

1 Acids and Bases

Definition 1.1: Arrhenius Acids and Bases

An Arrhenius acid dissociates in water to give hydronium ions. An Arrhenius base dissociates in water to give hydroxide ions.

Definition 1.2: Bronsted-Lowry Acids and Bases

A B-L acid is any species that can donate a proton, a base is any species that can accept a proton.

Theorem 1.3: Acid/Base Dissociation Constants

$$(K_a)(K_b) = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \underbrace{[\text{H}_3\text{O}^+][\text{OH}^-]}_{\text{water ion-product constant}} = 1.0 \times 10^{-14}$$
$$\text{p}K_a + \text{p}K_b = -\log(10^{-14}) = 14$$

Proposition 1.4: Structural Effects on Acidity

Stronger acids correlate with stabler conjugate bases.

- Electronegativity
 - A more EN atom bears a negative charge more easily and is a stabler anion
- Size
 - The negative charge is spread out over a greater region of space
- Resonance Stabilization
 - Negative charge is delocalized over several atoms
- Inductive Effects
 - Electron-withdrawing atoms or groups absorb negative charge through sigma bonds depending on strength and proximity

Definition 1.5: Lewis Acids and Bases

Lewis bases are species with available electrons that can be donated to form new bonds. Lewis acids are species that can accept these electron pairs to form new bonds.

Remark. A Lewis acid is an **electrophile** while a Lewis base is a **nucleophile**.

2 Structure and Bonding

Definition 2.1: Bond fission

Heterolytic fission occurs when both electrons move to one of the bonding species.

Homolytic fission occurs when one electron moves to each of the bonding species.

Proposition 2.2: Bond length

- Atoms with larger van der Waals radii demand longer bonds

Example. $\text{CH}_3\text{F} < \text{CH}_3\text{Cl} < \text{CH}_3\text{Br} < \text{CH}_3\text{I}$

- More s -character means shorter bonds

Example. $\text{C}_2\text{H}_6 > \text{C}_2\text{H}_4 > \text{C}_2\text{H}_2$

Proposition 2.3: Bond strength

Shorter bonds generally require more energy to break

Definition 2.4: Resonance

Two or more valence-bond structures differing **only** in the placement of electrons (most commonly π and non-bonding, delocalized electrons)

Proposition 2.5: Determining major contributors

- Maximum number of octets
- Maximum number of bonds
- Minimum separation of charge
- Negative charges reside on more electronegative elements

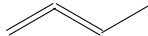
Remark. Delocalization is possible only if adjacent p -orbitals are parallel.

Remark. Hybridizations are constant between resonance structures.

Definition 2.6: Conjugation

Electron delocalization over at least three sets of p -orbitals.

Example. buta-1,3-diene  is planar, so electrons delocalize over the entire molecule.

Counterexample. buta-1,2-diene  is non-planar (note the sp C).

Definition 2.7: Polar Bond

A bond between atoms with differing electronegativities.

Proposition 2.8: Factors for molecular polarity

Notation. μ is dipole strength: the vector sum of individual dipoles.

- Polar bonds

- Molecular geometry
- **Unshared** valence electrons

Definition 2.9: Intermolecular forces

Forces *between* molecules. There are three types:

Lemma 2.10: London dispersion forces

Exist in all molecules. Magnitude depends on *polarizability*, a function of

- Number of electrons
- Shape of the molecule (i.e. surface area)

Lemma 2.11: Dipole-dipole interactions

Only present in polar molecules.

Lemma 2.12: Hydrogen bonding

Only present in molecules containing an $\text{H}-\text{N}$, $\text{H}-\text{O}$, or $\text{H}-\text{F}$ **and** a lone pair of electrons.