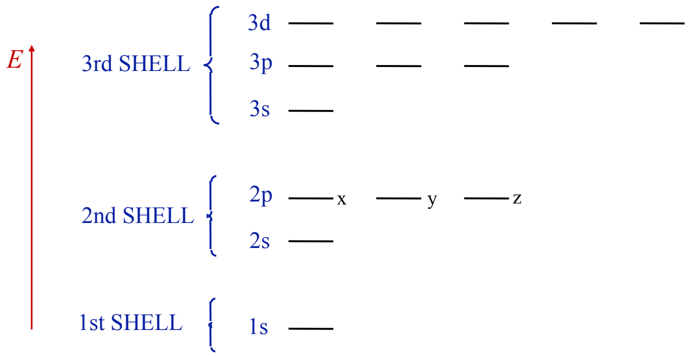
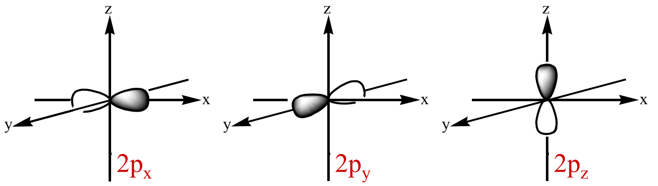
Atomic Structure

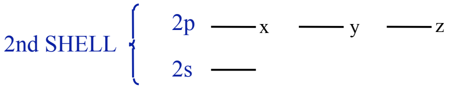
Electron Configuration

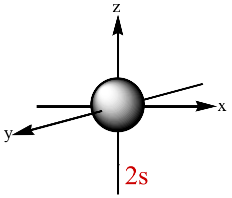


Atomic Structure

Electron Configuration







Atomic Structure

Ground State Configuration

- Lowest energy orbitals fill first

  (*Aufbau principle*)

- Each orbital can contain up to two electrons
  - electrons have opposite spins

  (*Pauli exclusion principle*)

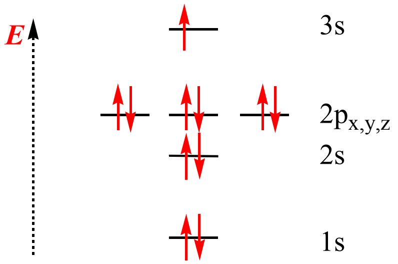
- Orbitals of equal energy fill evenly

  (*Hunds rule*)

Atomic Structure

Ground State Configuration

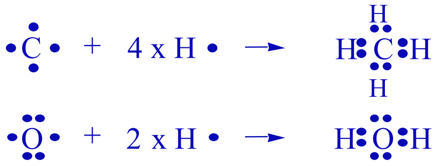
Eg. Sodium. 11 electrons



Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

Covalent Bonding

- **Sharing** of electrons
  - Eg. Carbon is $1s^2\ 2s^2\ 2p^2$ (half full)



H																	
Li												B	C	N	O	F	
Na	Mg											Al	Si	P	S	Cl	
K			Ti		Cr	Mn				Cu	Zn				Se	Br	
									Pd				Sn			I	
							Os				Hg						

Covalent Bonding

Remember:

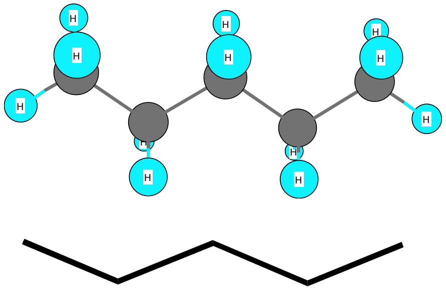
- A pair of bonding electrons is represented as a straight line

Lewis structure

Kekule structure

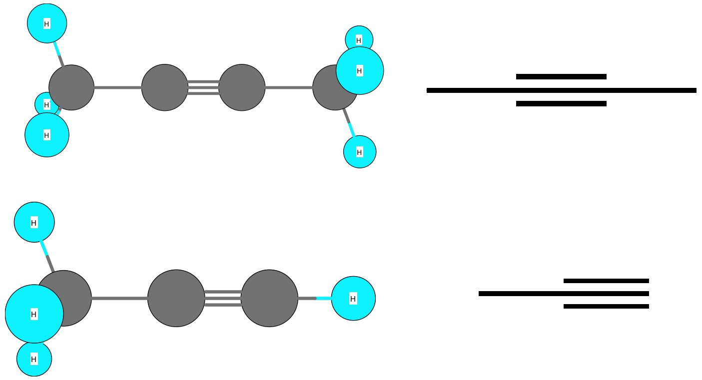
Organic Chemists Shorthand

Hydrogens are ignored and carbons are corners and terminals



Quick and convenient

Alkynes



Polar Covalent Bonds

- continuum of possibilities between ionic and covalent based on 'degree of sharing'

X : X

covalent

$\delta+$ $\delta-$
X : Y

polar covalent

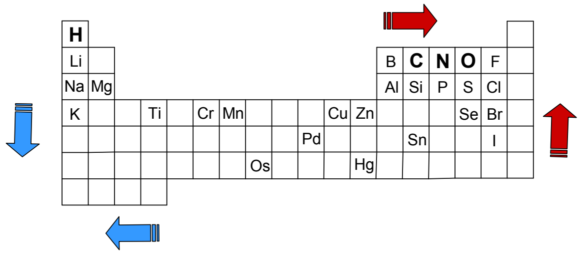
$+$ $-$
X Y:

ionic

δ = 'just a little bit'
"partial charge", not a "full charge"

Polar Covalent Bonds

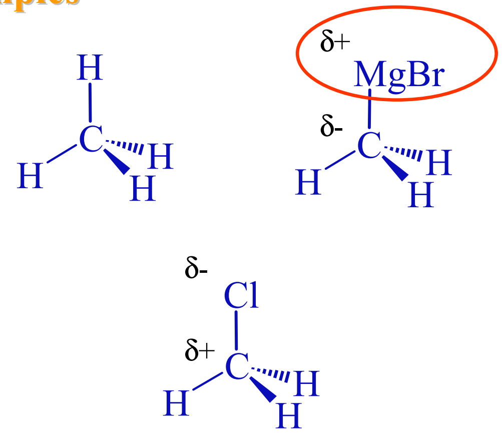
Electronegativity



- Eg. K=0.8 , H=2.1 , C=2.5 , O=3.5 , F=4.0

Polar Covalent Bonds

Examples

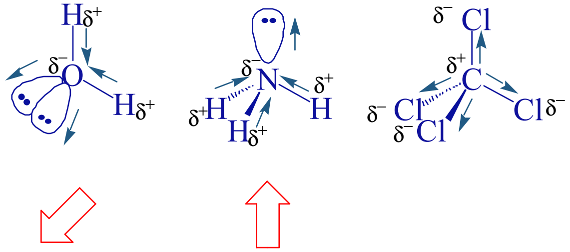


Polar Covalent Bonds

Dipole Moment

- overall polarity of a molecule
  - sum of all individual polarities

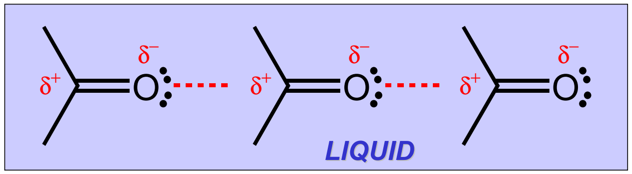
Example



Intermolecular Bonding

Dipole-dipole

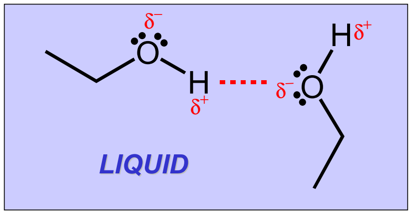
- Molecules with dipole moment
- Attraction of permanent partial charges
- MEDIUM strength
  - Eg Propanone (acetone)



Intermolecular Bonding

Hydrogen Bonding

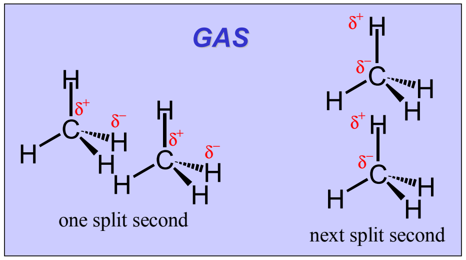
- Strong form of dipole-dipole interaction
- Require H bonded to highly electronegative atom (N, O or Halogen)
  - Eg. Ethanol



Intermolecular Bonding

Van der Waals forces

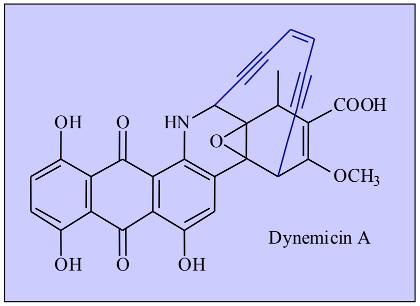
- Non polar molecules
- ‘Instantaneous’ dipole arises due to electrons random movements in atoms
- WEAK
  - Eg. Methane



Structures in 3D!!!

Alkynes as Pharmaceuticals

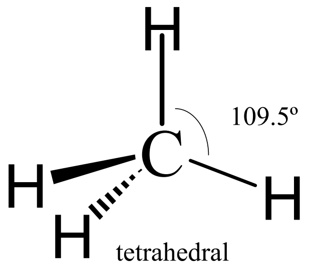
- anti-cancer compounds



Dynemicin A

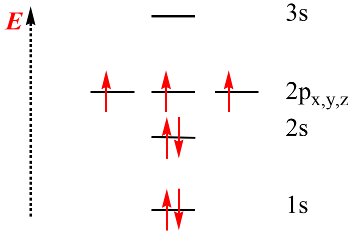
Structure

- **V.S.E.P.R.** – Valence Shell Electron Pair Repulsion
  - Useful for predicting structure
  - Electron pairs repel
  - Shape reflects this. *eg* **METHANE**

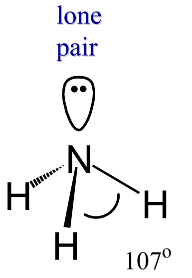


Structure

- **V.S.E.P.R.** – Valence Shell Electron Pair Repulsion
  - eg **AMMONIA**



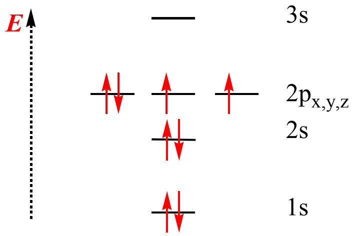
Nitrogen



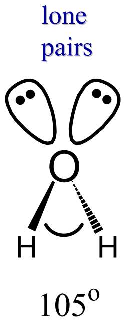
VSEPR predicts 109.5°

Structure

- **V.S.E.P.R.** – Valence Shell Electron Pair Repulsion
  - eg **WATER**



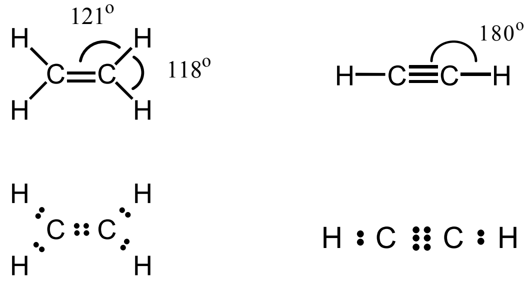
Oxygen



VSEPR predicts 109.5°

Structure

- **V.S.E.P.R.** – Valence Shell Electron Pair Repulsion
  - Multiple bonds

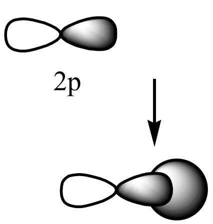


VSEPR predicts 120°

Covalent Bonding

Combining Atomic orbitals

- Sharing of electrons requires orbital overlap
- singly occupied atomic orbitals of individual atoms overlap



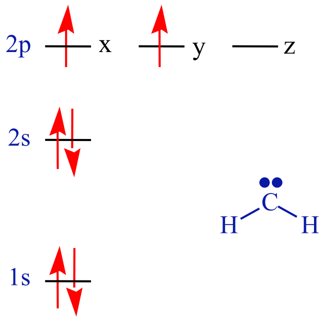
Hybridisation

Hybrid Orbitals

- Carbon ‘re-organises’ its orbitals for covalent bonding
- New orbitals derived from a mathematic combination of s and p atomic orbitals
- Why does it bother?

Hybridisation

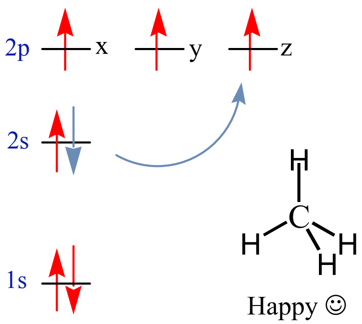
- Electron configuration of carbon:



Remember:
Only SINGLY occupied orbitals can overlap

Hybridisation

- carbon ‘promotes’ a 2s electron to the $2p_z$ orbital

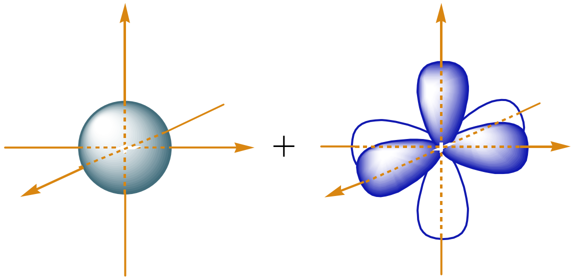


Happy ☺

Not quite this simple!

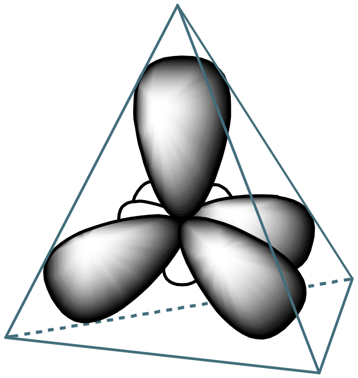
Hybridisation

- one s and three p orbitals **hybridise** to give four sp^3 orbitals



Hybridisation

- one s and three p orbitals **hybridise** to give four sp^3 orbitals



Hydridisation

Why?

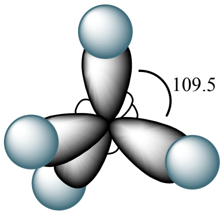
- sp^3 orbitals allow better overlap and form stronger bonds

  (stronger bonds = more stable compounds)

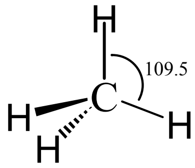
- the concept of **hybridisation** also explains the **structure** of carbon based molecules

Structure

- sp^3 hybridised carbon based molecules are **TETRAHEDRAL**.
- New single bonds are called sigma bonds
- **Bond angles 109.5º**



sp^3 hybridised



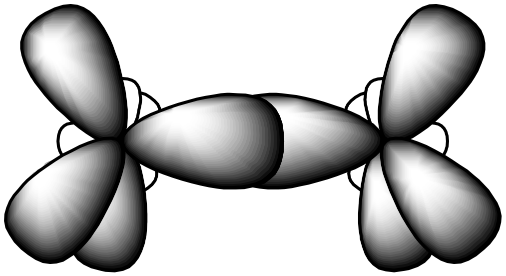
Solid wedge (towards you)

Dashed wedge (away from you)

Structure

Ethane

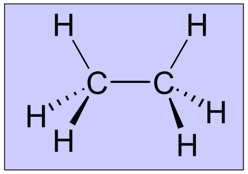
- sp^3 hybridised
  - four sigma bonds for each carbon

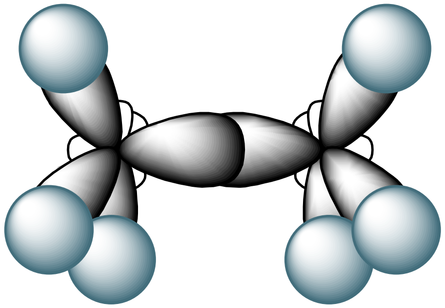


Structure

Ethane

- sp^3 hybridised

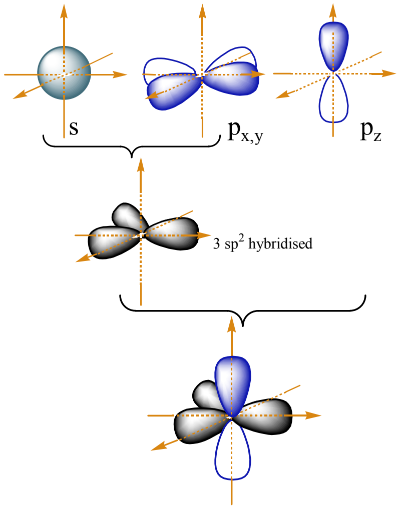


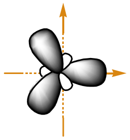


Hybridisation

sp^2 hybridisation

- One s orbital and two p orbitals **hybridise** to give three sp^2 orbitals



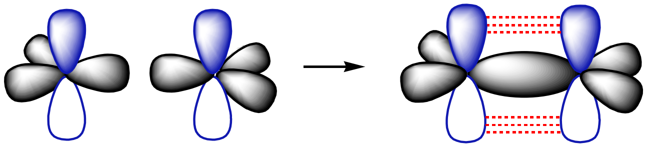


Trigonal planar

Structure

sp^2 hybridisation

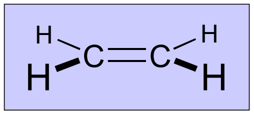
- **Bonding**
  - Each carbon has three sigma (σ) bonds
  - And one pi (π) bond



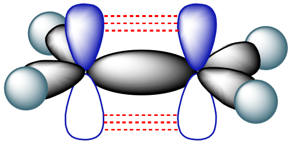
Structure

sp² hybridisation

- **Ethene**
  - 5 sigma (σ) bonds
  - one pi (π) bond



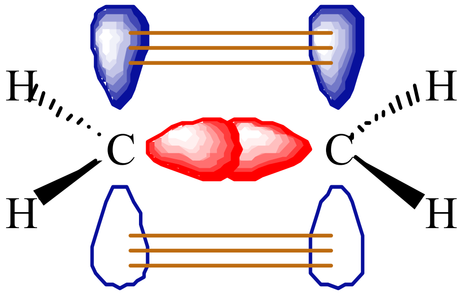
Flat



Structure

Hybridisation

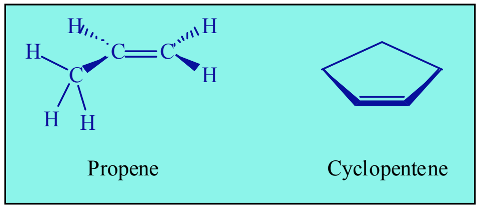
- The double bond itself = one σ and one π bond



Alkenes

Introduction

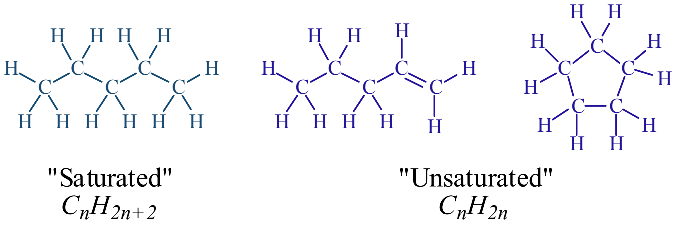
- Hydrocarbons containing one or more C-C double bond
- General formula: C_nH_{2n}



Alkenes

Degree of Unsaturation

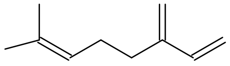
- Alkenes are said to be **'unsaturated'**
  - double bonds = unsaturation
  - rings also = unsaturation



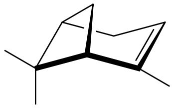
Alkenes

Degree of Unsaturation

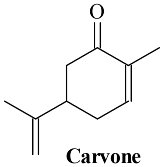
- Degree of unsaturation gives the number of double bonds and rings
  - Refered to as the number of 'double bond equivalents' (or DBEs)



Myrcen
(oil of bay)



α-Pinene
(Turpentine)

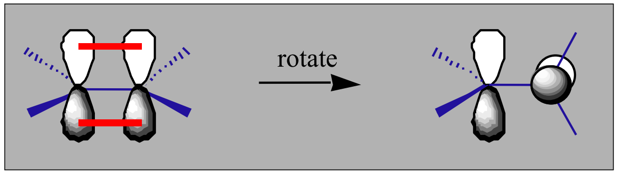


Carvone
(spermint oil)

Alkenes

Stereoisomers

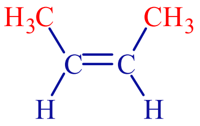
- Rotation about C-C double bond would require breaking the π bond
- Does not occur under normal conditions



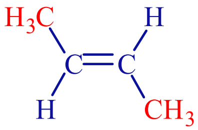
Structure

Cis-Trans Isomerism

- Restricted rotation gives rise to *cis/trans* isomerism
  - same side = cis (Z)
  - opposide sides = trans (E)



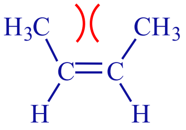
cis

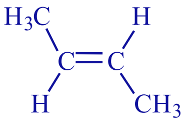


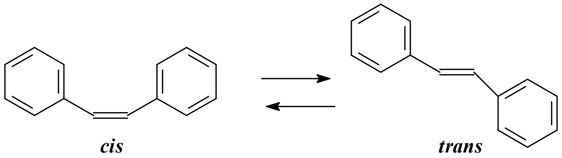
trans

Stability

- Trans (*E*) form has steric strain minimized ∴ more stable



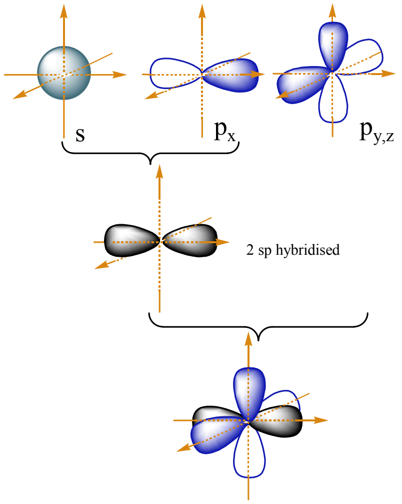




Hybridisation

sp hybridisation

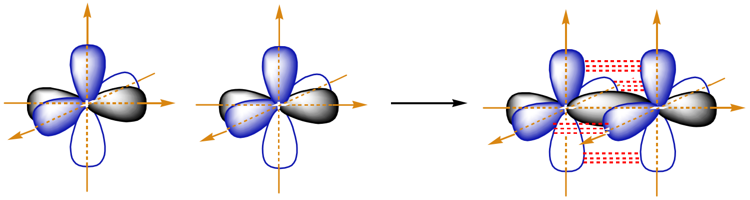
- One s orbital and one p orbital **hybridise** to give two sp orbitals



Structure

sp hybridisation

- **Bonding**
  - Each C has two sigma (σ) bonds
  - two pi (π) bonds



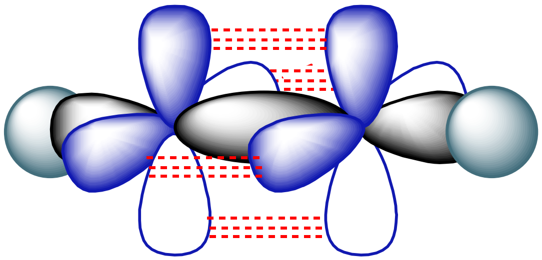
Structure

sp hybridisation

- **Ethyne**
  - two pi (π) bonds

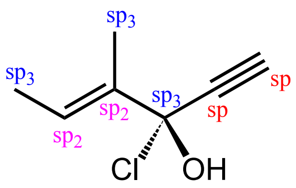
H–C≡C–H

Linear



Hybridisation and structure

- Hybridisation 'reshapes' atomic orbitals for better bonding
- sp^3 (4σ bonds)
  - Tetrahedral
  - Eg methane, ethane
- sp^2 (3σ +1π bond)
  - Flat, planar
  - Eg. Ethene
- sp (2σ +2π bond)
  - Linear
  - Eg. ethyne



Reactions and Mechanisms

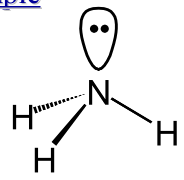
- Acid Base
  - Formal charges
  - Lowry–Bronsted theory
  - K_a and pK_a
  - Lewis theory
- Reaction Types
  - Addition, substitution, elimination and rearrangement
- Reaction Mechanisms

Formal Charges

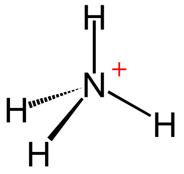
- Compounds with an unusual number of e-

  (a covalent bond is two shared electrons, each atom "owns" one electron)

Example



N "owns" 5e-
N has 5 valence e-
no charge



N "owns' 4e-
N has 5 valence e-
1+ charge

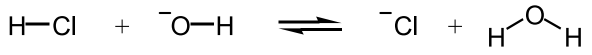
Acids and Bases

The Lowry-Bronsted Definition

- an acid is a substance which donates a proton (H^+)
- a base is a substance which accepts a proton (H^+)

Example

H-A	+	$^{-}$:B	$\rightleftharpoons$	A:$^{-}$	+	B-H
acid		base		conjugate base		conjugate acid



Acids and Bases

Acidity Constant (K_a)

- acids differ in their H^+ donating ability
- measured based on their ability to donate H^+ to water

$$\text{H-A} + H_2O \rightleftharpoons A^- + H_3O^+$$

- position of the eq. relates to acid strength
  - equilibrium favors the rhs ⇒ strong acid
  - equilibrium favors the lhs ⇒ weak acid

Acids and Bases

- quantified by measuring the eq. constant

$$H\text{-}A + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- often expressed as pK_a (= $-\log K_a$)

Acids and Bases

Relative Acid Strengths

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Acid	pK_a	K_a
CH_3CH_2OH	16.0	10^{-16}
H_2O	15.7	$10^{-15.7}$
CH_3COOH	4.8	$10^{-4.8}$
HNO_3	-1.3	$10^{1.3}$
HCl	-7.0	10^{7}

increasing acid strength

Acids and Bases

The Lewis Definition

- a lewis acid is an electron pair <u>acceptor</u>.
- a lewis base is an electron pair <u>donor</u>.

<u>Example</u>

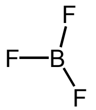
$$H^+ + {:}NH_3 \longrightarrow H\text{—}\overset{+}{N}H_3$$

lewis acid — lewis base

Acids and Bases

- Lewis acids require a unfilled low energy orbital

H^+ No electrons, ∴ empty s orbital



Only <u>six</u> electrons, ∴ empty 2p orbital

- Lewis bases require a lone pair of electrons