H, P

  that is, F wants it most, P wants it least in that list
- Differences in electronegativity account for type/character of bonding (shown in later slide)

Electronegativity Quantitated

V·T·E

Periodic table of electronegativity by Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group → / ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

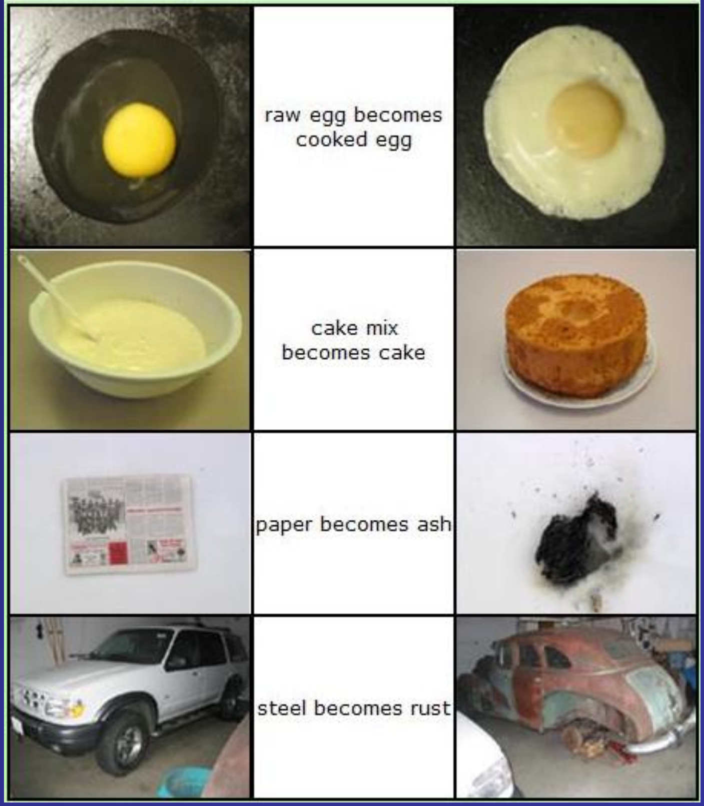
Values are given for the elements in their most common and stable oxidation states.

http://en.wikipedia.org/wiki/Electronegativity

Chemical Reactions

- Bond breaking and formation
- Movements of electron (singly or as pairs) from one atom or molecule to another
- Atoms or molecules acquiring electrical charges positive or negative (or losing them: uncharged)

Common, daily chemical reactions

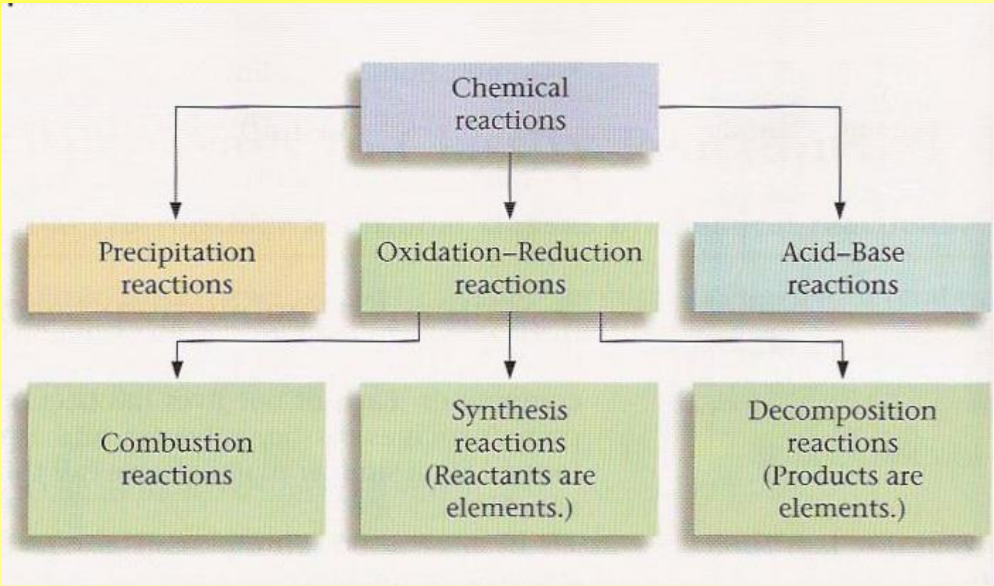


https://wikis.engrade.com/science1012011/chemicalreactions

Types of Chemical Reactions

6 Types of Reactions

1. Combustion $C_{10}H_8 + 12\ O_2 \rightarrow 10\ CO_2 + 4\ H_2O$
2. Synthesis $8\ Fe + S_8 \rightarrow 8\ FeS$
3. Decomposition $2\ H_2O \rightarrow 2\ H_2 + O_2$
4. Single Displacement $Mg + 2\ H_2O \rightarrow Mg(OH)_2 + H_2$



5. Double Displacement
   $Pb(NO_3)_2 + 2\ KI \rightarrow$
   $PbI_2 + 2\ KNO_3$
6. Acid-Base
   $HBr + NaOH \rightarrow$
   $NaBr + H_2O$

http://quinton.pbwiki.com/f/textbookfig712edit.jpg

Balancing Mass & Charge

Laws of conservation of mass and electrical charge require that chemical (reaction) equations be balanced for mass and charge

$$CaCO_3\,(s) \leftrightarrow Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$
$$CO_2\,(g) \leftrightarrow CO_2\,(aq)$$
$$CO_2\,(aq) + H_2O \leftrightarrow H_2CO_3\,(aq)$$
$$H_2CO_3\,(aq) \leftrightarrow H^+\,(aq) + HCO_3^-\,(aq)$$
$$HCO_3^-\,(aq) \leftrightarrow H^+\,(aq) + CO_3^{2-}\,(aq)$$
$$H_2O \leftrightarrow H^+ + OH^-$$

http://ion.chem.usu.edu/~sbialkow/Classes/3600/Overheads/Carbonate/image020.gif

coefficients

$$\underbrace{2H_2 + O_2}_{\text{reactants}} \rightarrow \underbrace{2H_2O}_{\text{products}}$$

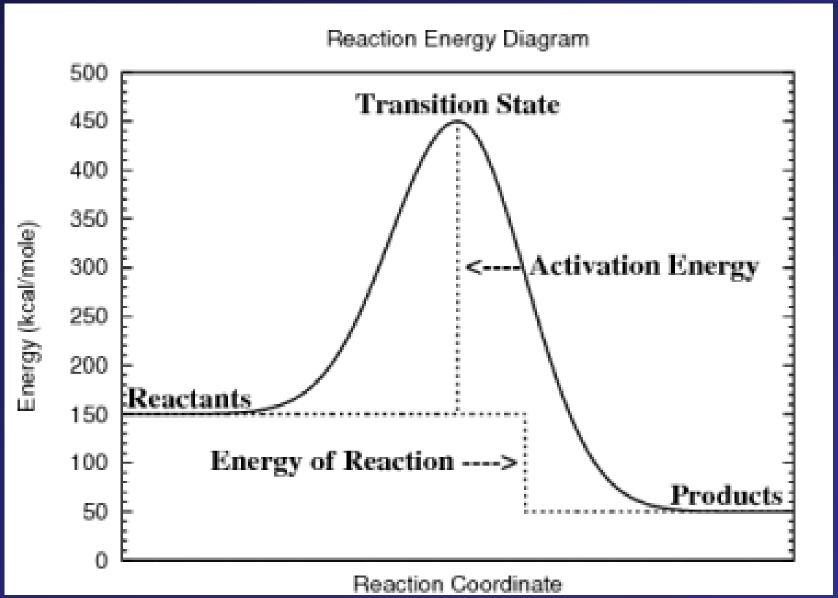
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

C=1		C=1
H=4	=	H=4
O=4		O=4

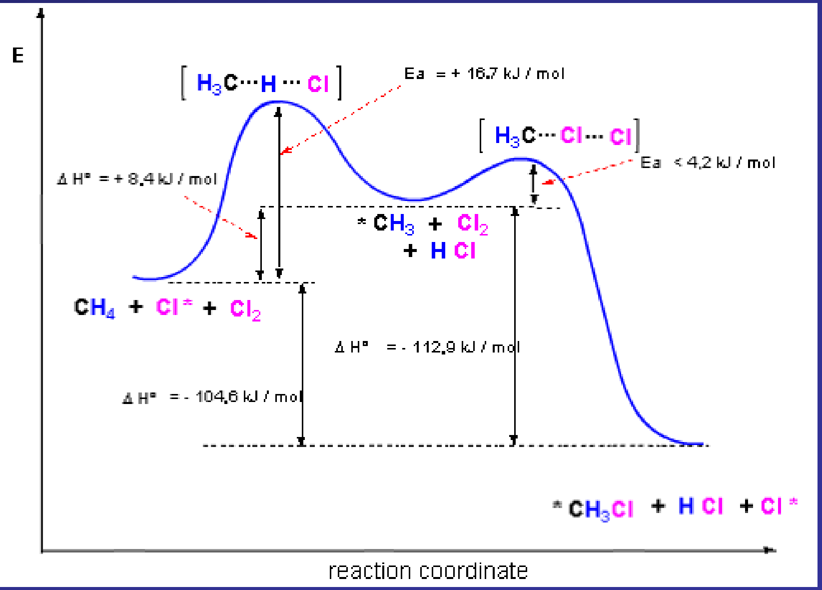
http://www.mikeblaber.org/oldwine/chm1045/notes/Stoich/Equation/balance4.gif

Reaction Energy Diagrams

- Diagrams show changes in the (potential) energy along a "reaction coordinate"
- A reaction coordinate is basically a state of the reaction: reactants, activated complexes or transition states, products
- Often show detail of energy values



http://www.personal.kent.edu/~cearley/gen50/review/rxnEnergy.png



Endothermic & Exothermic

- Exothermic Reactions

  reactions releasing energy: work done, heat released

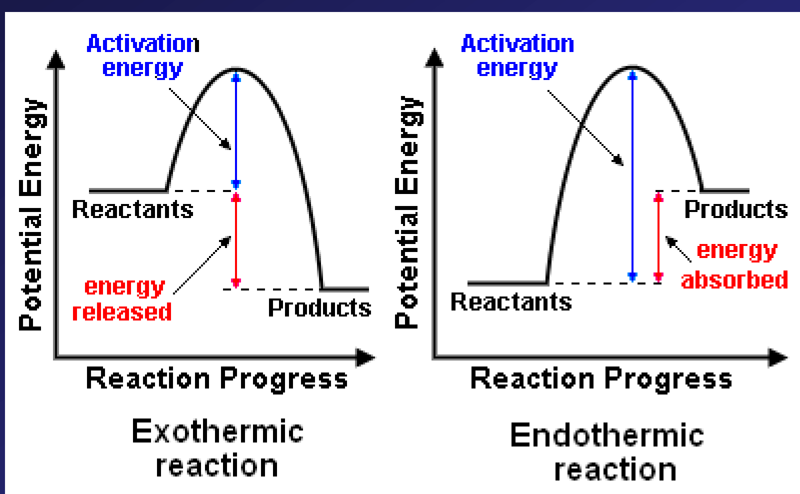
  gasoline combustion

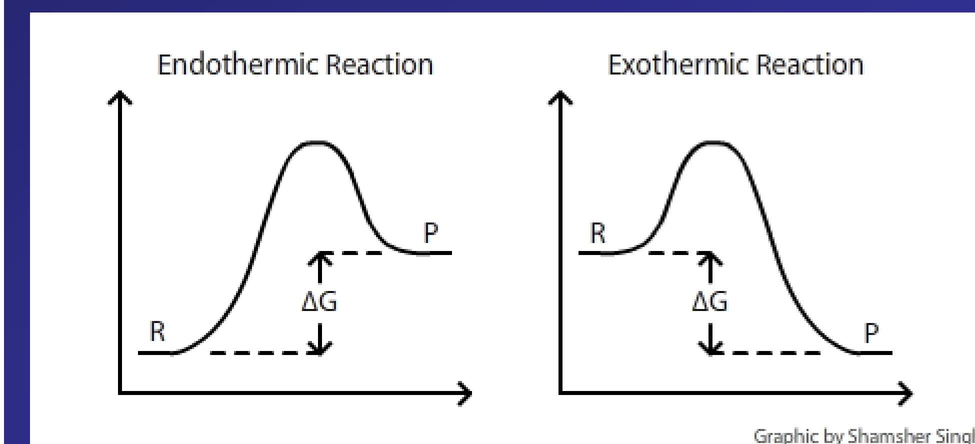
- Endothermic Reactions

  reactions requiring energy: put them on the hot plate

  dissolving urea in water

http://en.citizendium.org/images/f/fb/ExoEndo_Reax.png





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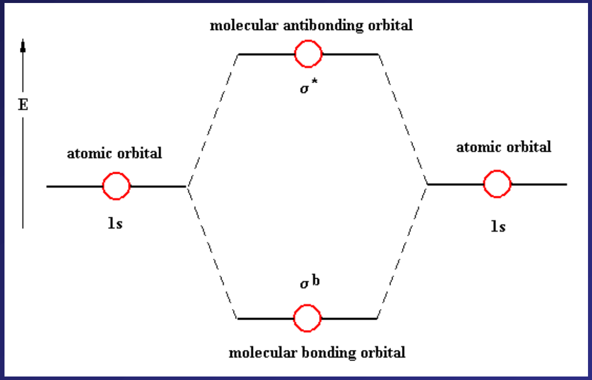
Bonding



- Atoms bond using electrons

  remember: chemistry is really about the electrons
- Electrons in atomic orbitals (AOs) come together between atoms in molecular orbitals (MOs), forming a bonding MO
- MOs have two paired (opposite spin) electrons just like AOs
  - *s* subshell AOs form σ (sigma)-type MOs (bonds)
  - *p* subshell AOs form π (pi)-type MOs (bonds)
  - there are anti-bonding MOs: they are an excited state type of orbital which, when filled with electrons, actually result in bond-breaking between atoms, not bond-making

Bonding Types & Strength

Type	**Description**	**Strength** (kcal/mol)
Ionic / Electrostatic	One atom gives up its electron(s) to another which really wants them: the result is ionized atoms bonding because of electrical attraction (unlike charges)	50-150
Covalent	Two atoms share the electrons in the bond, neither having a strongly competitive affinity for the electrons (small difference in electronegativity)	50-100 (single) 100-200 (double) 200-250 (triple)
Hydrogen Bonding	The hydrogen (H) atom is "shared" between two *more* electronegative atoms	2-10
Hydrophobic	A "bonding" driven by solvent with polar molecule (H_2O) that prefers to bond to itself (oil & water don't mix)	ND
van der Waals	bonding caused by "induced polarity" from one molecule to another causing a temporary weak electrical attraction	0.5-1.0

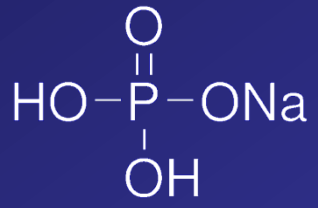
The Covalent Bond

- Two atoms that share equally the pair(s) of electrons

  Atoms bonding with selves (diatomic molecules) should always be covalent

  H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2

- Can be single, double, and triple bonds between atoms
  - $H_3C—CH_3$ (ethane) sigma bond
  - $H_2C{=}CH_2$ (ethene) sigma + pi bond
  - $HC{\equiv}CH$ (ethyne/acetylene) sigma + 2 pi bonds
  - H—H, O=O, N≡N, F—F, Cl—Cl, Br—Br



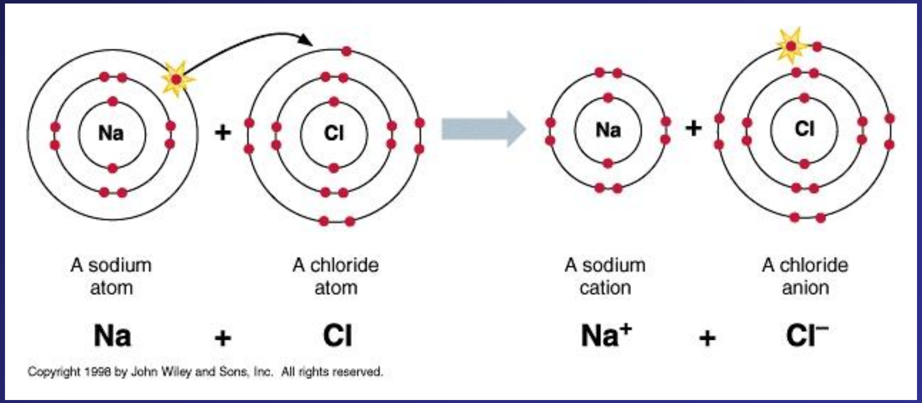
The Ionic / Electrostatic Bond

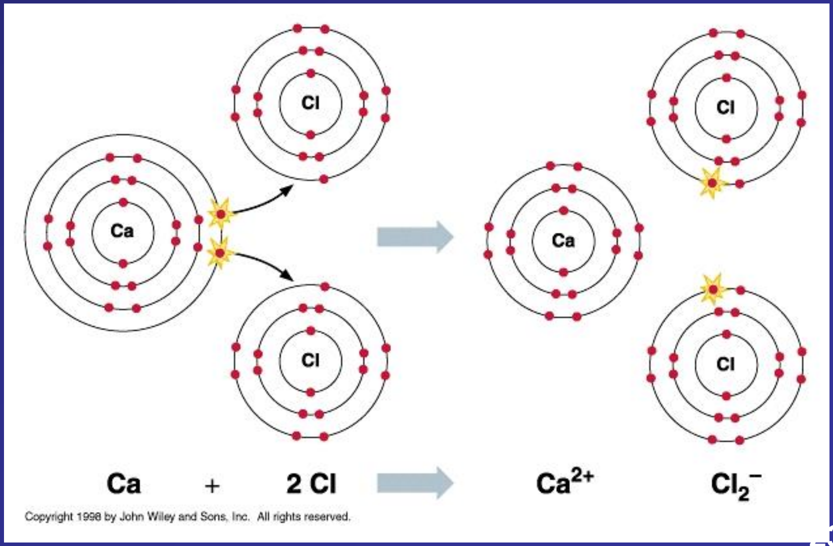
The bond created by an electrostatic attraction between positive and negative charges resulting from the complete transfer of electrons from one atom to another

$Na \rightarrow Na^+ + e^-$

$Cl + e^- \rightarrow Cl^-$

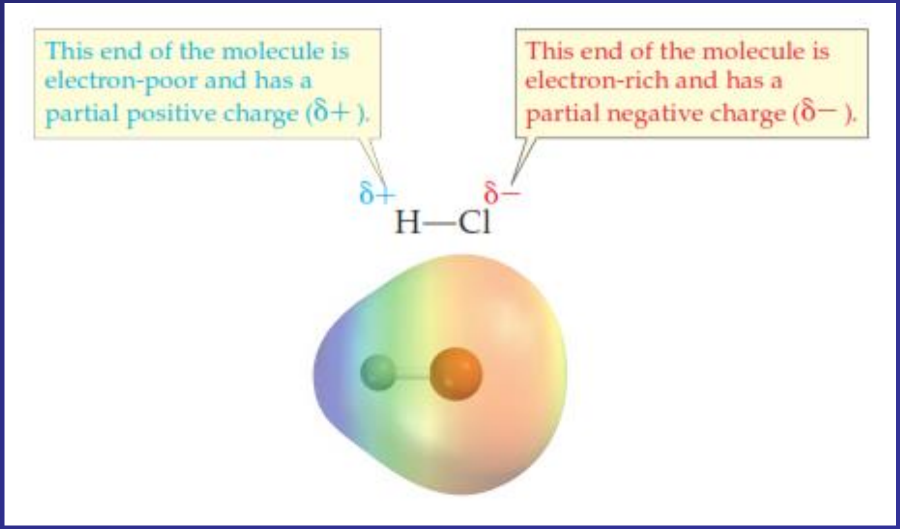
$Na + Cl \rightarrow Na^+ + Cl^-$





A Polar Covalent Bond

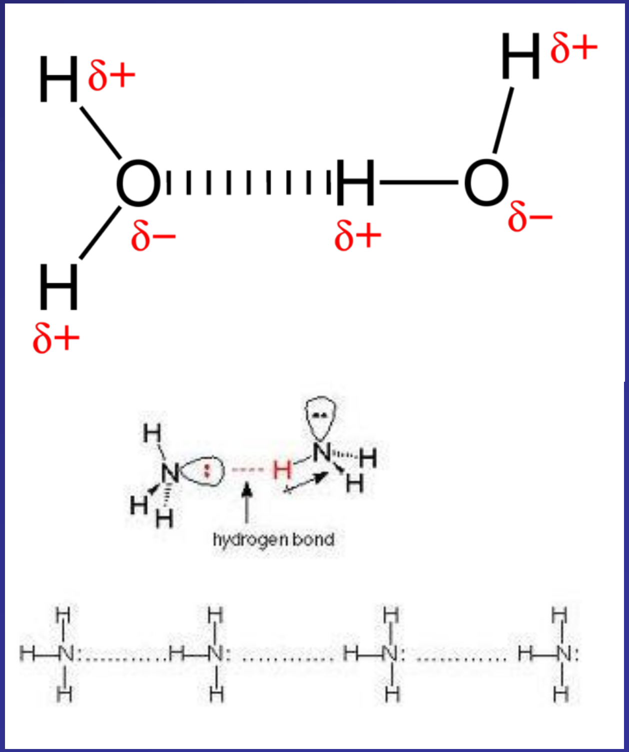
- A type of bond that has a mix of covalent and ionic character
- The difference in electronegativity of atoms is not such that one atom fully grabs another
- Bonds that are polar covalent:
  O–H, N–H, H–Cl/F (list shown later)
- The polar covalent bond accounts for the hydrogen bond



The Hydrogen Bond

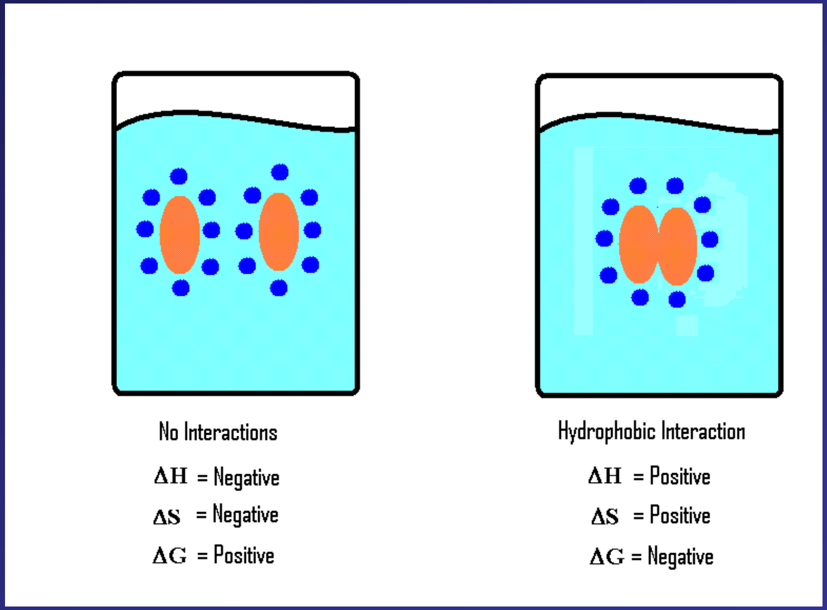
- The bonding of an H atom already covalently bonded to a more electronegative atom to another more electronegative atom on different molecule
- The presence of (a) nonbonding electron pairs in the more electronegative atom is a factor

- The presence of N–H and O–H groups in countless biomolecules makes the hydrogen bond significant in all aspects of biochemistry
- The double-strandedness of DNA and RNA is because of H-bonding. Polypeptide folding in proteins makes use of H-bonding



Hydrophobic Interactions

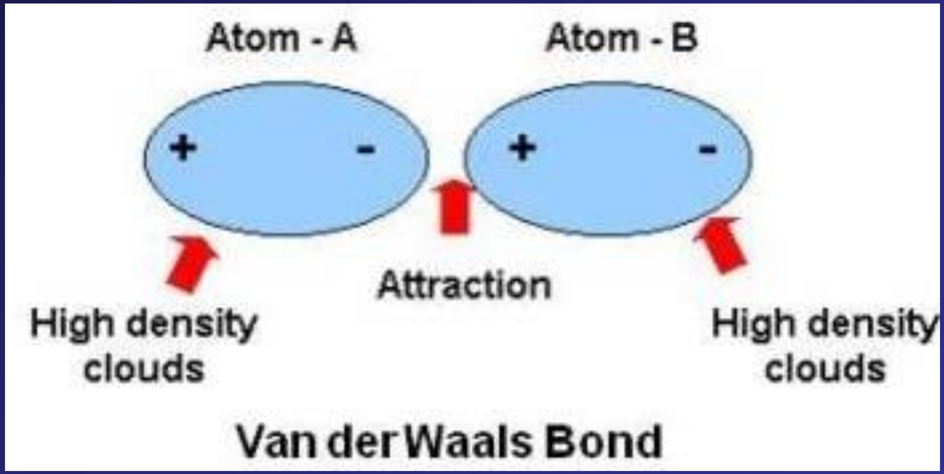
- There are no real forces between molecules in hydrophobic molecules associating or clustering together
- Instead, the free energy (G) of the solution favors water bonding with itself (by H-bonding) rather than interacting with molecules with which it has no affinity

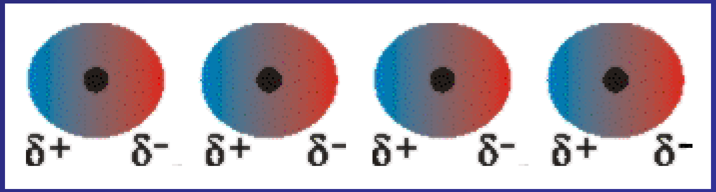


http://chemwiki.ucdavis.edu/@api/deki/files/8648/image9.GIF

van der Waals Forces

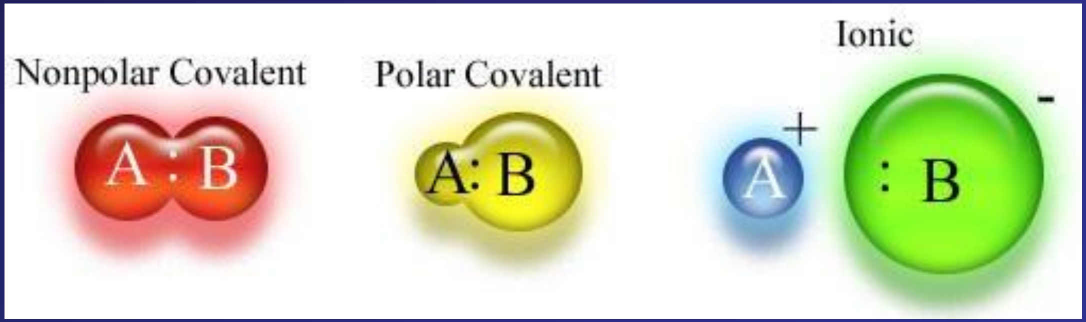
- The spatial location of negative charge ("electron cloud") is not perfectly radially distributed about the spherical atom at each moment in time
- This transient change in charge symmetry in one atom affects neighboring atoms





Spectrum of Sharing

- Covalent ←→ Polar Covalent ←→ Ionic bonding is a spectrum of atomic affinity for electrons
- The spectrum is evidenced by the differences of the electronegativity of atoms



- (Nonpolar) Covalent

  N—O, diatomic forms (H_2, O_2, N_2), C—H, C—S
- Polar Covalent

  O—H, N—H, O—C, N—C, O—P
- Ionic

  Metal + nonmetal: Na+ –Cl, K+ –Cl, Na+ –OH,

- Electronegativity Values

H: 2.20 , C: 2.55 , O: 3.44, N: 3.04, P: 2.19 S:2.58

- Criteria: Electronegativity Difference (Δ)
  - $\Delta < 0.4$: covalent
  - $0.4 < \Delta < 2$: polar covalent
  - $\Delta > 2$: ionic
- Common Bonded Atoms in Biology

O—H 3.44 – 2.20 = 1.24 polar covalent

C—H 2.55 – 2.20 = 0.35 covalent

C—O 3.44 – 2.55 = 0.99 polar covalent

C—N 3.04 – 2.55 = 0.49 polar covalent

N—H 3.04 – 2.20 = 0.84 polar covalent

P—O 3.44 – 2.19 = 1.25 polar covalent

C—S 2.58 – 2.55 = 0.03 covalent

S—O 3.44 – 2.58 = 0.86 polar covalent

Ions

- electrically charged atoms and molecules
- ionized atoms: Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}
- ionized molecules

  H_3O^+, HPO_4^{2-}, NH_4^+
  $C_4H_4O_4^{2-}$ (succinate: molecular formula)
  $^-OOC\text{-}CH_2\text{-}CH_2\text{-}COO^-$ (succinate: structural formula)
- cations: positively charged ions

  move toward cathode (– pole)
- anions: negatively charged ions

  move toward anode (+ pole)

The Molecule

- Atoms that are covalently bonded to each other
- Ionic compounds (and their solid forms crystals) (e.g. NaCl, table salt) are not molecules because the bonding is not covalent
- A group of bonded atoms that are all non-metal atoms is a molecule

Organic Chemistry

Functional Groups (moieties)

- alkyl (methylene $–CH_2$-)
- alkenyl ($-CH_2=CH_2-$)
  double-bond geometry (*cis*- or *Z*-, *trans*- or *E*-)
- hydroxyl (R-OH)
- carbonyl (aldehydes, ketones) (-C=O)
- aminyl ($-NH_2$)
- carboxyl (-C[=O]-OH)
- esteryl (-C[=O]-O-R)
- amidyl (-C[=O]-NH-R)

Substance Quantitation

prefixes: giga 10^9, mega 10^6, kilo 10^3, deca 10^1, deci 10^{-1}, centi 10^{-2}, milli 10^{-3}, micro 10^{-6}, nano 10^{-9}, pico 10^{-12}, femto 10^{-15}, atto 10^{-18}

- Mass
  - units: grams, kilograms, moles, # molecules
  - not weight!

  Conversions:

  When balancing or determining yields from chemical equations, always convert to moles first

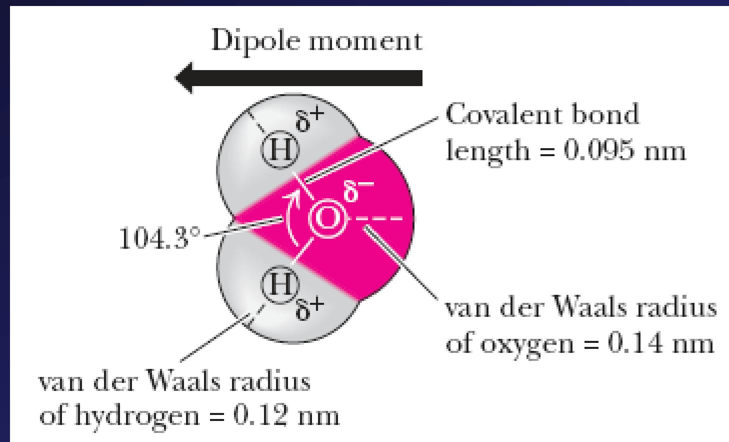
- Volume
  - units: cubic ___meters: cm^3, mm^3, L(iters)
  - Conversions: 1 mL = 1 cm^3, 1 L = 1000 ml

Substance Quantitation

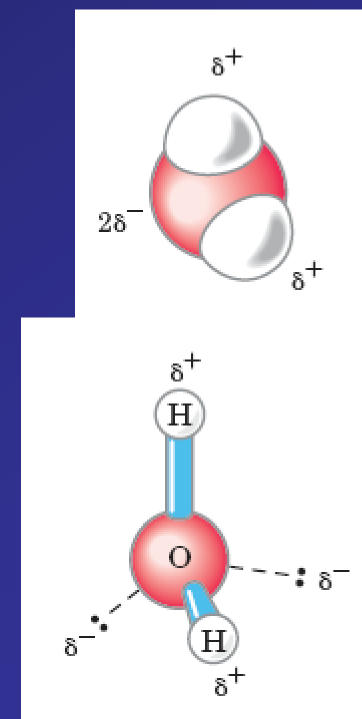
- Solution Density (Concentration)
  - units: G/L, mol/L, M, %(w/v), %(v/v), ppm, etc, etc
  - mass of a solute in the volume of a solution
  - solution = solute + solvent
  - note density = mass/volume, but of a pure substance!
  - mass of solute = concentration × volume
  - stock solutions / reagents

    [g ←AW/MW→ mole] weighed out: add solvent to final volume
  - dilutions: $C_{concentrated} \times V_{concentrated} = C_{dilution} \times V_{dilution}$

H_2O – Structure



- O atom more electronegative
  - greater affinity for electrons
  - both bonding and nonbonding electrons (electron pairs)
- O-H bond covalent ("shared" bonding electrons) but polar

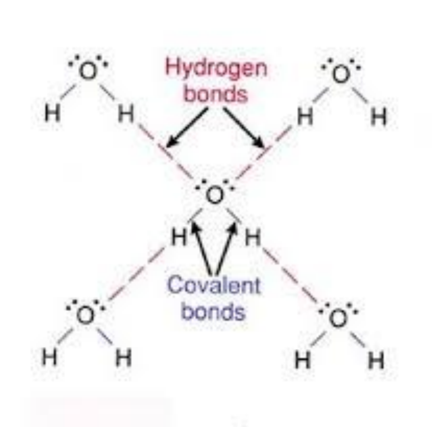


Garrett & Grisham, *Biochemistry* (5ed, 2013)

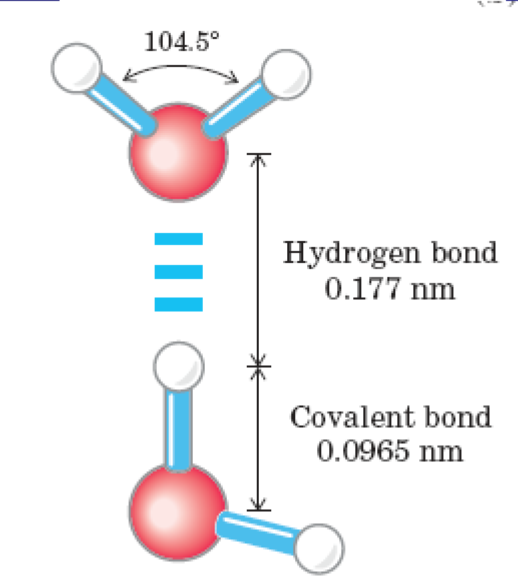
Lehninger, *Biochemistry* (4ed, 2005)

Water – Hydrogen Bonding

- H-bonding: the H atom covalently bonded to an O atom in one H_2O molecule forms a weak bond with one of the two unbonded pairs in the valence shell of the O atom of another H_2O molecule
- A "weak" bond is a relatively lower energy bond than the covalent bond, but still significant
- Water (liq H_2O) forms at temperatures < 100°C with H bonds
- These are broken when water boils

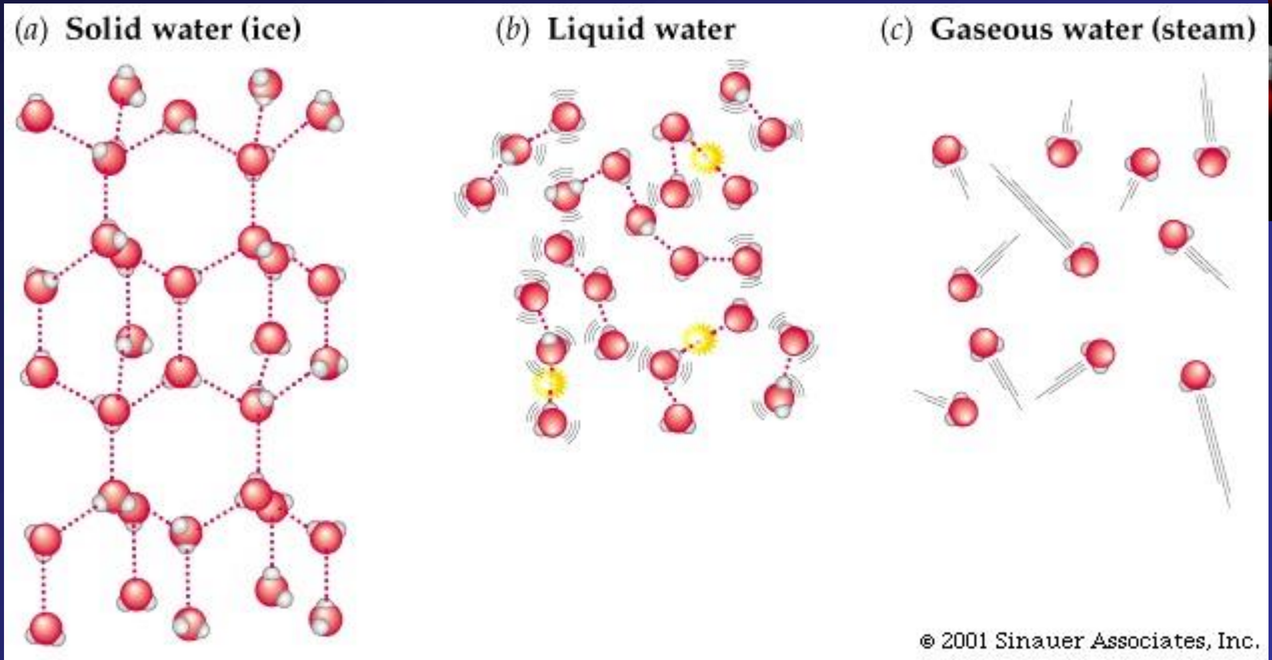


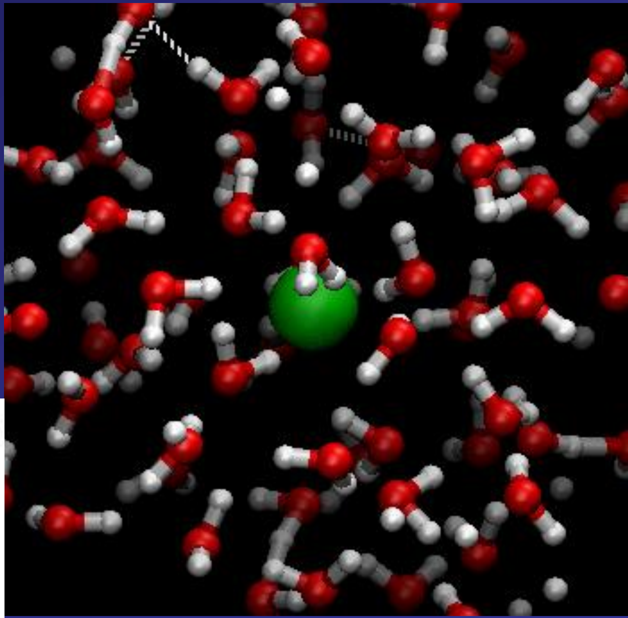
Hydrogen bonding in water.



H_2O Phases

- ice: H-bonded in a less dense space
- water: H-bonds formed & unformed rapidly in more dense space
- vapor: no H-bonding as they gallivant through space





- animation shows H_2O as water solvating a chloride ion. Note yellow flashes are H-bonds forming & unforming

Water – Properties

- High specific heat   1 cal/g/°C

This enables water to resist changes in temperature when heat energy enters or exits

- Polar

A great many organic and inorganic solutes dissolve in it, providing the environment for biochemical reactions

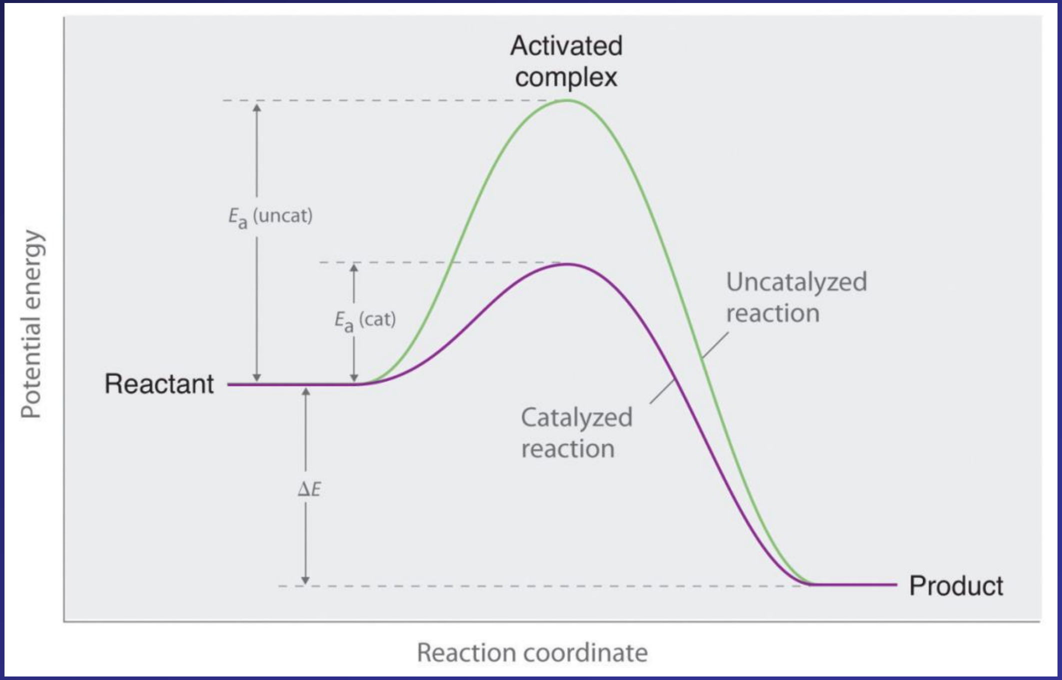
- Cohesive because of the H-bond

Water's surface tension resists loss of solvent as well as accounts for capillary flow exploited by organisms

Organisms composed of 70-90% water

Catalysis

- A substance that promotes a chemical reaction by lowering its activation energy (E_a)
- Note that this does not change the relative potential energies of the reactants or products (ΔE)



Reading (Sources)

- Marieb: Chapter 2
- Becker's WotC: Chapter 2
- Raven: Chap 2