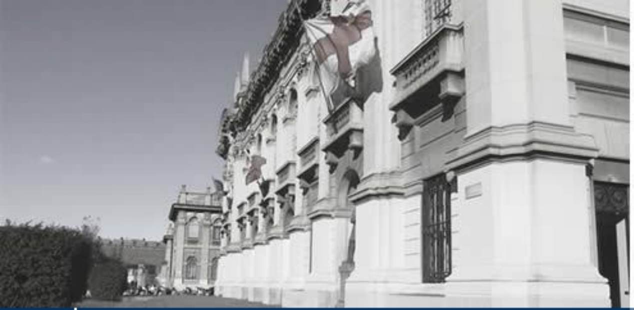


Scuola di Ingegneria Industriale e dell’Informazione

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO





The Chemical Level of Organization.

Prof. Attilio Citterio (and Ada Truscello)

Dept. CMIC

https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

Overview.

Atoms and Molecules

- Structure of an atom
- Electrons
- Bonds

Chemical Notation

Chemical Reactions

- Basic energy concepts
- Types of reactions
- Acids and bases
- pH

Inorganic Compounds

- Carbon dioxide and oxygen
- Water
- Acids and bases
- Salts

Organic Compounds

- Carbohydrates
- Lipids
- Proteins
- Nucleic acids

ATP

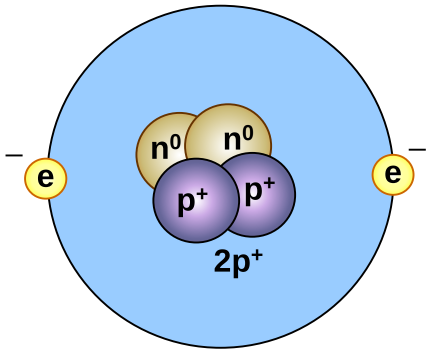
Matter, Elements, and Atoms.

Matter: anything that occupies space and has mass

- 3 states
  - Solid
  - Liquid
  - Gas

All matter composed of elements

- Cannot be broken down
- Smallest component of an element is an atom
- Each element has a unique chemical symbol



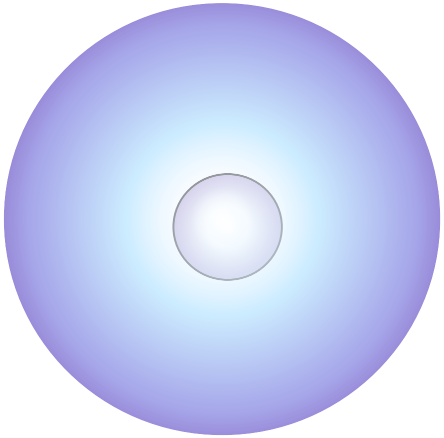
Helium (He)

Atom has 3 subatomic particles

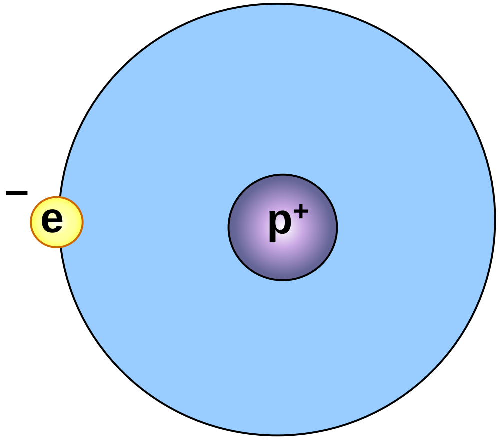
- Proton
- Neutron
- Electron

Structure of an Atom.

- Protons and neutrons are found in the nucleus
- Electrons found in the electron cloud (shell) – These particles characterize the dimension of the atom (Å) and the chemical reactivity (*kinetics and thermodynamic*)



(a) Electron cloud or space filling model



(b) Electron-shell model

Structure of an Atom and Elements.

Atomic number = **Z** = # of protons

- And also # of electrons in a neutral atom.

Mass number = **A** = # p + # n

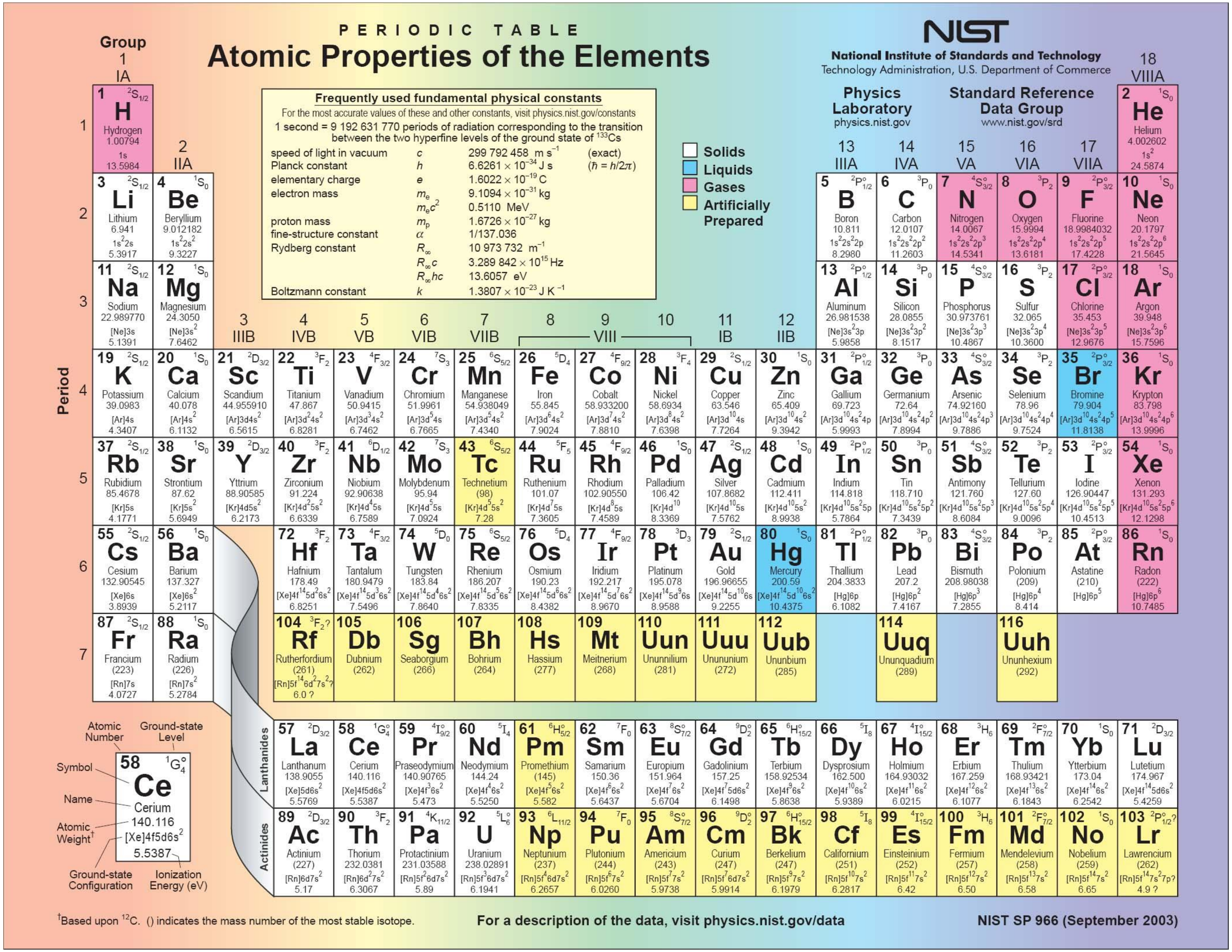
Atoms which differ for A but have the same Z are called **isotopes** $({}^{12}_{6}C,\ {}^{13}_{6}C,\ {}^{14}_{6}C)$

<u>Elements</u> represent the natural distribution of isotopes.

(1) Cl = (0.758) ^{35}Cl + (0.242) ^{37}Cl

$${}^{A}_{Z}\mathrm{Na}$$

Periodic Table (according to NIST).



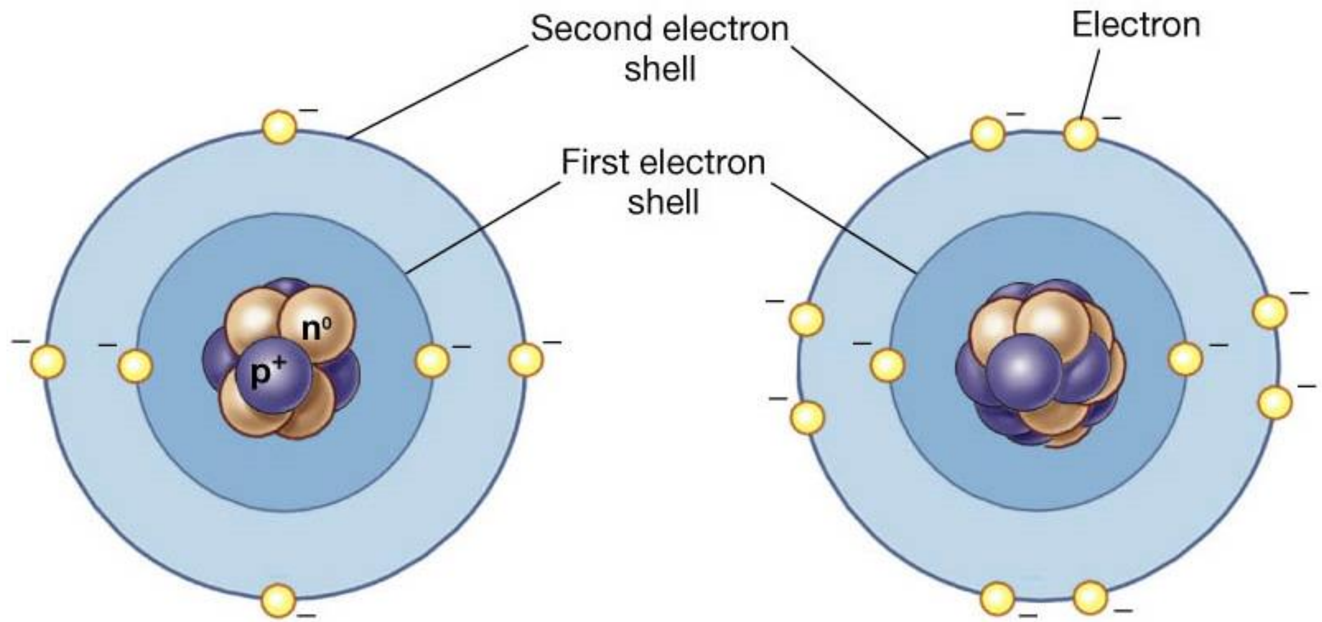
Electrons and Electron Shells.

Only outer shell electrons can interact (form bonds)!

- If outermost shell is full, element is stable (He)
- If outermost shell is not full, unstable and can bond

The 1st shell can hold 2 electrons

The 2nd shell can hold 8 electrons



(a) Carbon atom ($6p^+$, $6n^0$, $6e^-$)

(b) Neon atom ($10p^+$, $10n^0$, $10e^-$)

Molecules and Compounds.

Atoms become stable by:

- Sharing electrons
- Gaining electrons
- Losing electrons
- This is called a *chemical reaction*
  - Molecules and compounds are the result

Elemental molecules are chemical structures containing 2 or more atoms of the *same element*

- Ex: O_2 , O_3 , S_8

Compounds contain 2 or more atoms from different *elements*

- Ex: H_2O , CH_3COOH , H_2NCH_2COOH

Important Bonding Concepts.

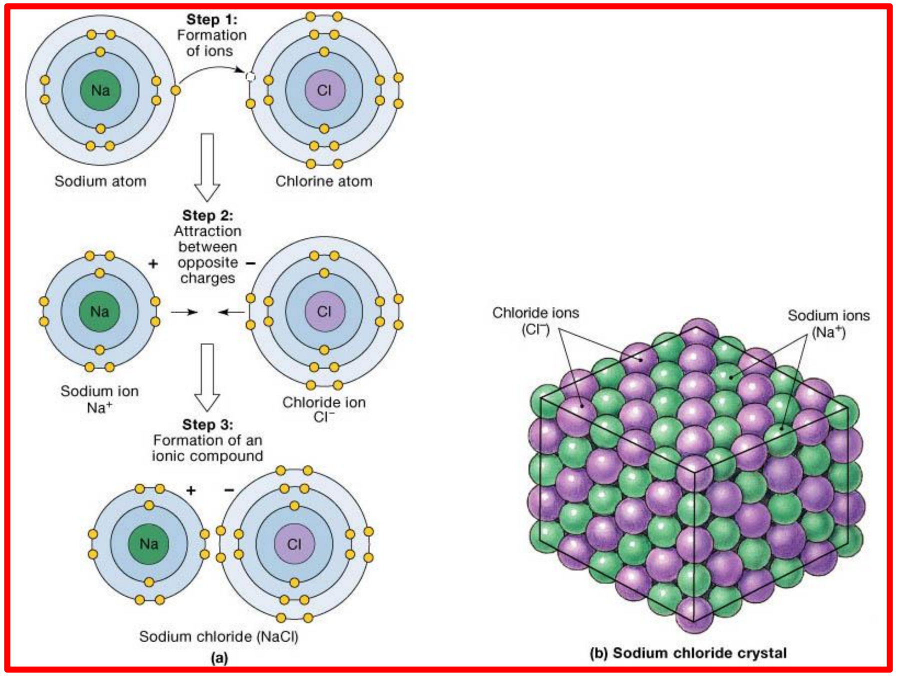
- All atoms want to be stable!
  - Stability (commonly) means having 8 electrons in the outer shell
    - Unless it does not fill the first shell (2 electrons) (or higher *d*, *f* orbitals)
- Opposites attract!   (positive/negative ions: Na^{+} Cl^{-})
- Atoms are electrically neutral!   (N° p^{+} = N° e^{-})
- 3 types of bonds
  - **Ionic**
  - **Covalent**
    - Polar
    - Nonpolar
  - **Metallic**
- *Interactions*
  - Hydrogen bonds, Van der Waals, and other

Ionic Bonds.

Ions are atoms or group of atoms with a positive or negative charge:

- Anion
  - Ions with a negative charge
  - Atom *gains* electrons (electron acceptor)
  - More electrons than protons
- Cation
  - Ions with a positive charge
  - Atom *loses* electrons (electron donor)
  - More protons than electrons
- Ionic bonds are between an anion and a cation

  Ex: NaCl, KCl, $CaBr_2$



Covalent Bonds.

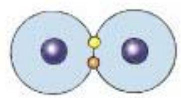
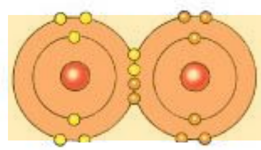
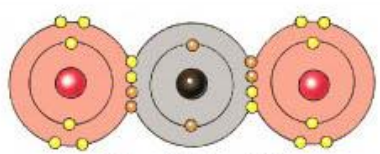
Form a bond by sharing electrons

Single covalent bond

- Share one pair of electrons

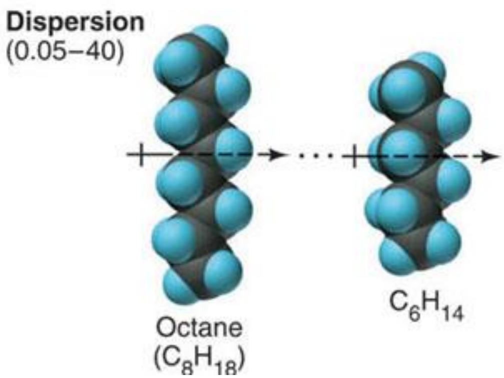
Double (**triple**) covalent bond

- Share two (three) pairs of elec.

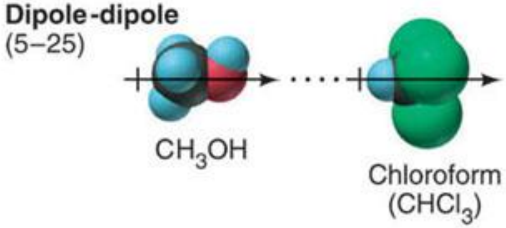
	ELECTRON-SHELL MODEL AND STRUCTURAL FORMULA	SPACE-FILLING MODEL
(a) Hydrogen (H_2)	 H–H	
(b) Nitrogen (N_2)	 N≡N	
(c) Carbon dioxide (CO_2)	 O=C=O	

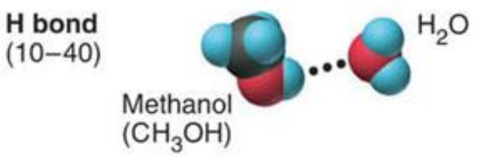
Covalent Bonds and Intermolecular Bonds.

- Nonpolar covalent bonds
  - Electrons are equally shared
  - Carbon atoms
    - Create stability of macromol. in the body
  - Typically tetrahedral



- Polar covalent bonds
  - Unequal sharing of electrons
  - Water is great example
  - Typically contain O, N, F (high χ)

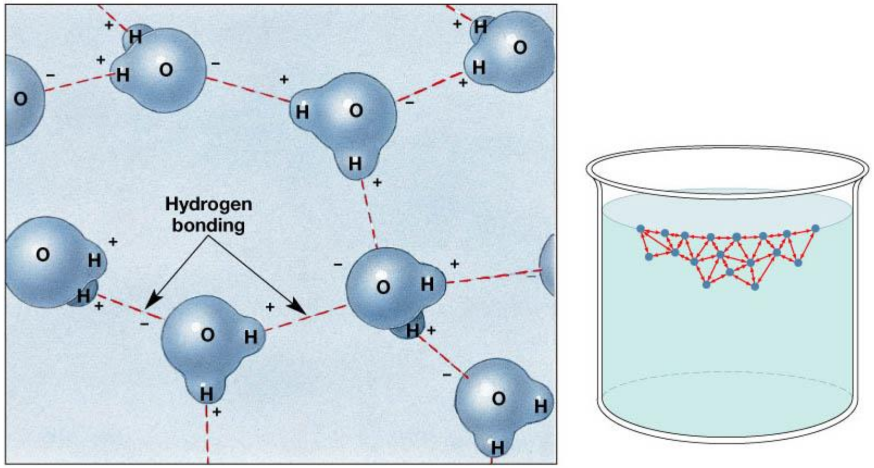




Intermolecular Interactions: Hydrogen Bonds.

Simple interaction not a common chemical bond.

- Weak (20-60 kJ·mol^{-1})
- Attraction between hydrogen atom of a molecule and partially negatively charged atom in other molecules (is mainly electrostatic)
- Do not create molecules
  - Alter molecule shape
- Water is best example
  - Reason for
    - surface tension
    - capillary force
    - Lower density of ice vs. liquid water



(a) (b)

Rules of Chemical Notation for Atoms.

- Abbreviation of element (symbol) represents 1 atom (also subscript on left indicates the number of protons) $_{6}C$
- # before abbrev. of element indicates more than 1 atom (5 O)
- An arrow separates the Reactants (left) from Products (N.B. reagents and products have different chemical formula – *exception Isomers*!)
- Superscript on right indicates an ion
  - + = loss of 1 electron (Na^{+})   2+ = loss of two electrons (Ca^{2+})
  - - = gain of 1 electron (F^{-})   etc.
- Superscript on left indicates an isotope (^{235}U and ^{238}U)
- Chemical reaction must be balanced: Mass is conserved in a chemical reaction – atoms in raw materials and in wastes are the same; therefore, they are equally usable.

Chemical Reactions.

- Bonds between atoms are broken and atoms are rearranged into new combinations
- Very important in every cell:
  - Allow to obtain unstable products non accumulated in nature
  - Provide energy
- Metabolism is all of the chemical reactions that occur in the body
  Important chemical reaction:

$$C_6H_{12}O_6 \rightarrow 6CO_2 + 6H_2O + ATP$$

- 3 main types of reactions (important in biochemistry):
  - Decomposition reactions
  - Synthesis reactions
  - Exchange reactions

Basic Energy Concepts.

- **Work**: movement or change in physical structure of matter
- **Energy**: capacity to do work
  - *Kinetic energy*
    - Energy in motion (released)
  - *Potential energy*
    - Stored energy
  - *Electrical energy*
    - Energy associated to the motion of electrons
  - *Chemical energy*
    - Energy stored in chemical bonds of molecules and solids.
  - Easily convertible between different types
  - Energy can be released in the form of heat (**Enthalpy**)
  - Originate also by a change of configuration of a system (**Entropy**)

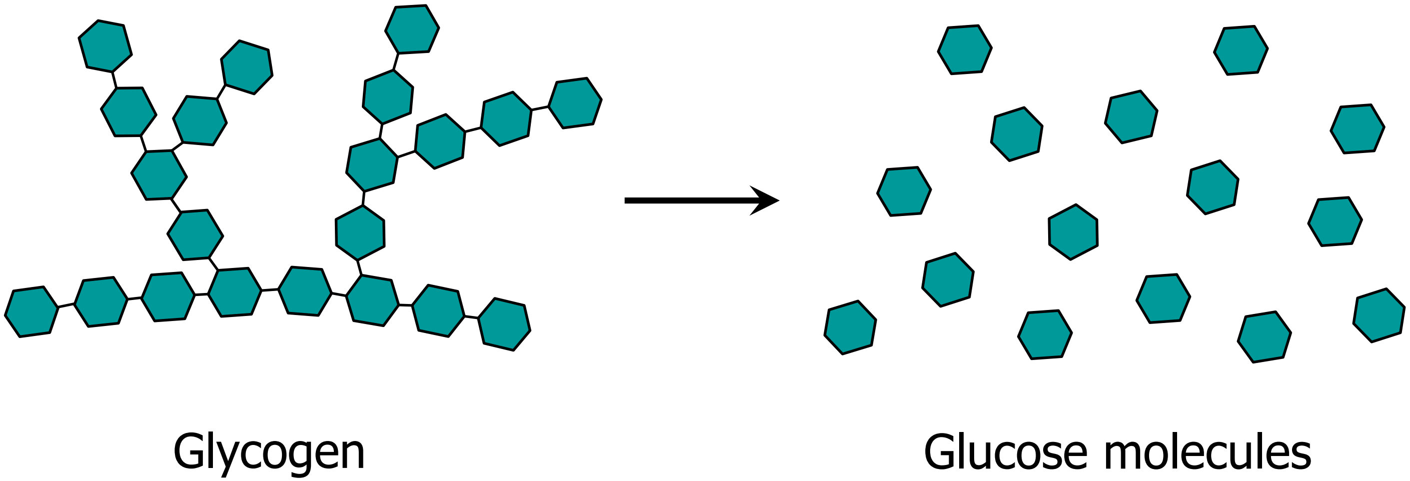
Decomposition Reactions.

AB → A + B   Catabolism

(dissociation)

$Cl_2 \rightarrow 2\ Cl^{\bullet}$

Will energy be released or stored?



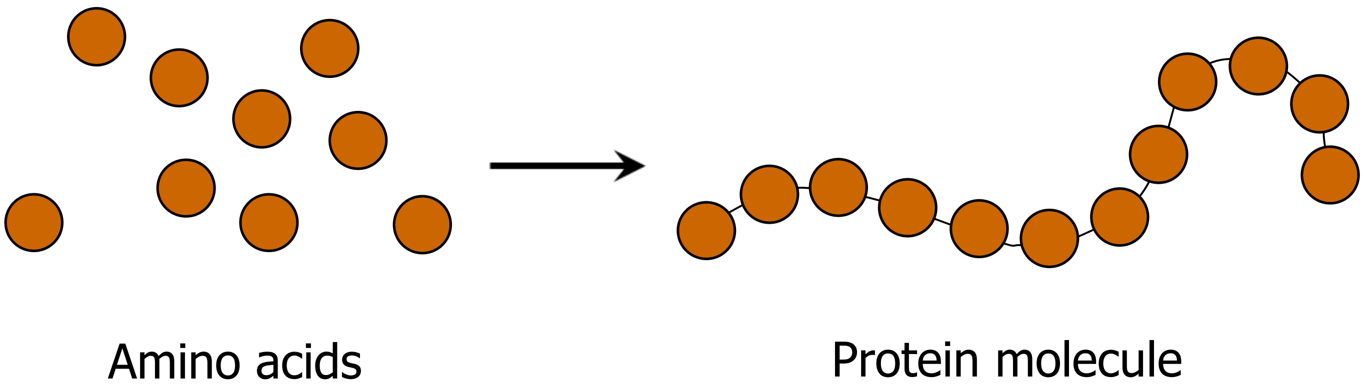
Example of a decomposition reaction: breakdown of glycogen to release glucose units.

Synthesis Reactions.

A + B → AB

Anabolism

Energy is stored in chemical bonds of the macromolecule.



Example of a synthesis reaction: amino acid are joined to form a protein molecule.

Exchange Reactions.

AB + CD → AD + CB   AB + CD ⇄ AD + CB (reversible)

Combination of decomposition and synthesis reactions

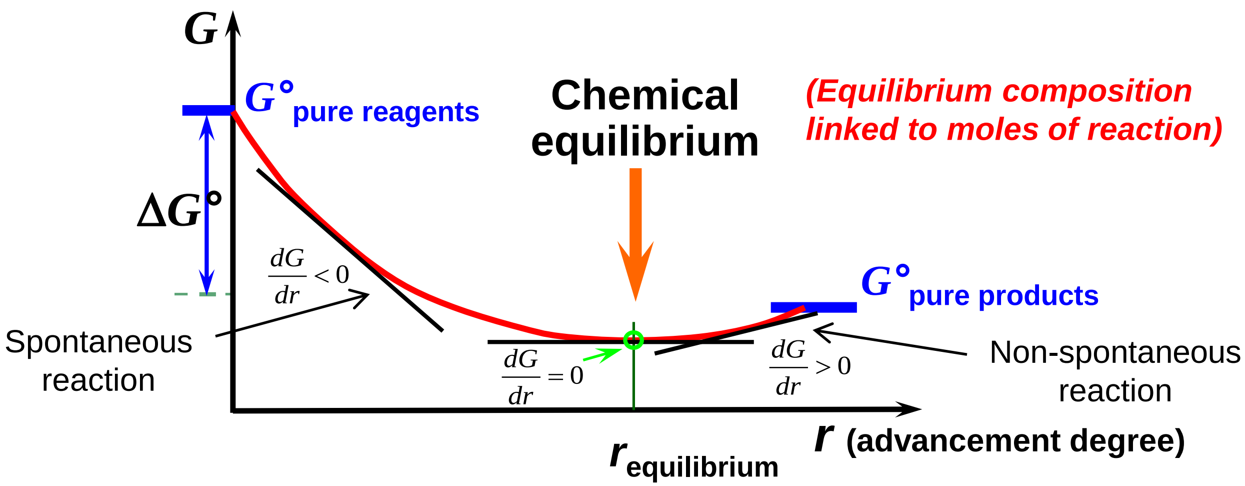
Exothermic reaction ($\Delta H < 0$)

- If decomposition stronger than synthesis; Energy released

Endothermic reaction ($\Delta H > 0$)

- If synthesis stronger than decomposition (Energy provided)

Spontaneous reactions: ($\Delta G < 0$) : reaction occurs from reagents to products and stop at the equilibrium point.



Acids and Bases in Aqueous Solutions

Acids produce H^+ and the conjugate base.

Example: $CH_3COOH \rightleftarrows H^+ + CH_3COO^-$

Bases produce OH^- and the conjugate acid.

Example: $NH_3 + H_2O \rightleftarrows OH^- + NH_4^+$

Most of the compounds exhibit both acidic and basic properties. Such compounds are called **amphoteric compounds**.

Acids react with bases and produce a salt (which can be another base at the same time) and water (which also can act as an acid).

Example:

$$H_2O + CN^- \rightleftarrows HCN + OH^-$$

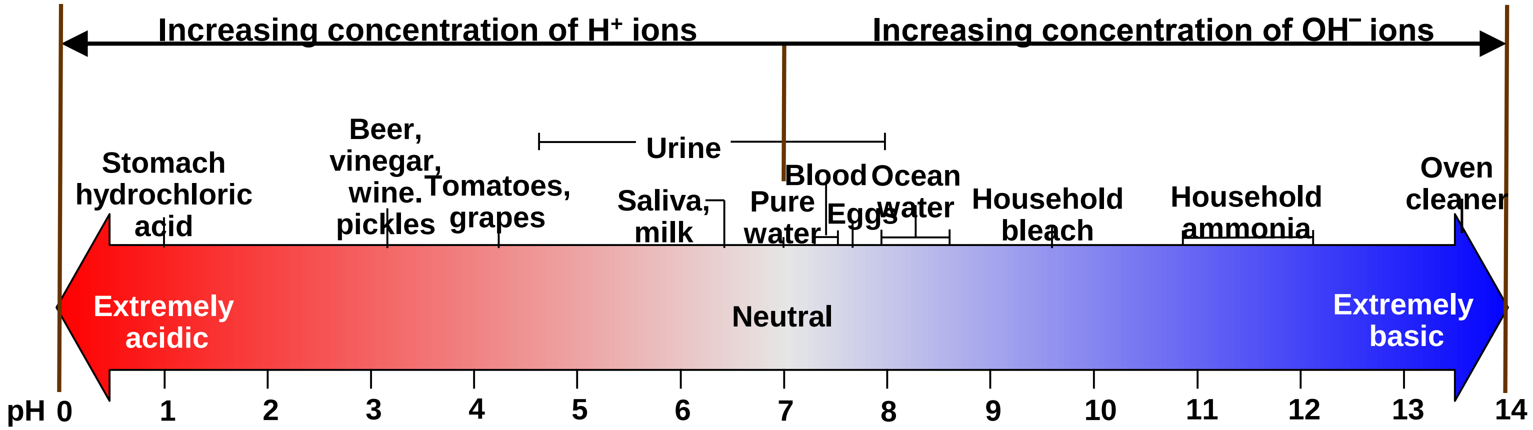
Acid 1 (H_2O)   Base 1 (CN^-)   Base 2 (OH^-) (conjugate base for Acid 1)

Acid 2 (HCN) (conjugate acid for Base 1)

This equilibrium is shifted toward the weaker acid and the weaker base. A stronger acid has a lower value of pK_a and a weaker conjugate base. Proton Acid-Base reactions are fast processes ($k \approx 10^{-9}\ M^{-1}\cdot s^{-1}$ at 25°C) and their equilibrium are instantaneously established.

pH Scale.

- Measures the $[H^+]$ at equilibrium in a water medium
  - If too many, disrupt structure and function
- pH ranges from 0-14; neutral is 7 (distilled water)
- pH below 7 = acidic; pH above 7 = basic
- Cells in biological systems must maintain the pH between a specific range around 7 (i.e. Blood is buffered between 7.35-7.45)
- Buffers: Stabilize pH by removing or replacing hydrogen ions
  Can you think of any other examples?



Electrolytic Dissociation.

1. **Acids** produce H^+ and the anion of the conjugated base.
   Example: $HCl \rightarrow H^+ + Cl^-$
   Presentation in reaction schemes: HCl (or another acid), H^+, H_3O^+

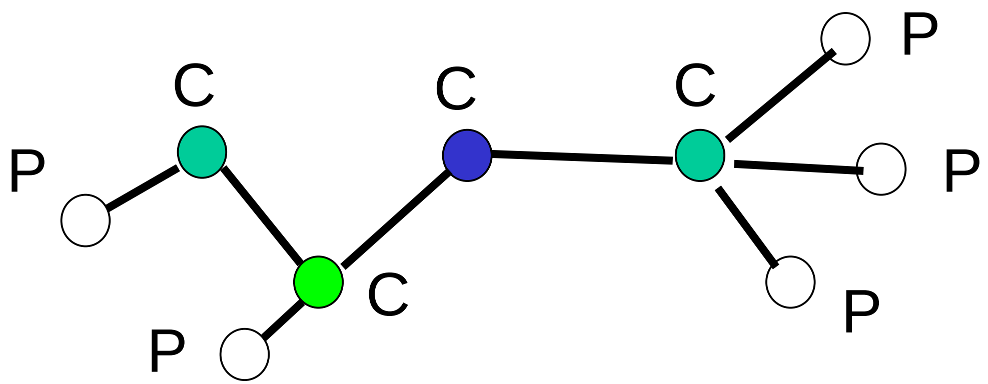
2. **Hydroxides of alkali and alkali earth metals** produce $OH^−$ and the cation of the corresponding metal.
   Example: $NaOH \rightarrow Na^+ + OH^−$
   Presentation in reaction schemes: NaOH (o another hydroxide), $OH^−$

3. Salts produce cations of the metal (or cationic complex) and anions (or anion complex) of the rest of the ionic compound.
   Example 1: $Na_2Cr_2O_7 \rightarrow 2\ Na^+ + Cr_2O_7^{2-}$
   Presentation in reaction schemes: $Na_2Cr_2O_7$, $Cr_2O_7^{2-}$ (reactive anion)

   Example 2: $Hg(CH_3COO)_2 \rightarrow Hg^{2+} + 2\ CH_3COO^−$
   Presentation in reaction schemes: $Hg(CH_3COO)_2$, Hg^{2+} (reactive cation)

   Example 3: $[(CH_3)_4N]\ [Al(OH)_4] \rightarrow [(CH_3)_4N]^+ + [Al(OH)_4]^−$
   Presentation in reaction schemes: complete notation in square brackets.

Identification of Acid Centres in a Molecule.



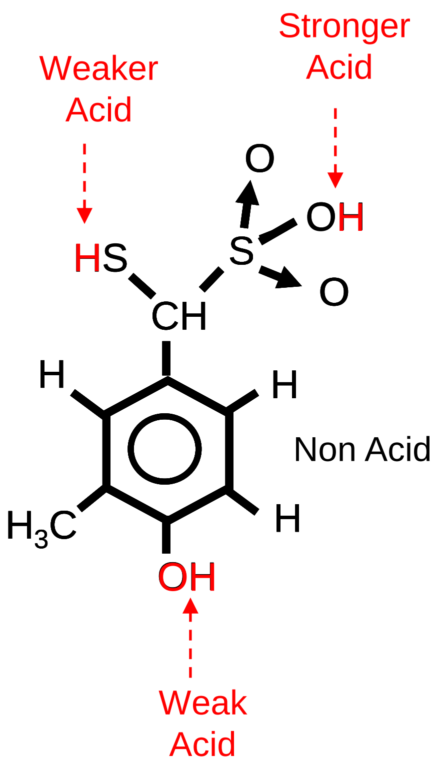
Once known the structural formula, whatsoever complex, is known, it is sufficient:

1) analyse **the peripheral atoms** and select **H**

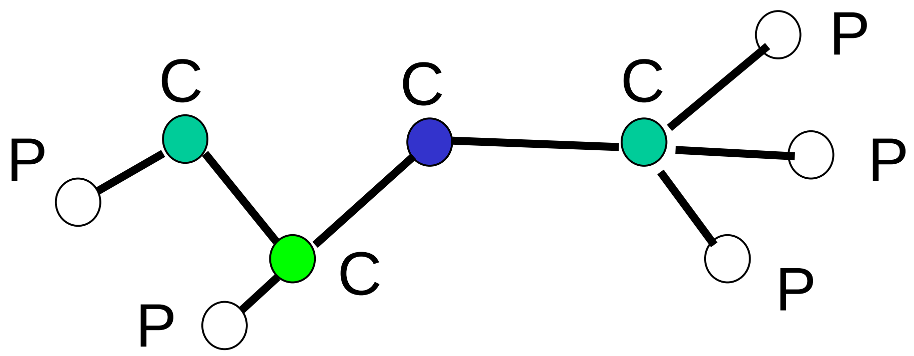
2) Analyse central atoms directly linked to H

3) Sort by electronegativity of central atom X (the hydrogens linked to the more electronegative atoms are more acid)

4) If more X-H groups exist for the same X, the one in which X is bound to a maximum number of electronegative atoms is the more acid.

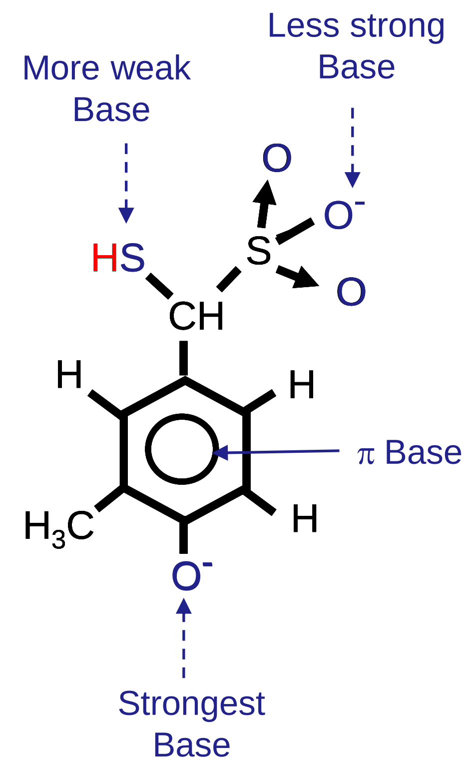


Identification of Basic Centres in a Molecule.



Once the structural formula of a compound is known, whatsoever complex, it is sufficient:

1) analyse **all atoms (C** and **P)** and select those unshared electron pair
2) Sort the atoms by electronegativity of central X atom (more loosely bound electrons define make the more basic)
3) If negative charges are present, the atom which bring charge is basic atoms.
4) If there are more X atoms of the same element, the more basics are the ones in which X is bonded to lowest number of electronegative atoms and to the highest number of electropositive groups .



Lewis Acid and Bases.

- Lewis Acid = acceptor of electron pair.
- Lewis Base = donor of electron pair.
  - The definition includes any atom of the molecules or ions which have these properties, included metallic ions and solvents;
  - Overcomes all other concepts and is now the model more used
    - Examples: $BF_3 + :NH_3 \rightarrow H_3N:BF_3$ (o $BF_3 \bullet NH_3$ o $BF_3 \leftarrow NH_3$)
      $Ag^+ + 2\ :NH_3 \rightarrow [Ag(NH_3)_2]^+$ [*coordination ion*]
      $Ni + 4\ :CO \rightarrow Ni(CO)_4$ [*metal complex*]

The bond which is formed in the Lewis acid-base interaction shows variable strength depending on the involved partners and is strictly linked to the interaction between the filled orbitals at higher energy (HOMO) of Basic centers and the empty orbitals at lower energy (LUMO) of Acid centers involved.

Biochemistry.

- **Nutrients**: essential elements and molecules
- **Metabolites**: all molecules synthesized or broken down by chemical reactions in the body
- Both can be classified based on atom type and molecule complexity:
  - **Inorganic compounds** (all combinations of elements without C)
  - Coordination Compounds (combinations of atoms organized around central metal atoms);
  - **Organic Compounds** (all combination of C atom networks containing also other important elements (H, O, N, P, S, Cl);
  - Organometallic Compounds (all combinations of C atoms networks containing also metal elements).

Main Class of BioOrganic Compounds.

- Contain H and C
  - Are characterized by strong covalent sigma C-C and C-H bonds.
- Carbohydrates
  - Monosaccharides
  - Disaccharides
  - Polysaccharides
- Lipids
  - Fatty acids
  - Fats
  - Steroids
  - Phospholipids
- Proteins
  - Protein function
  - Protein structure
  - Enzymes
- Nucleic acids
  - Structure
  - Function
- Organophosphates: ATP
- Secondary metabolites:
  - Terpenes
  - Phenols
  - Alcaloids

Organic Nomenclature worth remembering.

Alkanes C_mH_n

Examples: Methane, ethane, propane, butane...

Alkenes RC=CR'

Examples: ethene or ethylene $H_2C=CH_2$, a plant hormone and isoprene C_5H_8 or $(CH_2=CH\text{-}C(CH_3)=CH_2$, a diene.

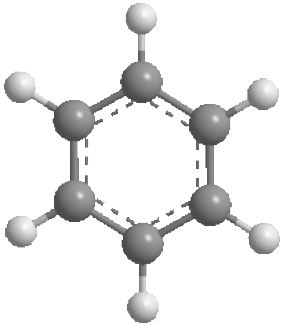
Alkynes

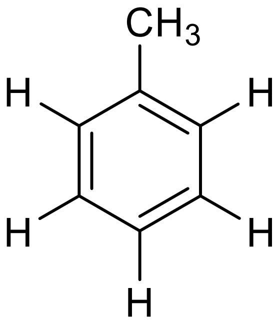
Example: Acetylene or ethyne $HC\equiv CH$

Aromatic Hydrocarbons

Based on the benzene ring

Example: Toluene





Organic Nomenclature worth remembering (2).

Alcohols R-CH_2OH

Example ethanol CH_2CH_3OH

Ethers R-O-R'

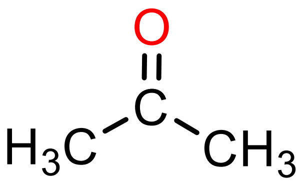
Example diethyl ether $CH_3CH_2OCH_2CH_3$

Aldehydes R-CHO

Examples formaldehyde H_2CO; acetaldehyde CH_3CHO

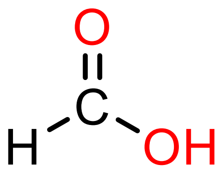
Ketones R-C(O)-R'

Example Acetone

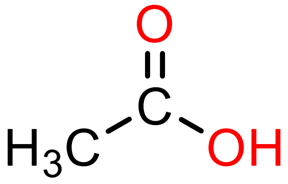


Carboxylic acids R-COOH

Examples Formic acid



acetic acid



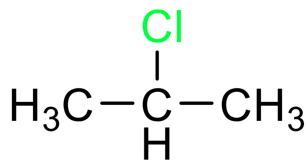
Formate $HCOO^-$

acetate CH_3COO^-

More organic nomenclature worth remembering (3).

Organic Halides

Example:



called 2-chloropropane, or 2-propyl chloride, or isopropyl chloride

***Freons**

Examples: CFC-11, Trichlorofluoromethane, $CFCl_3$

CFC-12, Dichlorodifluoromethane, CF_2Cl_2

Halons (used in fire extinguishers)

Example: Halon 1011 (bromochloromethane, CH_2BrCl)

HCFC's (Freon substitutes)

Example: HCFC-123, CF_3CHCl_2

Sulfur Compounds

Examples: CH_3–SH, methanethiol.

CH_3–S–CH_3, dimethyl sulfide (DMS).

More Organic Nomenclature worth remembering: N compounds.

Amines, RNH_2

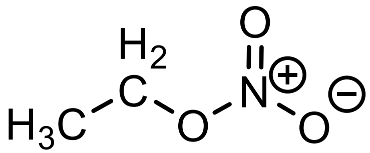
Example CH_3NH_2, methylamine (a primary amine).

Nitriles, Nitro Compounds and Organic Nitrates

Examples acetonitrile : $CH_3\text{-}C\equiv N$

A nearly unique marker for biomass burning.

Alkyl nitrates, such as ethylnitrate



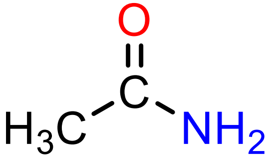
Methyl nitrite CH_3ONO.

Nitryl Chloride $ClNO_2$ (ClONO).

All NOx reservoirs.

Amides, $RC(O)NH_2$

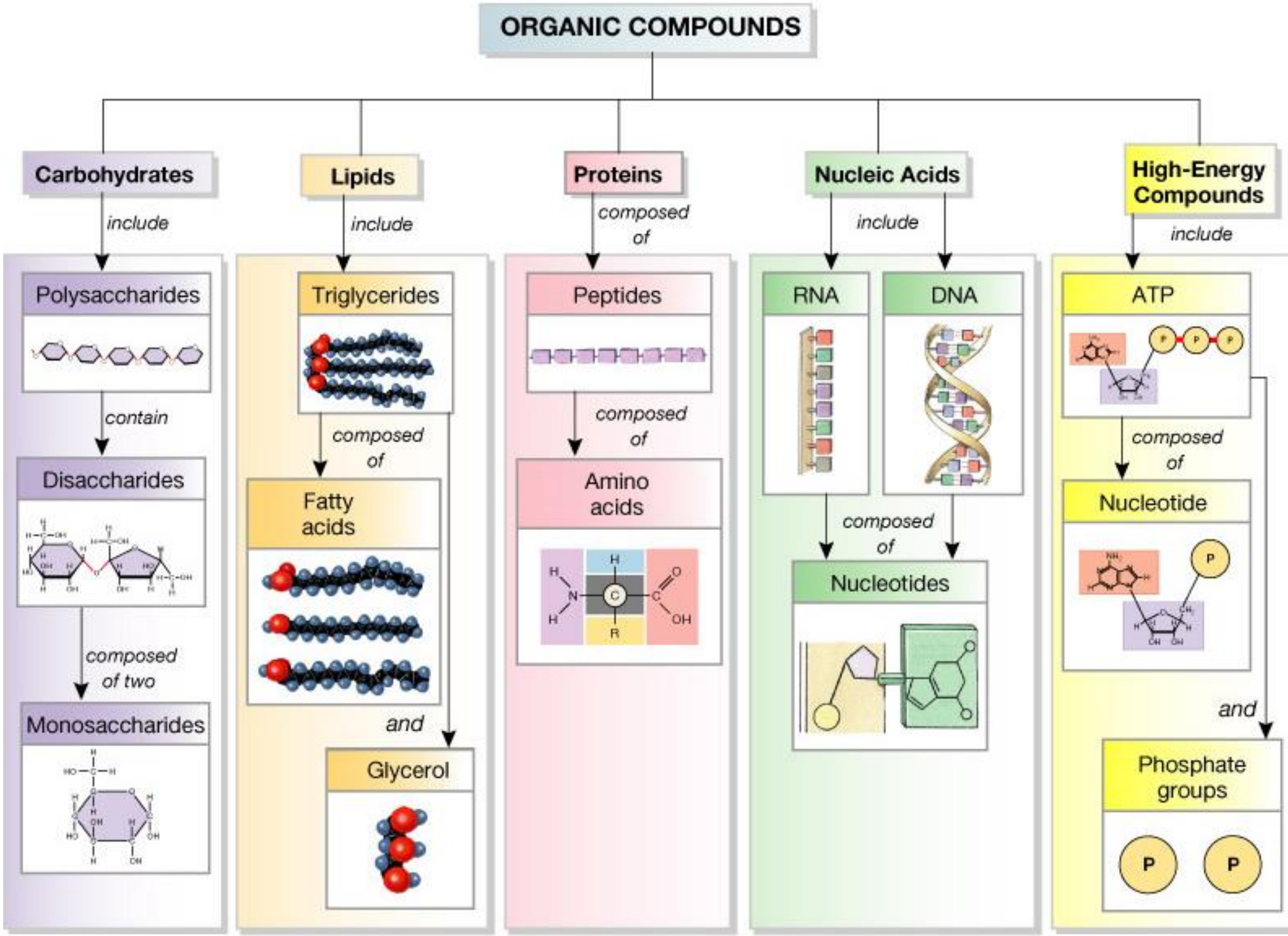
Example ethanamide:



Amino acids, $H_2N\text{-}CH(R)\text{-}COOH$ building blocks of proteins and enzymes.

Urea, $(NH_2)_2CO$

Main Organic Compounds in Living Systems.

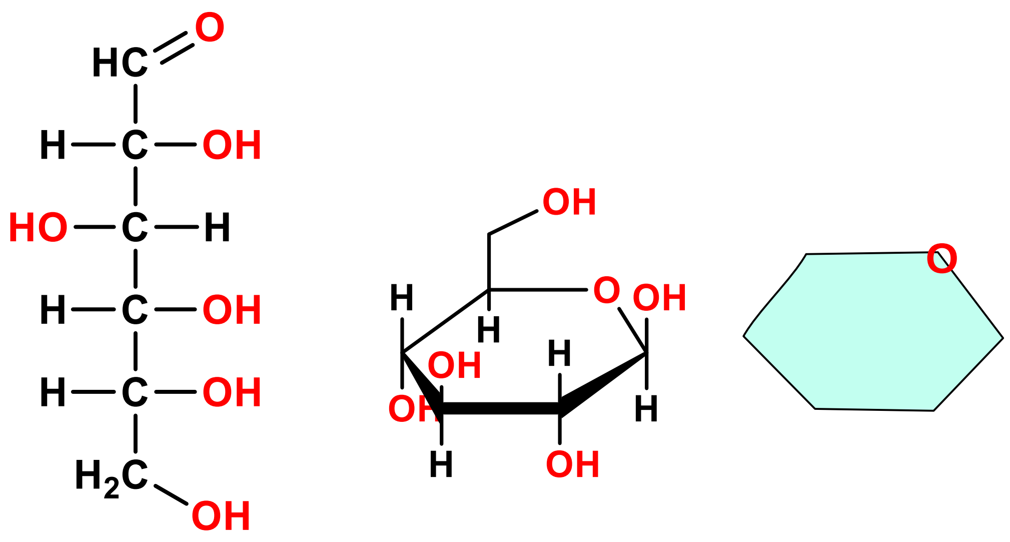


Carbohydrates.

- 1:2:1 ratio of carbon, hydrogen, and oxygen
- Most important source of energy by disproportionation or oxidation with O_2
  - Account for only 3% total body weight!
- 3 major types
  - Monosaccharide
  - Disaccharide
  - Polysaccharide

- Monosaccharides: Simple sugar; contains 3-7 C.

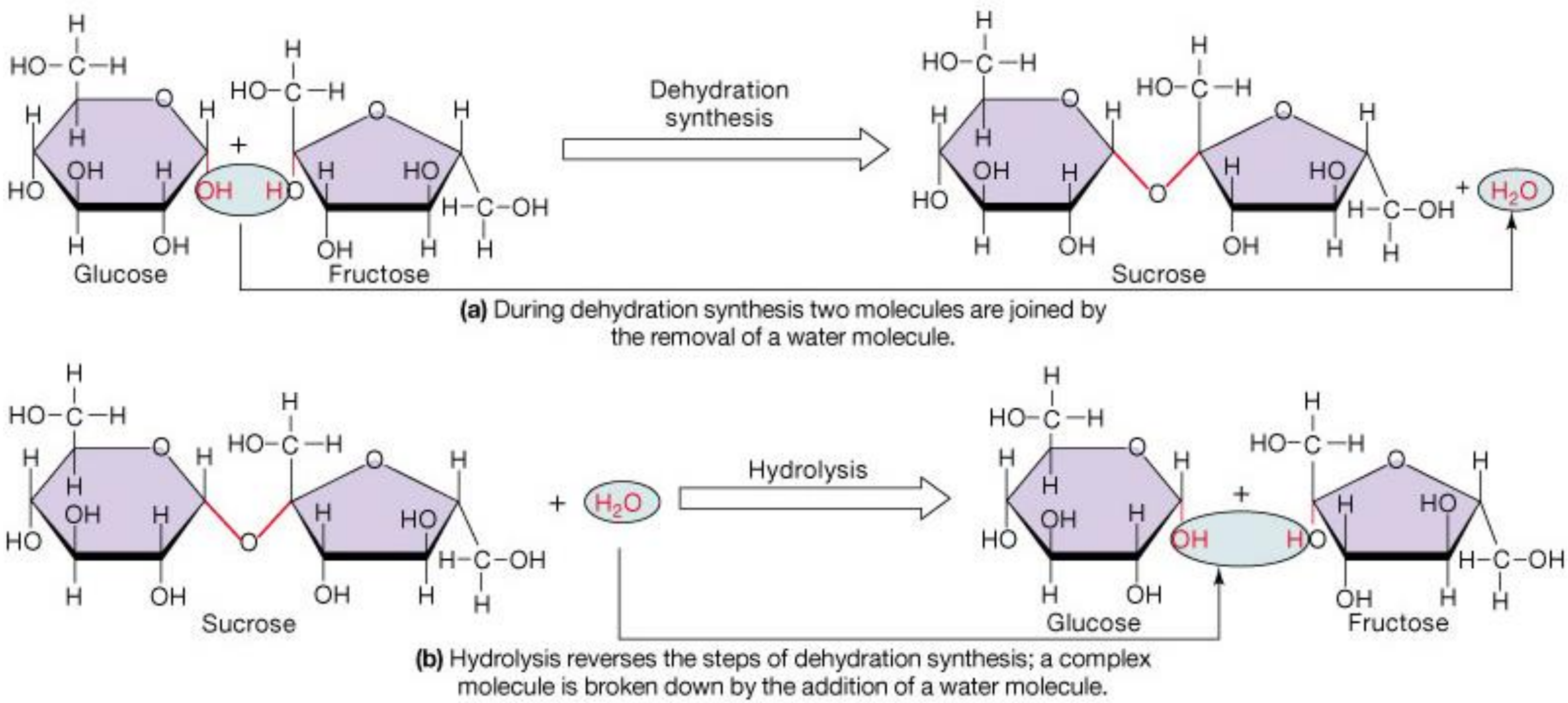
Glucose (most important fuel for body), fructose, etc.



(a) (b) (c)

Disaccharides.

- Formed from two simple sugars through condensation (dehydration)
- Sucrose, lactose, maltose
- Can be broken down to form simple sugars
  - Hydrolysis rxn



(a) During dehydration synthesis two molecules are joined by the removal of a water molecule.

(b) Hydrolysis reverses the steps of dehydration synthesis; a complex molecule is broken down by the addition of a water molecule.

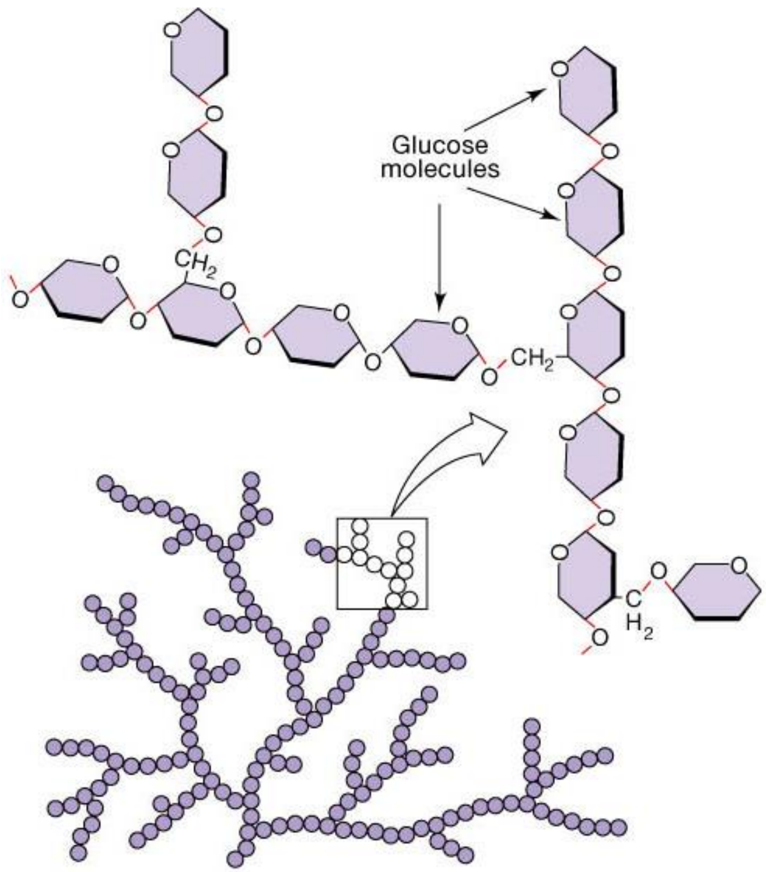
Polysaccharides.

➢ **In Plants**

- Starches
- Cellulose
- Pectins
- Complex polysaccharides

➢ **In Animals**

- glycogen
  - Long chains of glucose
  - Does not dissolve in water
  - Stored in liver and muscle tissue
  - Broken down into glucose when fuel is needed
- Complex polysaccharides



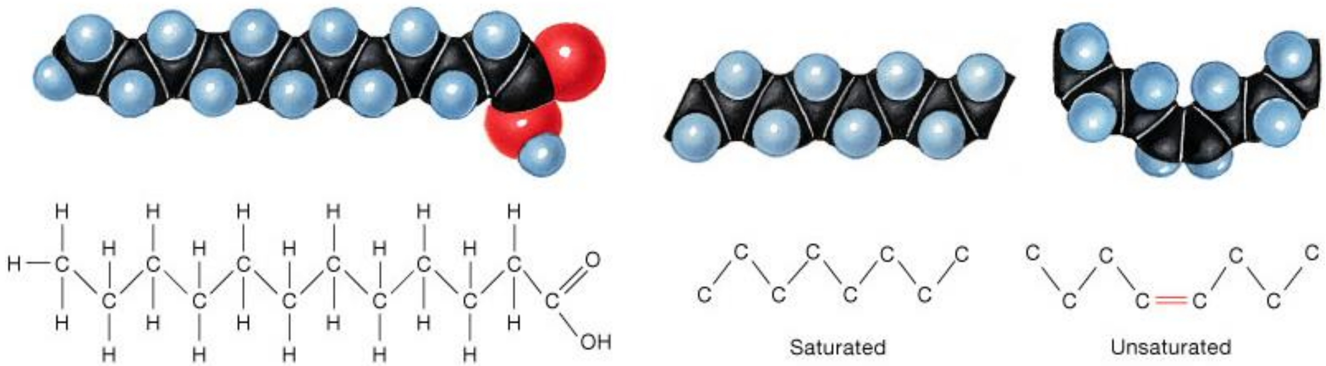
(c) Glycogen, a branching chain of glucose molecules, is stored in muscle cells and liver cells.

Lipids.

- Contain H, O, C, P, S, or N
- Fats, oils, waxes
- Insoluble in water
- Form essential structural components of cells
- Are useful as energy storage
  - Provide 2Xs amount of energy as carbohydrates
- 12% of body weight
- Are commonly partitioned in:
  - Fatty acids,
  - Fats,
  - Steroids,
  - Phospholipids

Fatty Acids.

- Long hydrocarbon chains with a COOH group at the end
- Saturated FA
  - Single covalent bonds between carbons (C-C)
- Unsaturated FA
  - Double covalent bonds between C (but also C-C)
    - Not as many Hydrogens
- They have an essential role as energy reserve and as constituents of cell walls.

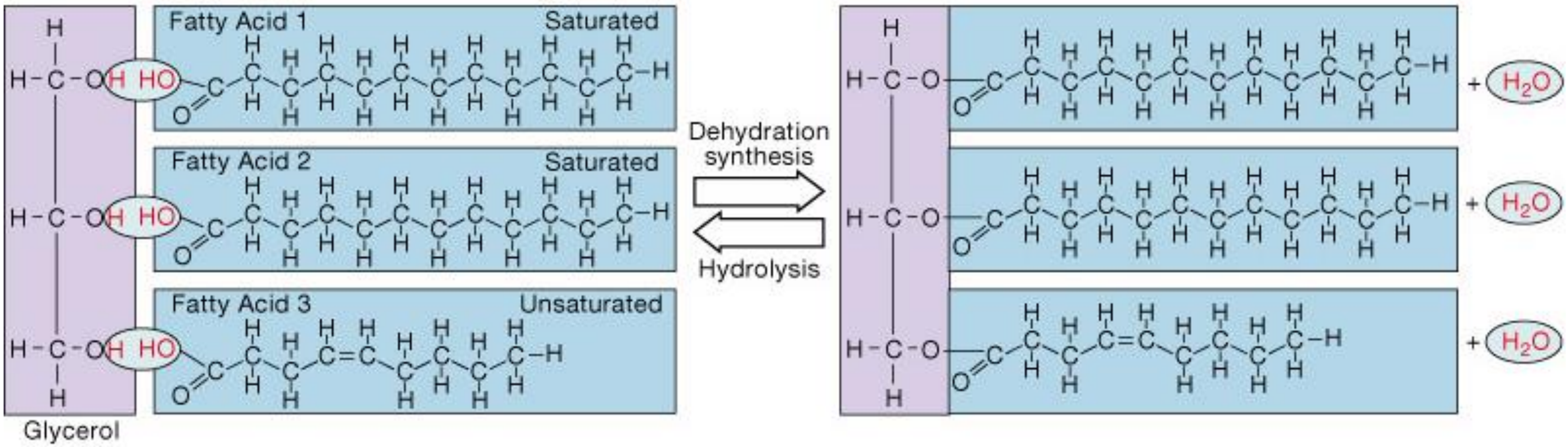


(a) Lauric acid ($C_{12}H_{24}O_2$) (b)

Fats.

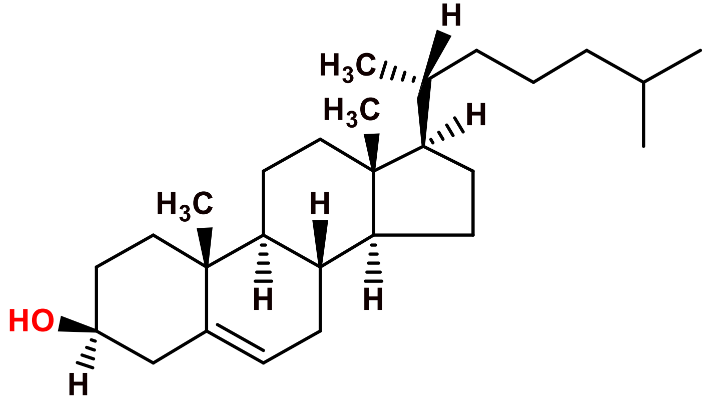
Triglycerides

- 1 glycerol molecule and 3 fatty acid molecules
- Their role is to store energy

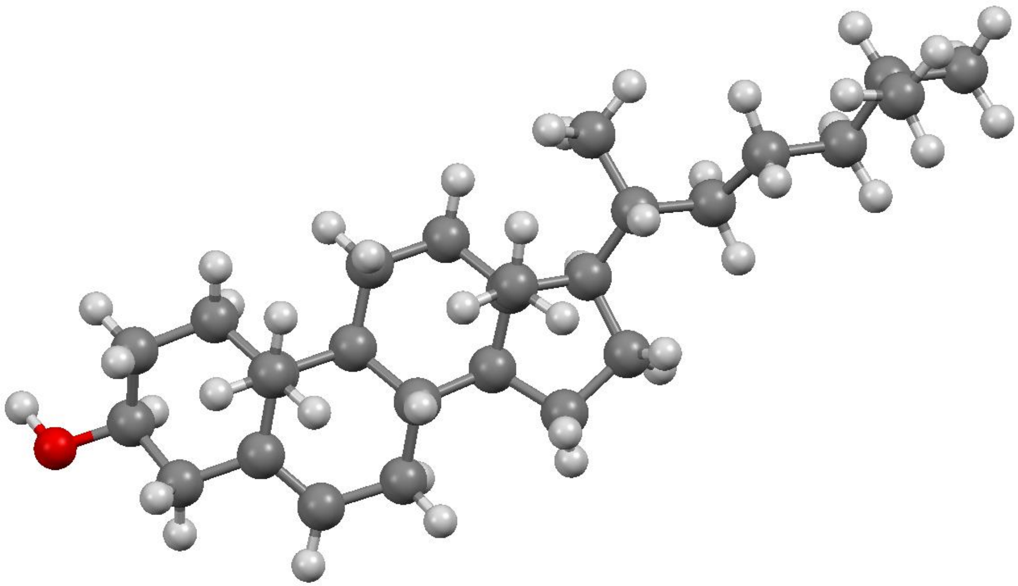


Cholesterol

- Found in:
  - Cell membranes
  - Hormones
    - Estrogen and testosterone

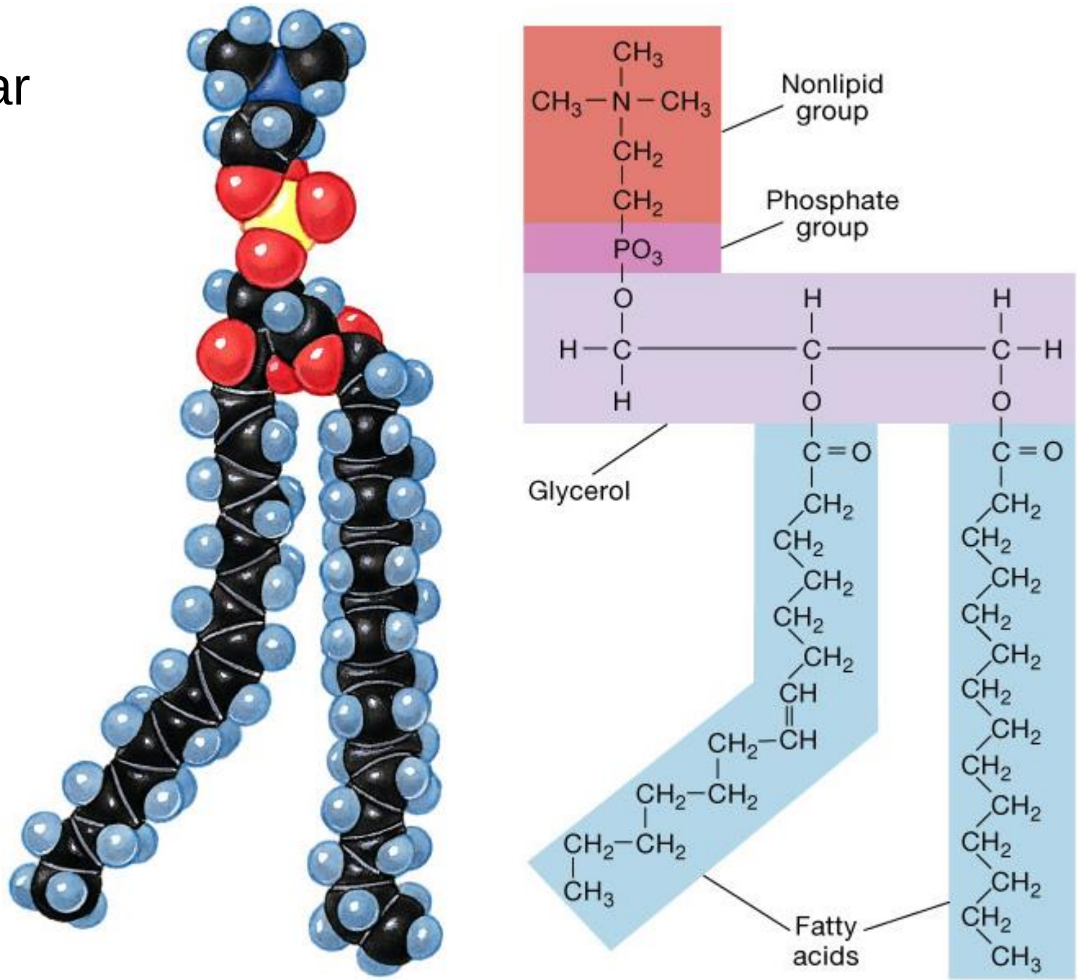


- Comes from:
  - Diet
  - Liver



Phospholipids.

- Consist of diglyceride and phosphate group
- Have polar and nonpolar regions
- Constitutes cell membrane



Proteins.

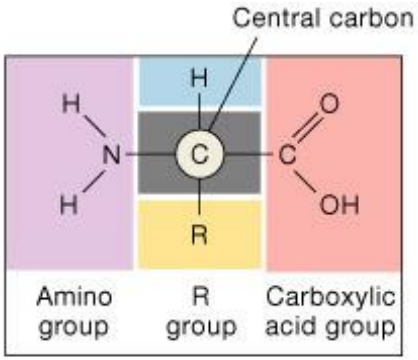
- Most abundant and diverse
  - 100,000 different kinds in the body
  - 20% of body weight
- Contain C, H, O, N, some S
- Function
- Structure
- Enzymes

Protein Functions.

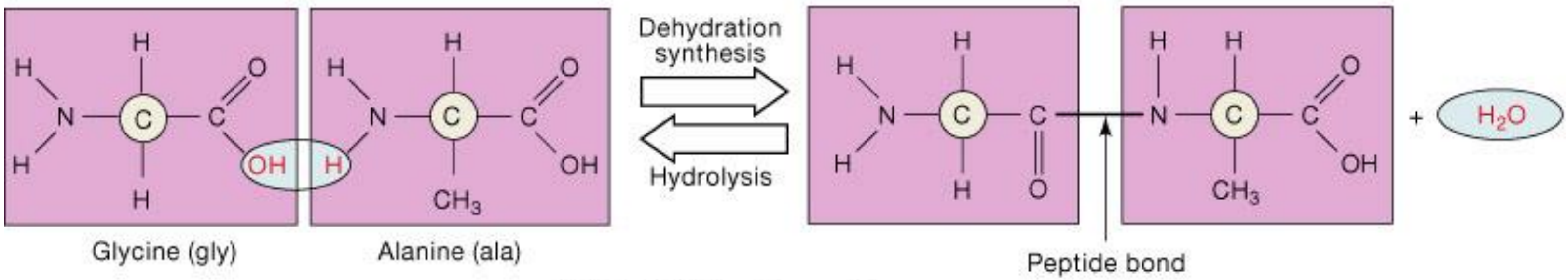
- Support
- Movement
- Transport
- Buffering
- Metabolic regulation
- Coordination, communication, and control
- Defense

Protein Structure.

- Composed of chains of amino acids
- Typical protein contains 1000 amino acids
  - Largest contains 100,000 aa or more
- Peptide bond connects aa
  - Dipeptide
  - Polypeptide



(a) Structure of an amino acid



(b) Peptide bond formation

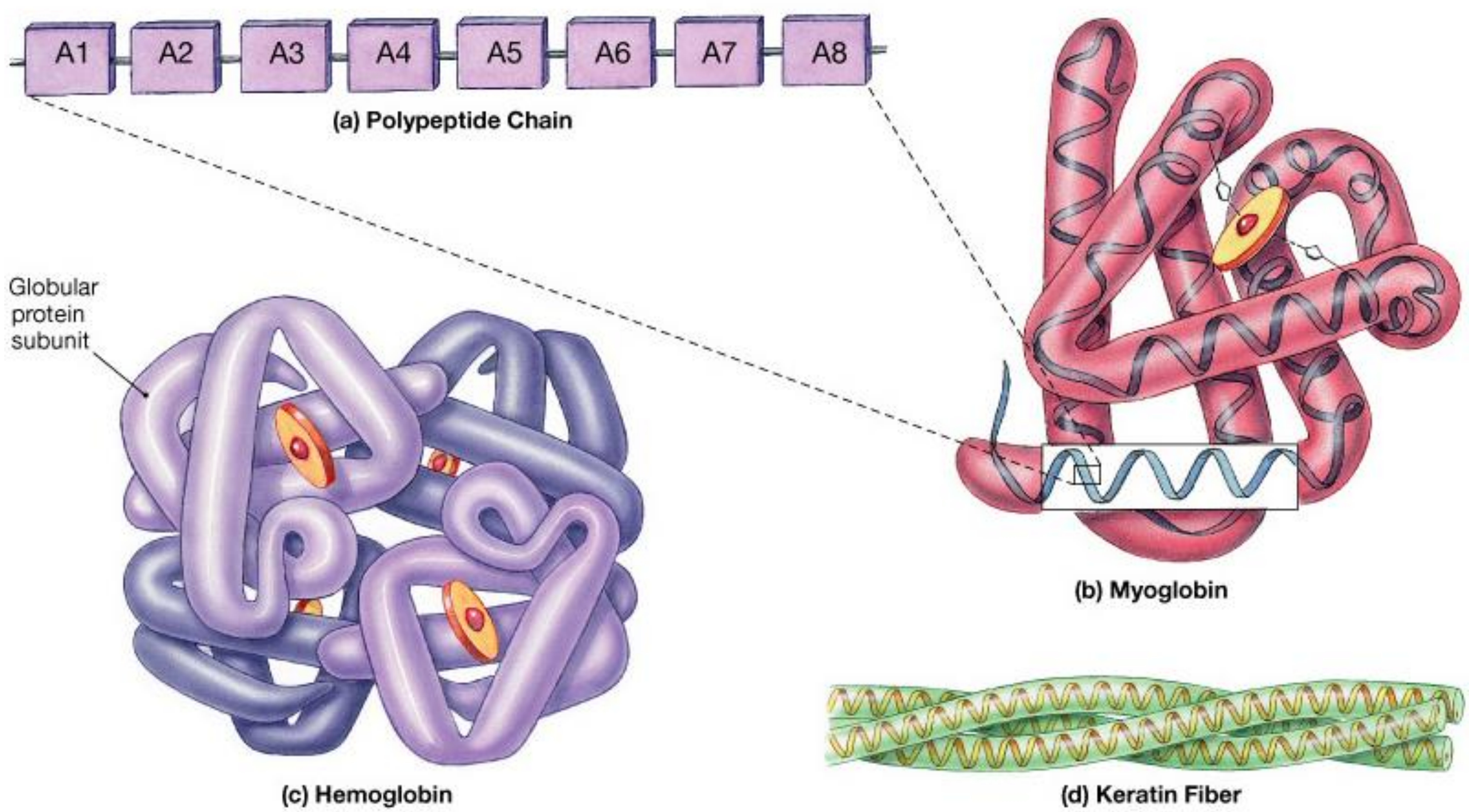
Protein Structure (2).

- Shape of a protein depends on amino acid interactions:
  - R group
  - Hydrogen bonds
  - Surrounding water molecules

- Shape = function!!!!
  - 1 tiny change can change the function!
  - Changes:
    - Changing an amino acid
    - Temperature
    - pH

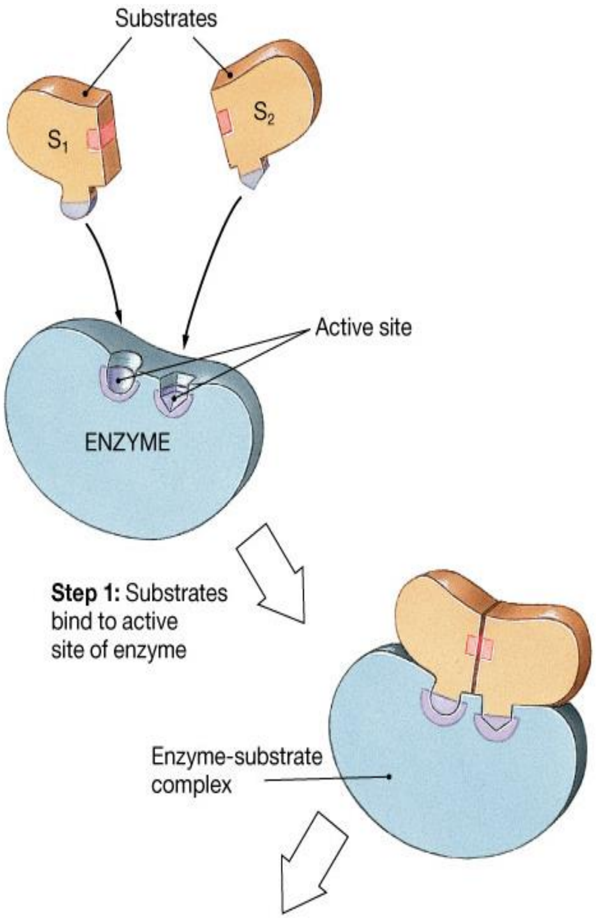
- Denaturation
  - It temp too high, proteins lose their shape and become functionless
    - If this continues, death ensues

Protein Structure: Globular vs. Fibrous Proteins.



Enzymes and Chemical Reactions.

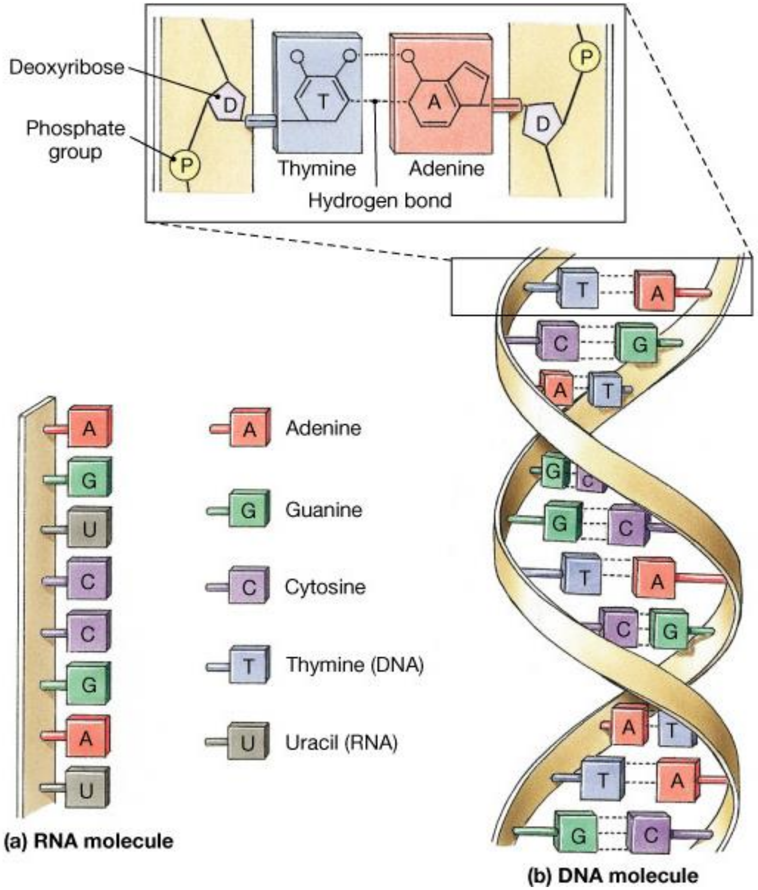
- Most chemical reactions do not occur spontaneously or occur so slowly that we would all be dead!
- Enzymes speed up the rate of chemical reactions
  - They do not become part of the reaction!



Enzyme Action

Nucleic Acids.

- C, H, O, N, P
- Store and process information at the molecular level
  - Found in cells
- 2 main types
  - DNA (deoxyribonucleic acid)
  - RNA (ribonucleic acid)
- Composed of nucleotides
  - 3 components
    - Sugar
    - Phosphate group
    - Nitrogenous base



High Energy Compounds.

- Energy obtained by catabolism of organic compounds (glucose)
- High energy bonds
  - Covalent; store large amount of energy
- ATP (adenosine triphosphate)
  - Generated from ADP (adenosine diphosphate)