

# I Structures and Properties of Organic Compounds

## I.1 Objectives

- a) Basic electronic structures and properties of organic compounds
- b) Introduction to functional groups and isomerization

## I.2 Introduction

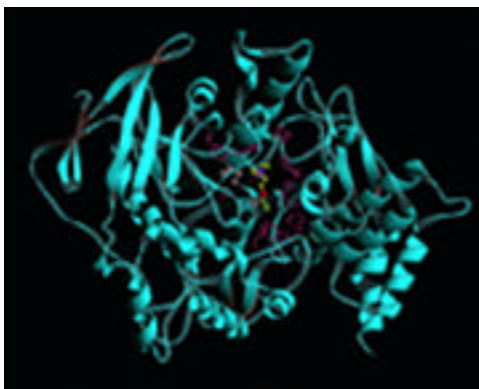
'Organic chemistry is the study of compounds that contain carbon C' (Jons Jakob Berzelius)

all life on earthy is based on organic chemistry

DNA (nucleotides)



Proteins (amino acids)



before 1800: all organic compounds have to come from nature e.g. you can NOT make them (vital force theory)

1828 Friedrich Wöhler prepared urea from ammonium hydroxide and lead cyanate

1859 first oil well drilled to produce oil

1908 first synthetic plastic (polymer)

1928 Discovery of Penicillin

1953 Structure of the DNA was determined (Watson and Crick)

Today: Billions of pounds of plastics are produced every year  
New drugs are developed every year  
Detailed understanding of natural processes  
Understanding of environmental processes  
Design of new bio-materials (bone transplants, cell membranes, organs)  
Better food supplies (genetically altered plants)

For all these accomplishments a detailed understanding of 'organic chemistry' is necessary

## 1.3 Atomic Structures and Properties

**Elements:** Fundamental building blocks of all substances

**Atoms:** Smallest particle of an element

**Neutron:** Neutral subatomic particle

**Proton:** Positively charged subatomic particle (+1 charge)

**Electron:** Negatively charged subatomic particle (-1 charge) (comprise virtually all of the volume dominant role in determining chemical and physical properties)

**Nucleus:** Center of an atom; contains protons and neutrons (very small)

An atom consists of a nucleus surrounded by electrons that are equal in number to the protons of the nucleus

**Atomic number:** Number of protons in the nucleus

A# for C is 6 (6 protons in the nucleus)

**Mass number:** Sum of protons and neutrons

**Isotopes:** Same atomic numbers BUT different mass numbers

C<sup>12</sup> 6 protons plus six neutrons (98.89%)

C<sup>13</sup> 6 protons and seven neutrons (1,11%)

The periodic table of the elements is arranged by atomic numbers.

Horizontal rows: Periods

Vertical Columns: Groups (Carbon is in Group 4)

### 1.3.1 Atomic Orbitals

- Electrons do not exist at random locations around the nucleus but in shells.
- Each Shell has a certain capacity for electrons.

Shell Number	Maximum Number of e <sup>-</sup>	Orbitals
1		
2		
3		
4		

- Within each shell, electrons occupy specific **atomic orbitals**
- An orbital is a defined region in space with the capacity to be occupied by electrons
- Each orbital can hold a maximum of TWO electrons with opposite spins
  
- The shape and orientation is described s, p, d, and f
- An s orbital is spherical
  
- A p orbital has two lobes with the nucleus located between the two lobes
  
- The first orbital of each shell (the orbital with the lowest energy) is a single s-orbital
- The next three orbitals are p-orbitals ( $p_x$ ,  $p_y$ ,  $p_z$ ) and have the same energy they are called degenerated orbitals (orbitals with the SAME energy)
- The first shell has only 2 e<sup>-</sup> (1s)

- The second shell has 8 e<sup>-</sup> (2s, 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub>)
- Aufbau principle: Electrons occupy the orbitals nearest the nucleus first

**The closer the orbital is to the nucleus the lower the energy**

*How to determine the electronic configuration of an atom? Example carbon:*

- Valence electrons are the electrons in the outermost shell  
they determine the chemical reactivity

**Octet Rule:** Atoms are most stable if they have a filled shell or an outer shell of **eight** electrons

*Summary:*

- ⇒ *atoms are made of neutrons, protons, and electrons*
- ⇒ *electrons are in shells and atomic orbitals*
- ⇒ *electrons populate the lowest energy orbitals first*
- ⇒ *every atoms tries to get to an eight electron outer shell*

**Q1:** What is the electronic configuration of Nitrogen and Chlorine?

### 1.3.2 Atomic Properties

- Shapes of atoms are spherical
- Atomic radii increase from the right to the left of the periodic table and from the top to the bottom (nuclear charge increases from the left to the right electrons are drawn closer to the nucleus)

**Electronegativity:** Ability of an atom to attract its outer shell electrons and electrons in general (Linus Pauling)

- Electronegativity increases from the left to the right of the periodic table and from the bottom to the top

**Q2:** Most electronegative atom?

Hydrogen (2.1) is LESS electronegative than Carbon (2.5)

Nitrogen (3.0), Oxygen (3.5), Chlorine (3.0), and Bromine (2.8) are more electronegative than Carbon

- Elements on the far right and top of the periodic table are called **electronegative** atoms Elements with electron-attracting capabilities
- Elements of the far left (such as sodium) are called **electropositive** atoms Elements with electron-donating capabilities
- When an element acquires an electron, energy is released. The release is called the **electron affinity**

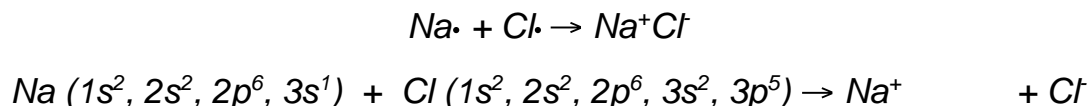
## 1.4 Bonding

### 1.4.1 Ionic Bonds

***Ionic Bond:*** Bond between two atoms caused by electrostatic attraction of plus and minus charged ions

- Involves complete transfer of electrons between two atoms of **widely** different electronegativities to form ions
- Positively charged ions are called **cations**
- Negatively charged ions are called **anions**
- Sign and magnitude of the charge on an ion is called **ionic charge** ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ )

*Example NaCl:*



The formation of NaCl can be shown by **Lewis Structures**

Na:

Cl:

## 1.4.2 Covalent Bonds

**Covalent Bond:** Bond formed by sharing of electrons (in pairs) between two atoms

Remember: Only TWO electrons can be in each orbital

- One electron from each of two atoms form a covalent bond (two electrons total)
- Covalent bonds are formed between atoms of similar electronegativity
- **Bonding electron pair:** outer-shell electron pair involved in a covalent bond
- **Non-bonding electron pair:** a lone outer-shell electron pair NOT involved in a bond between atoms

*Example  $H_2$ :*

**Q3:** Lewis structure for  $Cl_2$  and HCl

## Covalent bond formation and the periodic table

Group	Outer shell dot structure	Covalent compound with H	# of Covalent bonds
I	A·	A·H	1
II	·A·		
III			
IV			
V			
VI			
VII			

**Kekulé Structures:** electron pairs are drawn as lines and NOT as dots

**Condensed Structures:** All electrons are omitted

*Example HCl*

*Summary:*

⇒ *bond between atoms of very different electronegativity: ionic bond*

⇒ *bond between atoms of very similar electronegativity: covalent bond*

### 1.4.2.1 Covalent Bonds in Organic Molecules

- Carbon can form FOUR covalent bonds
- It loves to share electrons with its own kind

*Example Methane CH<sub>4</sub>:*

*Example Ethane CH<sub>3</sub>CH<sub>3</sub>*

- A single covalent bond between elements is called **single bond** or sigma (  $\sigma$  ) bond
- Elements can share MORE than one pair of electrons between each other
  - four electrons are shared (two bonds): **double bond**
  - six electrons are shared (three bonds): **triple bond**

*Example Ethylene CH<sub>2</sub>CH<sub>2</sub>*

*Example Acetylene CHCH*

### 1.4.2.2 Polar Covalent Bonds

- A polar covalent bond exists between atoms that form a covalent bond but have different electronegativity
- The more electropositive atom has a partial positive charge (  $\delta^+$  )
- The more electronegative atom has a partial negative charge (  $\delta^-$  )

*Example HCl*

### 1.4.3 Formal Charge

**Formal Charge:** Difference between the number of outer-shell electrons 'owned' by a neutral free atom and the same atom in a compound

- Ownership of electrons:

Unshared electrons 'belong' to the parent atom

1/2 of bonded electrons between a pair of atoms is assigned to each atom

formal charge = [# of valence e<sup>-</sup>] - [# of non-bonding e<sup>-</sup>] - 1/2 [# of bonding e<sup>-</sup>]

*Example NH<sub>3</sub> and NH<sub>4</sub>*

*Example CH<sub>3</sub>NC*

### 1.4.4 Resonance Theory

- Electrons that are fixed between two atoms are called **localized**

A single Lewis structure can describe a molecule

- In some molecules a single Lewis structure CANNOT describe the electronic structure adequately

Several Lewis structures are needed

- The negative charge is **NOT localized** at one atom but **delocalized** over several atoms

*Example Acetic Acid Ion  $\text{CH}_3\text{CO}_2^-$*

The negative charge is NOT located at only one Oxygen atom but on both

How do we know this?

- single bonds are longer than double bonds
- however, both C-O bond have the same length they are the same
- hybrid between single and double bond

The molecule has therefore a **delocalized** charge and is **resonance stabilized**

**Resonance Structures:** Valid Lewis structures with the same connectivity, differing only in the location of the electrons. Individual resonance structures DO NOT exist.

**Resonance Hybrid:** 'average' of the resonance forms used to describe a molecule or ion that cannot be described by a single structure

*Example Acetic Acid Ion  $\text{CH}_3\text{CO}_2^-$*

**Q4:** Draw the resonance structures of Benzene  $\text{C}_6\text{H}_6$ :

## 1.4.5 Hybrid Orbitals

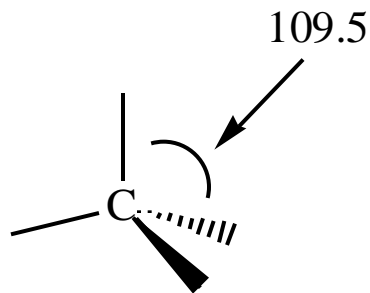
Carbon undergoes 4 covalent bonds

However it does only has two single occupied p orbitals and one filled s orbital in its outer shell

When it undergoes four bonds it is tetrahedral (bond angle of

109.5°)

e.g. methane



How to explain?

- It undergoes an orbital hybridization (Linus Pauling)

**Hybridization:** combination of atomic orbitals to form NEW orbitals of different shapes and orientations     **Hybrid Orbitals**

- sp hybrid orbitals have the same energy
- sp orbitals undergo covalent single sigma bonds

### Carbon bonded to four atoms:

Carbon atoms that have FOUR covalent bonds undergo an orbital hybridization of the 2s and the 2p<sub>x</sub>, 2p<sub>y</sub>, 2p<sub>z</sub> orbitals

They form FOUR new and equivalent sp hybrid orbitals

You are using one s orbital and three p orbitals, they are called sp<sup>3</sup>

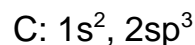
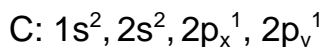
They are directed toward the corners of the tetrahedron

The carbon is said to be **sp<sup>3</sup> hybridized**

It undergoes rotation around the C-H bonds

The four new orbitals can undergo four **sigma** bonds

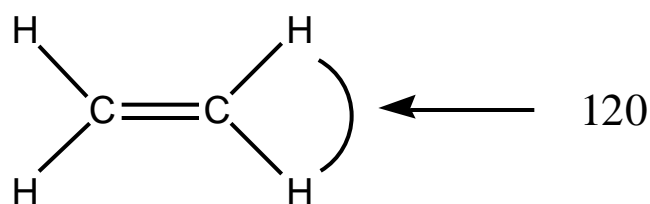
Each new sp<sup>3</sup> orbital has 25% character of a s orbital and 75% of a p orbital



### Carbon bonded to three atoms:

- the new molecule is planar and NOT tetrahedral  
can NOT undergo sp<sup>3</sup> hybridization

e.g. ethene (ethylene)



Carbon atoms that are bonded to THREE atoms undergo an orbital hybridization of the 2s and only TWO p orbitals

They form three new sp orbitals

One p orbital is left

You are using one s and two p orbitals, they are called sp<sup>2</sup> orbitals

The carbon is **sp<sup>2</sup> hybridized**

There is NO rotation around the C=C double bond

Each new sp<sup>2</sup> orbital has 33% character of a s orbital and 66% of a p orbital

- Double bonds are using one hybrid orbital of each carbon and the left p orbital of each carbon
- The hybrid orbitals undergo a sigma bond
- The p orbitals are perpendicular to the plane of the hybrid orbitals and can overlap with each other forming a pi ( ) bond

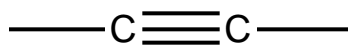
C: 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sub>x</sub><sup>1</sup>, 2p<sub>y</sub><sup>1</sup>

C: 1s<sup>2</sup>, 2sp<sup>2</sup>, p

Carbon bonded to two atoms with one triple bond:

the molecule is planar AND linear

e.g. acetylene



Carbon atoms that are bonded to TWO atoms including one triple bond undergo an orbital hybridization of the 2s and only ONE p orbital

They form two new sp orbitals

Two p orbital is left

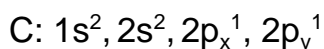
You are using one s and one p orbitals, they are called sp orbitals

The carbon is **sp hybridized**

There is NO rotation around the C-C triple bond

Each new sp orbital has 50% character of a s orbital and 50% of a p orbital

- Triple bonds are using one hybrid orbital of each carbon and the left two p orbital of each carbon
- The hybrid orbitals undergo a sigma bond
- The p orbitals are perpendicular to the plane of the hybrid orbitals and can overlap with each other forming two pi ( ) bond



### Effect of the hybridization on bonding:

- Single bonds are the longest bonds
- Triple bonds are the shortest bonds
- The shorter the bond the more stable
- The more s character the closer the electrons are to the nucleus

### *Summary:*

*⇒ bonding in organic chemistry can be explained using hybrid orbitals*

*⇒ four bonded carbons undergo  $sp^3$  hybridization*

*⇒ carbons with one double bond undergo  $sp^2$  hybridization*

*⇒ carbons with one triple bond undergo  $sp$  hybridization*

*⇒ all single bonds are sigma bonds*

*⇒ a double bond is made up of a sigma and a pi bond*

*⇒ a triple bond is made up of a sigma bond and two pi bonds*

*⇒ bond length:  $C-C > C=C > C\equiv C$*

*⇒ bond strength:  $C\equiv C > C=C > C-C$*

**Q5:** What is a diamond and what is graphite and what is the difference?

**Q6:** What is a Fullerene or buckyball?

**Q7:** How would you describe the bonding of carbon to oxygen and nitrogen?

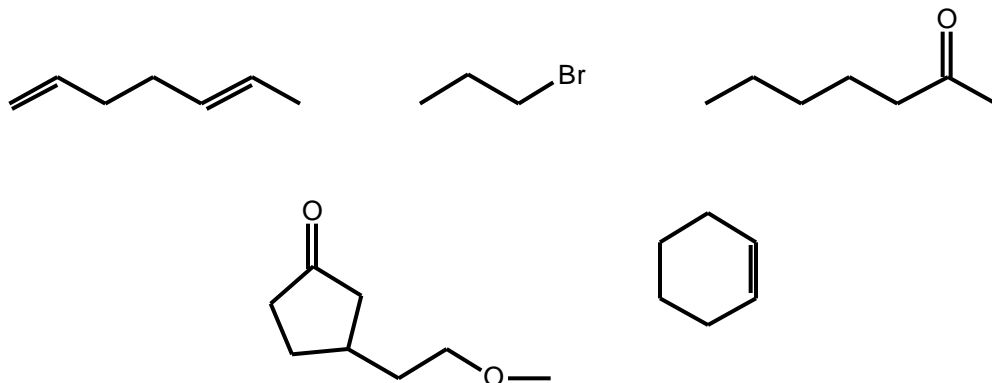
## 1.5 Functional Groups and Molecule Representation

**Functional Group:** A structural unit (grouping of atoms) in a molecule that characterizes a class of organic compounds and causes the molecule to display the characteristic chemical and physical properties of the class of compounds

**Q8:** Name all functional groups you know.

**Q9:** Name all the molecule representations you know.

**Q10:** What is the molecular formula of each of the following molecules?



## 1.6 Isomers

- Isomers:** Compounds with the same molecular formula but different structures
- Skeletal Isomers:** Compounds differ in their carbon skeleton
- Functional Group Isomers:** Compounds contain different functional groups
- Positional Isomers:** The position of the functional group differs

**Q11:** What are the isomers of  $C_3H_6O$  and  $C_4H_9R$ ?

## 1.7 Nomenclature

**Nomenclature:** Naming of organic compounds.

- Until the early 20th century, all organic compounds were named by the person who first found or synthesized it or by the organism it was found
- Today, organic compounds are named systematically by the 'International Union of Pure and Applied Chemists' (IUPAC)
- All names are based on three parts:
  - prefix: identifies the location of the functional groups
  - parent: indicated how many carbons are in the LONGEST skeleton
  - suffix: identifies most of the functional groups

**Q12:** Alcohols have a suffix of -ol. What is 2-pentanol?

## 1.8 Intramolecular Forces

There are other attractive forces besides covalent and ionic bonds (very important in biochemistry)

- **Dipole-Dipole Forces:** Molecular Dipoles attract each other  
+ of one end attracts the - of another
- **London Forces:** Attractive interactions between a temporary dipole (electron distortion) and an induced dipole (the ease with which you can distort electrons is called **polarizability**)
- **Hydrogen Bonding:** Attraction caused by hydrogen bonded to an electronegative element (O,N) being attracted to a non-bonding electron pair of another electronegative element  
Stabilization (increase in boiling point)
- **Hydrophobic Interactions:** non-polar compounds aggregate in water

Other interactions will be discussed during the course (arene-arene interactions)

## 1.9 Chemical Reactions in Organic Chemistry

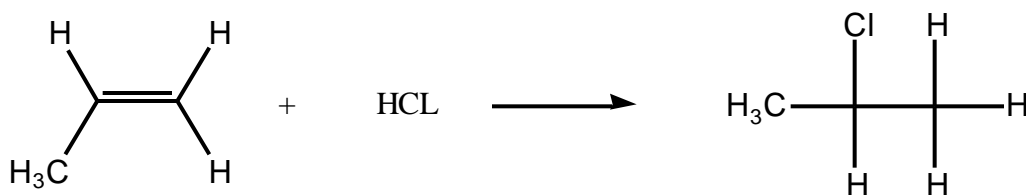
**Chemical Reactions** transform molecules from a starting material or reactant to a product

### 1.9.1 How to describe a chemical reaction?

• **Reaction Equation:** An equation that shows what happens in a chemical reaction by showing reactants and products

on the left side of the arrow are the reactants

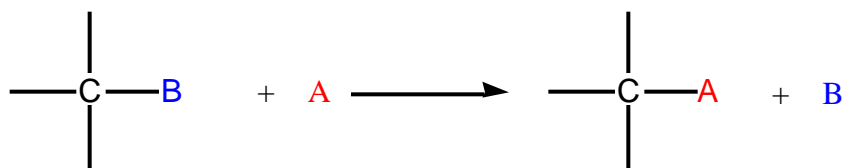
on the right side of the arrow are the products



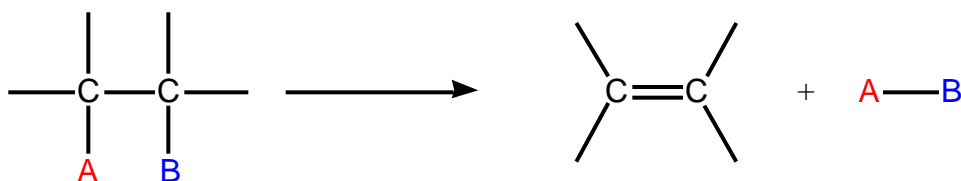
### 1.9.2 What are the types of reactions we are interested in?

Most organic reactions fall in these four categories:

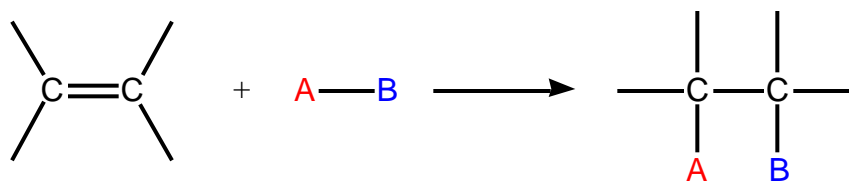
I) **Substitution Reaction:** A reaction in which an atom or group on a molecule is replaced by another atom or group



II) **Elimination Reaction:** A reaction in which atoms or groups are removed from adjacent atoms to form a double or triple bond



III) **Addition Reaction:** A reaction in which atoms or groups add to adjacent atoms of a multiple bond



IV) **Acid-Base Reaction:** A reaction between an acid and a base

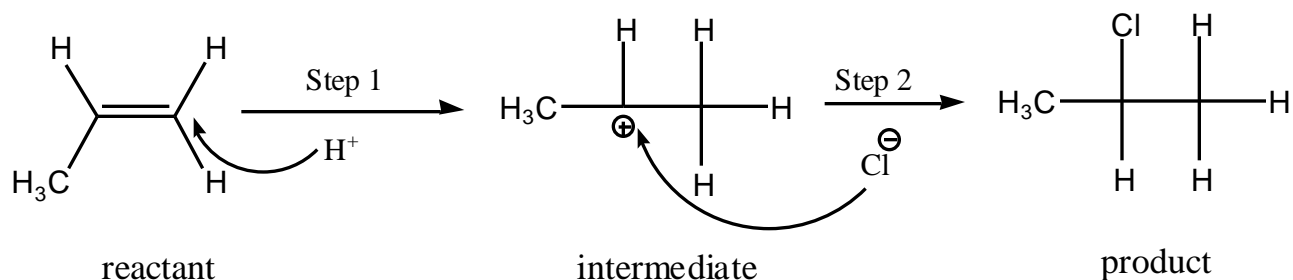


### 1.9.3 How to describe a more detailed picture of a chemical reaction?

• **Reaction Mechanism:** A step-by-step description of HOW a chemical reaction occurs

If the reaction occurs in a SINGLE step, bonds form and break simultaneously, it is called a **Concerted Reaction**

Most reactions occur in a series of steps. The reaction mechanism describes EACH individual step



**Reaction Intermediate:** An unstable, short lived (at least  $10^{-14}$  sec) species formed during a chemical reaction

Three major reaction intermediates:

Carbocation

Free Radical

Carbanion

**Carbocation:** A species with a carbon that has only three bonds, six outer-shell electrons and a positive charge

**Free Radical:** A neutral species with a carbon that has only three bonds and seven outer-shell electrons, one of which is unpaired

**Carbanion:** A species with a carbon that has only three bonds, eight outer-shell electrons including one non-bonding pair, and a negative charge

**Q13:** Why are these compounds unstable?

#### 1.9.4 How do you form these intermediates?

Free Radical:

Carbocation:

Carbanion:

**Homolytic Cleavage:** Bond cleavage in which the bonding electrons are evenly divided between the two parting atoms

**Heterolytic Cleavage:** Bond cleavage in which the bonding electrons are unevenly divided between the two parting atoms

**Homolytic Bond Formation:** Bond formation in which the bonding electrons are evenly divided between the two atoms that form the new bond

**Heterolytic Bond Formation:** Bond formation in which the bonding electrons are unevenly divided between the two atoms that form the new bond

### 1.9.5 Where do organic reactions occur?

- The reactivity is determined by the structure of an organic compound

There are sites on organic molecules that are electron deficient or have electron available that can react with each other

**Electrophile** (electron loving): An electron-deficient species that accepts electrons from nucleophiles in a chemical reaction. Electrophiles are also LEWIS ACIDS

**Nucleophile** (nucleus loving): A species with electron availability that donates electrons to electrophiles in a chemical reaction. Nucleophiles are LEWIS BASES

**Q14:** Classify the following molecules as either electrophiles or nucleophiles:  $\text{OH}^-$ ,  $\text{CH}_3\text{CH}^+\text{CH}_3$ ,  $\text{CH}_3^-$

### 1.9.6 How does the energy changes during a reaction?

- Energy is required to break and/or form bond

**Potential Energy Diagrams (Reaction Coordinate Diagrams):** a graphical depiction of energy changes during a chemical reaction

*Example:*

**Transition State:** A dynamic process of change in which bonds are being broken and formed in a reaction

**Energy of Activation:** The energy difference between reactants and a transition state

**Heat of Reaction:** The difference in energy between the reactants and the products

**Exothermic Reaction:** A reaction in which energy is released

**Endothermic Reaction:** A reaction in which energy is adsorbed

**Catalyst:** A reagent that influences the course and rate of a reaction without being consumed

## 1.10 Acid-Base Chemistry

### 1.10.1 Acid-Base Definitions

- **Brønsted Acid:** Acid that is a hydrogen ion donor in a chemical reaction
- **Brønsted Base:** Base that can accept protons during a reaction
  
- **Strong Acid:** Acid that is 100% ionized in a water solution

*Example:*

- **Weak Acid:** Acid that is only partially ionized in water solutions (most organic acids)

*Example:*

**Acid Base Reaction:** Reaction between an acid and a base

*Example:*

- **Conjugate Base:** Species formed by loss of a proton from an acid
- **Conjugated Acid:** Species formed by gain of a proton by a base

The stronger the base the weaker the conjugated acid and *vice versa*

The stronger the acid the weaker the conjugated base and *vice versa*

**Acidity Constant:**  $K_a$ , product of the concentrations of the ionized species of an acid divided by the concentration of the un-ionized form

**p $K_a$ :** negative logarithm of the acidity constant  $K_a$

• **Lewis Acid:** A substance that can accept a pair of electrons for sharing from a LEWIS base in a chemical reaction. Electrophiles are LEWIS ACIDS

*Example:*

• **Lewis Base:** A substance with an outer-shell non-bonding electron pair that it can share in a chemical reaction with a LEWIS acid. Nucleophiles are LEWIS BASES

*Example:*

Important LEWIS ACIDS:

Important LEWIS BASES:

*Summary:*

⇒ *Two Definitions of Acids and Bases*

→ *Brønsted definition is based on proton donors and acceptors*

→ *Lewis definition based on electron pair donors and acceptors*

## 1.10.2 Oxidation and Reduction Reactions

- **Oxidation:** Loss of an electron during a reaction; goes hand in hand with an increase in the oxidation state of the atom
- **Reduction:** Gain of electrons that result in a decrease of its oxidation state
- **Oxidizing Agent:** Substance that gets reduced during an oxidation-reduction reaction
- **Reducing Agent:** Substance that gets oxidized during an oxidation-reduction reaction

*Examples:*

## 1.10.2 Chemical Equilibrium

- all reactions are reversible

You can write an equilibrium equation of each reaction

The equilibrium between the right side of the reaction and the left side can be expressed by an equilibrium constant

- If the equilibrium constant is VERY LARGE the equilibrium lies VERY strongly on the side of the products and practically NO reactants remain

The reaction is said to go to completion

- In organic chemistry, you want to push EVERY reaction towards completion

*How can you do this?*

- 
- 
-

- in water the ionization constants are:
  - $K_a$  (acid ionization constant)
  - $K_b$  (base dissociation constant)

associated with the are the  $pK_a$  and the  $pK_b$

*Examples:*

### 1.10.3 Structure and Acidity and Electronegativity

**Q15:** What influences acidity?

-

-

**Inductive Electron Withdrawal:** Pulling electrons away through sigma bonds

*Examples:*

## Summary of Chapter 1:

⇒ *Atoms*

⇒ *How do atoms connect (bonds)*

→ *ionic bonds*

→ *covalent bonds*

• *hybridization*

• *resonance*

• *charges*

→ *intramolecular forces*

⇒ *Nomenclature*

⇒ *Isomers*

⇒ *Functional groups*

⇒ *Chemical Reactions*

→ *reaction equations*

→ *types of reactions*

→ *energy*

→ *mechanisms*

⇒ *Acid/Base Chemistry*

→ *acids and bases*

→ *oxidation and reduction*

→ *dissociation constants*

→ *inductive effect*