Quick Study ACADEMIC

ORGANIC CHEMISTRY
FUNDAMENTALS

TYPES OF ORGANIC COMPOUNDS

| HYDROCARBON	-O- ADDED	>C =O ADDED	>COO ADDED	NITROGEN ADDED	SULFUR ADDED
ALKANE $\begin{smallmatrix}C-H\\C-C\end{smallmatrix}$	**ALCOHOL** R–ÖH		**CARBOXYLIC ACID** $R-C\begin{smallmatrix}\ddot{O}\\ \ddot{O}H\end{smallmatrix}$	**AMINE** R–N̈–R	• thiol: R-SH
• ethane: C_2H_6	• methanol: Me-OH	**ALDEHYDE** $R-C\begin{smallmatrix}\ddot{O}\\H\end{smallmatrix}$	• ethanoic acid: Me-COOH	• methyl amine: H_3C-NH_2	• thioether: R-S-R'
• methyl (Me): $-CH_3$	(methyl alcohol)		(acetic acid)	• phenylamine: $Ar-NH_2$	• disulfide: R-S-S-R'
• ethyl (Et): $-C_2H_5$	• phenol: Ar-OH		• acetate ion: Me-COO⁻	(aniline)	• thiol ester: R-CO-SR'
ALKENE $\begin{smallmatrix}\\C=C\end{smallmatrix}$	• diol/glycol: (2 -OH)	• methanal: H_2CO	• benzoic acid: Ar-COOH	• R-NH₂ (1°), RR'NH (2°),	• sulfoxide: R-SO-R'
• ethene: C_2H_4	• glycerol: (3 -OH)	(formaldehyde)	**Dicarboxylic acid**	RR"R"N (3°)	• sulfone: $R-SO_2-R'$
• diene: two C=C	**ETHER** R–Ö–R	• benzaldehyde: Ar-CHO	HOOC-R-COOH	**NITRO** $R-NO_2$	• sulfonic acid: $R-SO_3H$
• triene: three C=C	• ethoxyethane: Et-O-Et		**ESTER** $R-C\begin{smallmatrix}\ddot{O}\\ \ddot{O}-R\end{smallmatrix}$	**DIAZO** R-N≡N	**HALOGEN ADDED**
ALKYNE $-C≡C-$	(diethyl ether)	**KETONE** $R-C\begin{smallmatrix}\ddot{O}\\R\end{smallmatrix}$		**NITRILE** R–C≡N	• haloalkane: R–Ẍ:
• ethyne: C_2H_2	**EPOXY** >C-O-C<		• ethyl acetate:	• methane nitrile: Me-CN	Me-Cl chloromethane
AROMATIC ⬡	• cyclic ether	• 2-propanone: Me-CO-Me	Me-CO-OEth,	**AMIDE** $R-C\begin{smallmatrix}\ddot{O}\\N-\end{smallmatrix}$	• halobenzene: Ar-X
• benzene: C_6H_6	**PEROXIDE** R-O-O-R'	(dimethyl ketone, acetone)	**Other derivatives:**		chlorobenzene: Ar-Cl
• arene: C_6H_5 (Ar-)		• diketone: R-CO-R"-CO-R'	• Peroxyacid: R-CO-OOH	• acetamide: $Me-CO-NH_2$	• acyl halide: R-CO-X
			• Acid anhydride: RCO-O-CO-R'		• aryl halide: Ar-X

FORMULAS AND ISOMERS

Molecular formula: elemental symbols with subscripts denote the composition of a compound

Empirical formula: subscripts denote the relative elemental composition
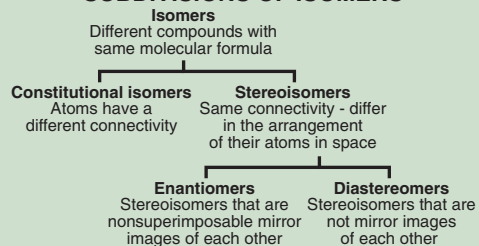
Graphical depiction:
- Dash formula: diagram all atoms, bonds as dashes
  - Bond line formula: hide H, show carbon skeleton as lines, other atoms explicit

Newman projection formula   Sawhorse formula
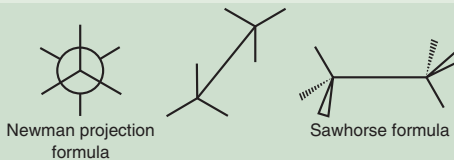
- Newman Projection: 2-d depiction
- 3-dimensional: wedges of sawhorse denote structure

SUBDIVISIONS OF ISOMERS

Isomers
Different compounds with same molecular formula

Constitutional isomers
Atoms have a different connectivity

Stereoisomers
Same connectivity - differ in the arrangement of their atoms in space

Enantiomers
Stereoisomers that are nonsuperimposable mirror images of each other

Diastereomers
Stereoisomers that are not mirror images of each other

constitutional isomers: different bonding connectivity (ex. rings, bonds, branching, substituent positions)

tautomers: easily interconverted structural isomers (ex. keto-enol for ketone)

chiral: not identical with mirror image

achiral: has plane of symmetry (superimposable on mirror-image)

epimers: a pair of diastereomers which differ only in the configuration of one atom

More than 1 chiral center:
- n chiral centers, ≤ 2^n stereoisomers
- **meso**: two chiral centers, 4 isomers: 3 stereoisomers, 1 achiral (mirror-plane)

FORMULAS AND ISOMERS



(c) CH₃ ... Arrows are clockwise
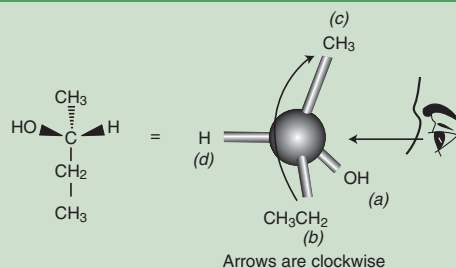
R/S notation: the four different atoms or groups attached to a central atom are ranked a,b,c,d, by molar mass. The lowest (d) is directed away from the viewer and the sequence of a-b-c produces clockwise (R) or counter-clockwise (S) configuration.

- **chiral (optically active)**: + or – rotation of plane polarized light. R/S: opposite effects
- **racemic**: 50/50 mixture of stereoisomers (no net optical activity)
- **nomenclature**: note R/S and +/- in the compound name; example: R (+) bromochloromethanol.

Fisher-projection: diagram depicts chiral/3-D structure
- **molecular conformations**: molecule exhibits structural variation due to free rotation about C-C single bond

Three-dimensional = Fischer projection
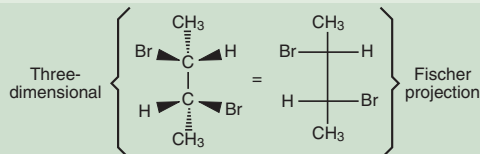
Newman-diagram: depict rotation about a C-C bond; **eclipsed** (high energy), **anti** (low energy), **gauche** (intermediate energy)
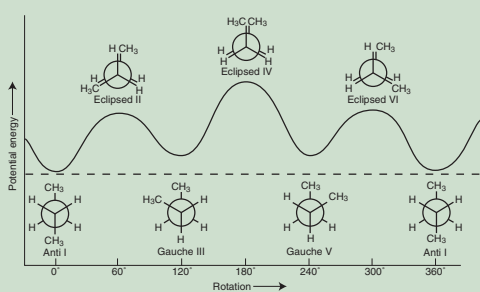
COMMON TERMS

aliphatic: non-aromatic
aromatic: benzene ring
heterocyclic: non-carbon atom in the ring structure
hydrocarbon: compound of H and C
paraffin: alkane
olefin: alkene
saturated: maximum # of H's (all C-C single bonds)
unsaturated: at least one C-C multiple bond

NOMENCLATURE

IUPAC - standard guidelines for naming compounds
Nomenclature Strategy - find longest carbon chain, identify and note location of functional groups and substituents by chain position number.
Classes of compounds are defined by the functional group. There are many common names and functional group names. Multiple names are possible.

CARBON CHAIN PREFIXES

# of C's	Prefix	R-group
1	meth-	methyl
2	eth-	ethyl
3	prop-	propyl
4	but-	butyl
5	pent-	pentyl
6	hex-	hexyl
7	hept-	heptyl
8	oct-	octyl
9	non-	nonyl
10	dec-	decyl

cyclo-: ring structure; example: cyclopropane 3-carbon ring molecule
iso-: two methyl groups on the terminus of a chain
n-: normal straight chain
t-: tertiary alkyl group
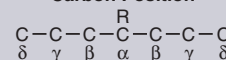**vic (vicinal)**: two substituents on adjacent carbons
gem (geminal): two substituents on the same carbon
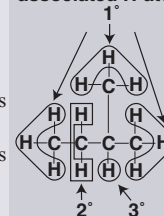**alkene isomers**: cis or trans
benzene substitution positions: ortho(1,2), meta (1,3), para (1,4)

Carbon atoms & associated H-atoms

1°   2°   3°

Carbon Position

C–C–C–Ç–C–C–C–C
δ   γ   β   α   β   γ   δ

(with R above the fourth carbon)

CHEMICAL BONDING IN ORGANIC COMPOUNDS

Bonds are usually **polar covalent**. Polarity arises from **electronegativity** difference; the larger the difference, the more polar the bond. The more electronegative atom is the negative end of the bond.

In $>C=O$, O is negative, C is positive.

LEWIS STRUCTURE: SIMPLEST MODEL

- Assign valence electrons as bonding electrons and non-bonding lone pairs.
- **Octet rule**: each atom is assigned 8 electrons; except H (2) and atoms with d-orbitals (the **"filled-shell rule"**)

$$
\begin{array}{ccccc}
H & H & : & H & \\
:N:C:O:C-H \\
H & H & : & H &
\end{array}
$$
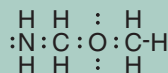
Bond Order (BO): # of bonds divided by the # of bonded neighbors. For a given pair of atoms, increased bond order reflects a stronger, shorter bond.

| Example:	BO	Length (Å)	Energy (Kcal/mole)
C-C	1	1.53	90
C=C	2	1.33	173
C≡C	3	1.20	230

Formal charge (effective atomic charge):

= (# of non-bonded electrons) + (1/2 # of bonded electrons) - (# of atomic valence electrons)

- The ideal formal charge of each atom is zero. Otherwise, minimize magnitude of charge by shifting charge to the more electronegative atom (especially for ions).

RESONANCE

The "average" of several Lewis structures provides a more accurate view of the bonding. Example: CO_3^- has 3 equal bonds, though each of 3 Lewis structures has 1 double bond and 2 single bonds.

- **delocalization**: resonance lowers the energy; electrons are dispersed, diminishing electron-electron repulsion
- **conjugated alkene**: has alternate single/double bonds:

$$>C=C-C=C-C=C<$$
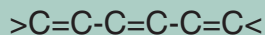
- **Hückel Rule:** A planar cyclic molecule with (4n+2) π-electrons is aromatic.

Ex: Benzene

- **antiaromatic**: 4n π-electrons: aromatic excited state.
- **heterocyclic**: heteroatom lone pairs join the planar π system
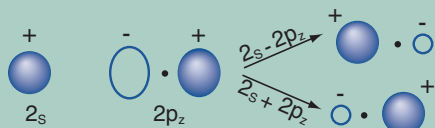
Examples:

Pyridine   Pyrrole   Furan   Thiophene

REFINED MODEL: VALENCE BOND THEORY

Overlap of atomic orbitals (AO's) or hybrids allows electrons to pair up, forming a chemical bond.

hybrid orbitals: valence AO's mix to accommodate "equivalent" bonded neighbors. Non-hybridized orbitals form lone pairs or π bonds.

MOLECULAR STRUCTURE AND HYBRID AO'S

VSEPR (Valence Shell Electron Pair Repulsion): bonding pairs (X) and lone pairs (E) define geometry of AX_n; reflects hybridization of A

sp^3 – AX_4: tetrahedral, bond angle of 109.4°; alkane; lone-pair larger than bonded pair, distorts geometry
Ex: AX_3E pyramidal; amines, NR_3, ammonia: AX_2E_2 bent: water: alcohol: R-O-H, ether: R-O-R'

sp^2 - AX_3 trigonal planar (120°); C-C-C in aromatic ring;
Ex: R-CO-R in ketone, aldehyde, carboxylic acid

sp - AX_2 linear;
Ex: alkyne -C≡C-; nitrile R-C≡N


QUANTUM MECHANICAL MODEL: MO THEORY

The **Schrodinger Equation**: $\hat{H}\psi = e\psi$, gives energy (e) and wavefunction (ψ); $\hat{H}$, Hamiltonian, the energy operator. ψ determines total energy, electron density and orbital energies.

- ψ is given by a set of MO's (**molecular orbitals**) formed by combining AO's. Each MO creates an energy level for two electrons.
- Constructive overlap of AO's : **bonding** = stable
- Destructive overlap of AO's : **anti-bonding** = unstable
- On-bond-axis: σ bonding ; σ* antibonding
- Off-bond-axis: π bonding ; π* antibonding
- Organic compound: focus on **s** and **p** orbitals
- Transition-metal atom: focus on **d** orbitals
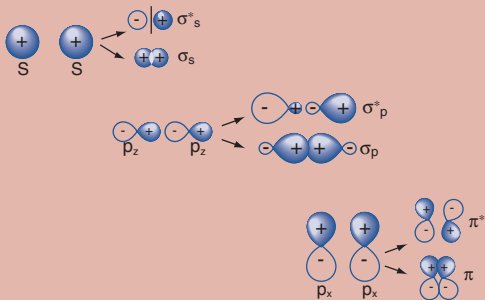
MO'S AND ENERGY

- # of MO's = # of AO's
- **bond order:** # of bonding electron-pairs - the # of antibonding electron-pairs
- **Aufbau & Pauli Exclusion Principles:** MO's are filled from lower to higher energy; each level holds up to two electrons with paired spins
- **HOMO**: Highest Occupied MO
- **LUMO:** Lowest Unoccupied MO
- **Hund's Rule:** For MO's of equal energy, maximize the total electron spin
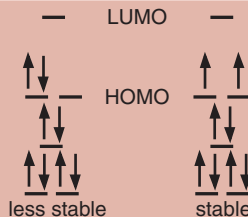
APPLICATIONS OF MO THEORY

Chemical Reactivity: The electrons in the **HOMO** are most likely to participate in nucleophilic attack (electron donor). These are the least stable (most reactive) valence electrons in the molecule.

- The **LUMO** is likely to represent an electrophilic site (electron acceptor). In photochemical processes electrons are excited to the LUMO.
- Molecules with **unpaired** electrons in MO levels exhibit a net electron spin which can be measured by **electron spin resonance spectroscopy (ESR)**.

INTERMOLECULAR FORCES

- **ELECTROSTATIC INTERACTIONS:** strong forces between ions; for charges q_1 and q_2; separated by r_{12}, and solvent dielectric constant, ε

$$\text{Energy} = \frac{1}{\varepsilon} \frac{q_1 \cdot q_2}{r_{12}}$$

Solvent with large ε stabilizes carbocation, carbanion
Solvents (ε) : water (80), ethanol (25), ethyl ether (4), methanol (33), acetone (21), hexane (1.9), benzene (2.2), toluene (2.4), phenol (9.8), aniline (6.9), pyridine (12), CCl_4 (2)

- **LONDON FORCES** (dispersion): attraction due to induced dipole moments; increases with α

Polarizability, α : measures distortion of electron cloud by electric field of other nuclei and electrons

- **DIPOLE-DIPOLE INTERACTION:** the positive end of one dipole is attracted to the negative end of another dipole. Increases with μ.
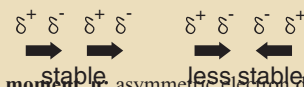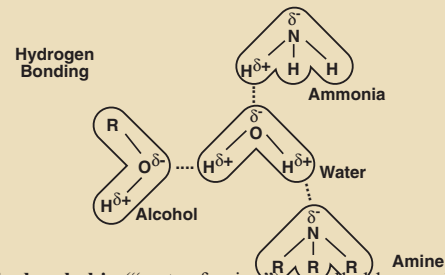

Dipole moment, μ: asymmetric electron distribution; one end on a polar molecule or bond will have partial charge (alcohol, ketone, ether, amine, carboxylic acid)
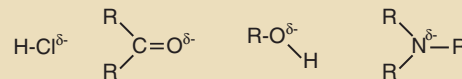
HYDROGEN BONDING

Enhanced dipole interaction between bonded H and the lone-pair of neighboring O, N or S. Can lead to dimer formation; gives "structure" to polar liquids.

hydrophobic ("water-fearing"): repelled by a polar group; attracted to "fat" or a nonpolar group
Examples: alkane or akyl group, arene, alkene
hydrophilic ("water-loving"): attracted to a polar group; repelled by a nonpolar group
Examples: -OH of alcohol, -NH of amine, -COOH of carboxylic acid

IMPACT ON SOLUBILITY

- Ionic material tends to dissolve in **water**, as do polar organic compounds, R-OH, R-COOH, $R-NH_2$.
- **Non-polar** compounds are usually **insoluble** in water, but tend to dissolve in non-polar solvents: alkanes, alkenes, alkynes, aromatics.
- **solvation:** process in which solute is surrounded by solvent molecules, creating a more stable system
- **miscible** (2 or more substances form 1 phase): liquids with similar molecular properties (polar+polar, non-polar+non-polar)
- **immiscible** (separate phases): aqueous and organic layers do not mix
- Compounds are partitioned between the layers based on chemical properties (acid/base, polar, nonpolar, ionic).
- **partition coefficient**: the ratio of the solubility limits of a material in two immiscible phases

ORGANIC REACTIONS

- Most reactions take place in several simple steps, producing an overall **mechanism**.
- Incomplete reactions may establish equilibria.
  - Each step passes through an energy barrier, characterized by an unstable configuration termed the **transition state (TS)**.
  - The height of the barrier is the **activation energy (Ea)**.
- The slowest step in the mechanism, the **rate-determining step**, limits the overall reaction rate.
- **Key principle:** examine the reactants and identify the points of excess and deficit electrons; organic reactions are best understood by "following the electrons."
  - The electron movement is often described using an **arrow** in the reaction mechanism.
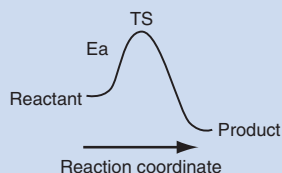
ACIDS AND BASES

Model Term	Acid	Base
Arrhenius	aqueous H_3O^+	aqueous OH^-
Bronsted-Lowry	proton donor	proton acceptor
Lewis	electron-pr. acceptor	electron-pr. donor
	electrophiles	nucleophiles

Organic reactions: use Bronsted-Lowry and Lewis models

Acid   HA <=> H+ + A−

- $K_a = [A^-][H^+]/[HA]$
- $pK_a = -log_{10}(K_a)$

strong acid: full dissociation; examples HCl, H_2SO_4 and HNO_3

weak acid: $K_a \ll 1$, large pK_a; organic acid: RCOOH
Examples (pK_a)**:** acetic (4.75), carbonic (6.37), HF (3.45), HCN (9.31), benzoic (4.19), citric (3.14), formic (3.75), oxalic (1.23)

Proton donor: acetylene (25), ethanol (16), phenol (9.9)

Base   BOH <=> B+ + OH−

$K_b = [OH^-][B^+]/[BOH]$
$pK_b = -log_{10}(K_b)$

strong base: full dissociation; examples NaOH, KOH
organic base: R-NH$_2$
weak base: $K_b \ll 1$, large pK_b
Examples: (pK_b): NH_3 (4.74), CN^- (4.7), hydrazine N_2H_4 (5.77), hydroxylamine (7.97), aniline (4.63), pyridine (5.25)

amphoteric: material which can react as an acid or a base. Example: **amino acid**; amine (base) and carboxylic acid functionality

zwitterion: self-ionization of the amino acid; the "acid" donates a proton to the "base"

OXIDATION-REDUCTION

- **oxidation:** loss of electrons; in organic reactions, add oxygen or remove hydrogen;

  examples: R => ROH => >C=O => RCOOH

- **reduction:** gain of electrons; in organic reactions, add hydrogen or remove oxygen;

  examples: hydrogenation of alkene/alkyne to alkane
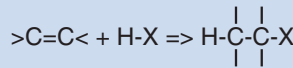
ORGANIC REACTIONS

ADDITION REACTIONS

Add groups to a pair of atoms joined by a multiple bond;
Ex: hydrogenation, halogenation, hydrohalogenation, hydration, hydroxylation. Two major types:

- **nucleophilic:** nucleophile attacks C of >C=O

$$X-Y + >\overset{|}{\underset{|}{C}}=O => X-C-OY$$
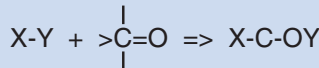
- **electrophilic:** π electrons donated to electrophile; forms carbocation, which may rearrange

$$>C=C< + H-X => H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-X$$

SUBSTITUTION REACTIONS

Replace existing group on an alkane or aromatic compound.

- **Nucleophilic substitution:** nucleophile (Nu-) seeks a "+" center (C of R group or >C=O), displaces leaving group -L.   **SN1 and SN2 mechanisms**

SN1   Step 1: R-L => R+ + L−
**   Step 2: R+ + Nu− => R-Nu**
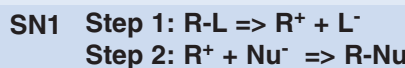
SN1: Favored for sterically hindered R; carbocation is stabilized by polar solvent (3°>2°>1°), therefore carbocation may rearrange; racemic mixture; first-order kinetics (formation of R^+ determines the reaction rate).

SN2   One Step
**   Nu− + R-L => Nu-R + L−**
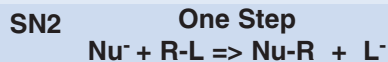
SN2: Backside attack of C bonded to L (the leaving group), inversion of stereochemical configuration; second order kinetics (Nu attack sets rate).

- **Nucleophilic aromatic substitution:**
  Two possible mechanisms:
  - elimination/addition via benzyne intermediate (dehydrobenzene), Ex.: Ar-Cl = > Ar-OH
  - addition/elimination (SNAr) mechanism; electron-withdrawing groups facilitate nucleophilic attack; ex: nitrochlorobenzene = > nitrophenol
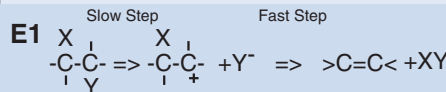
- **Electrophilic aromatic substitution:**
  - Electrophile, E^+ , attacks π electrons on the benzene ring, form arenium cation (ring stabilizes positive charge)
  - -H leaves, -E is attached to the ring
    ex: alkylation, nitration, halogenation of benzene
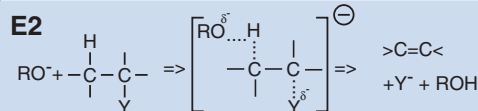
ELIMINATION REACTIONS

Reverse of addition, remove molecule "XY" from adjacent atoms, produces double bond.
Example: dehydrogenation, dehydrohalogenation, dehydration
Two possible mechanisms: E1 and E2

E1   Slow Step   Fast Step
$$-\overset{X}{\underset{Y}{C}}-\overset{X}{\underset{|}{C}}- => -\overset{X}{\underset{|}{C}}-\overset{|}{\underset{+}{C}}- +Y^- => >C=C< +XY$$

E1: slow step: Y- leaves, forms a carbocation which may rearrange;
fast step: X leaves, giving alkene; 1st order kinetics

E2

$$RO^- + -\overset{H}{\underset{Y}{C}}-\overset{|}{\underset{|}{C}}- => \left[\overset{\ominus}{RO^{\delta}\cdots H} \atop -\overset{|}{\underset{Y^\delta}{C}}-\overset{|}{\underset{|}{C}}- \right] => \begin{array}{l} >C=C< \\ +Y^- + ROH \end{array}$$

E2: Concerted reaction; base partially bonds to -H, weakens bond to Y, Y departs and H is removed by the base, producing alkene; 2nd order kinetics

ORGANIC REACTIONS

HYDROLYSIS REACTIONS

A type of solvolysis where water (the solvent) breaks a bond; adds -H and -OH to the molecule (or -H and -OR when solvent is alcohol).

Example: **saponification:** base-hydrolysis of ester

CONDENSATION REACTIONS

Two reagents combine via bridging O or N, produce water or alcohol molecule;
Example: peptide bond (N-H + RCOOH), nylon synthesis, formation of polysaccharide

REARRANGEMENTS

Change in bond connectivity; common with radical, carbocation and carbanion intermediates.
- **Driving force:** Bonds are altered to shift charge to a more substituted carbon; ex: resonance stabilization
- **Carbocation stability:** Ar>3°>2°>1° carbons

IONIC REACTIONS

Heterolytic cleavage of X-Y => $X^+ + Y^-$; ion pair, stabilized by resonance or polar solvent. Characteristic of ionic reactions involving nucleophiles and electrophiles.

RADICAL REACTIONS

- **Homolytic cleavage** of bond X-Y => X* + *Y
- **radical:** Reactive species with unpaired electrons
- **Reaction steps:** Initiation, propagation and termination. Radical geometries tend to be planar (sp^2 hybrid). Example: halogenation of alkane or alkene
- Radical stabilized by delocalization and rearrangement; relative stability: $Ar-C^*H_2 > R_2C=C^*H_2 > (CH_3)_3C^* > (CH_3)_2C^*H > CH_3C^*H_2$

EXAMPLES OF SPECIFIC REACTIONS

acylation: add RCO-
alkylation: add –R   Ex: **Grignard** (RMgX)
cyclization reaction:
  Diels-Alder: diene + alkene/alkyne
decarboxylation: lose CO_2 from a carboxylic acid
hydroxylation: add –OH
nitration: add –NO_2
pyrolysis: anaerobic thermal decomposition
sulfonation: add –SO_3H
Wittig: >C=O to >CH_2

MECHANISM TERMS

anti addition: add to opposite faces of substrate
carbene: divalent carbon; ethylene radical: $H_2C=$
carbocation: trivalent carbon, positive formal charge
carbanion: negative formal charge on carbon
electrophile: a Lewis acid; attracted to the electron density found in a chemical bond or lone pair
endo: prefix for closed structure-type
exo: prefix for open structure-type
nucleophile: a Lewis base; attracted to the + charge of a nucleus or cation
oxonium: positively charged oxygen species
syn addition: add to the same face of a substrate
ylide: a neutral molecule with a formally-charged C^- next to a P^+, or an electropositive heteroatom

SPECTROSCOPY AND INSTRUMENTAL METHODS

Chemical insight is gained by analyzing the interaction of matter and electromagnetic radiation (characterized by the wavelength, λ or frequency, ν).

MEASUREMENT METHODS

core electrons (X-ray)   electronic transitions (UV/Vis)
vibrations (IR)   nuclear spin (RF)

Energy of radiation is quantized in photons, $e = h\nu$; one photon excites one molecule to a higher energy state.

X-RAY

- **Structure determination:** x-ray λ is comparable to atomic-spacing, scattered x-rays give a diffraction pattern characteristic of a crystal structure
- **Photo-electron-spectroscopy (PES):** x-rays are energetic enough to dislodge core-electrons. Analysis of ejected electron energies gives MO and AO energies

ULTRAVIOLET/VISIBLE

- Probes electronic transitions; peaks are broadened by rotational, vibrational and solvent effects. The size of the peak depends on electronic energy spacing.
- For organic molecules, often corresponds to a transition from a π-type HOMO to a π^*-type LUMO.
- **Colorimetry - Beer-Lambert Law: A = abc**
Where **A** = absorbance; **a** = molar absorptivity (varies with λ); **b** = sample path length; **c** = molar concentration. A is related to transmission (T) by the equation: $A = -\log_{10}(T)$.

NUCLEAR MAGNETIC RESONANCE (NMR)
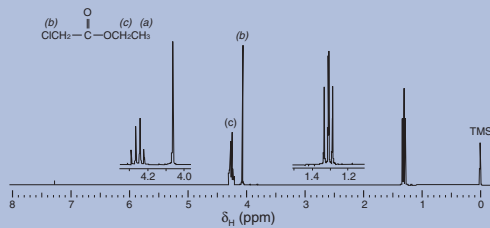
- **RF radiation** (radio waves) matches the spacing between nuclear-spin energy levels **artificially** split by a strong magnetic field.
- The **resonance** is characteristic of an atom's chemical environment; given as δ, in ppm, the shift relative to a reference compound; for H-NMR, TMS (tetramethylsilane).
- **shielding**: resonance shifts to greater magnetic field (larger delta, δ) due to chemical environment of the atom. Proton NMR is most common, though isotopes of C, O, F, Si can be studied as well.

Shift ranges (in ppm)

R(1°)	R(2°,3°)	R-X	ether	H-C=C-	H-C C-	Ar-H
1	1-2	2-3	3.5	5	3	6-10
Ar-CH₃	ket.	ald.	Ar-OH	R-OH	R-NH₂	RCOOH
2.5	2.5	9.5	5-8	1-6	1-5	10-13

- **H-NMR splitting patterns:** peak split by spin-spin interactions between adjacent H-atoms; "n" H's, give "n+1" peaks; example: -CH₂-CH₃ will have a quartet for the CH₂ and a triplet for the CH₃
- **Quantifying H-NMR data:** The strength of the resonance signal, given by the area under the curve, is proportional to the number of H's producing the resonance. The relative peak-area gives the fraction of H-atoms in the compound associated with that peak. Temperature dependent NMR is used to explore fluxional distortions.
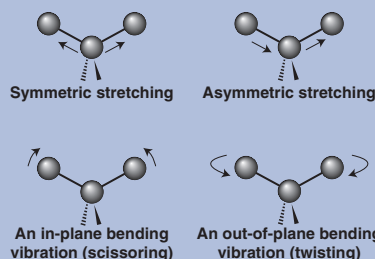
INFRARED (IR)
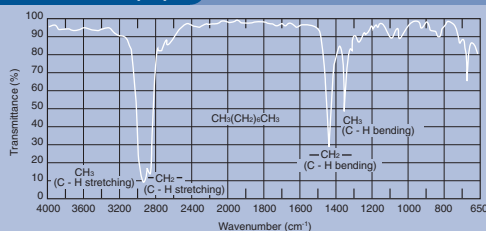
- IR excites vibrations which change the molecular dipole moment.
- Vibrational frequencies are characteristic of functional groups and bond-types; typically given in wavenumbers (ν, cm^{-1}), $1/\lambda$ (cm).

IR vibrational frequencies (wavenumber)

group	C=O	RO-H	R-OH	C-H	N-H
freq.	1700	3600	1200	2900	3400
group	H-Ar	>C=C<	-C≡C-	RC≡N	
freq.	3000	1650	2200	2250	

Symmetric stretching   **Asymmetric stretching**

An in-plane bending vibration (scissoring)   **An out-of-plane bending vibration (twisting)**

- **Isotope effects**: isotopic substitution changes the reduced mass (with little effect on spring constant), shifting the vibrational frequencies

MASS SPECTROMETRY
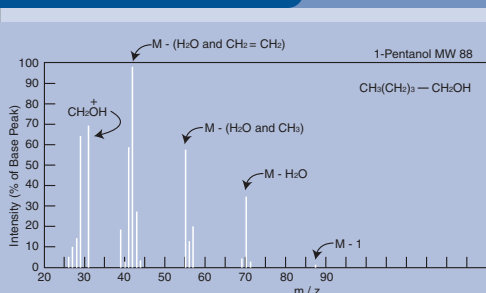
- An electron-beam ionizes and fragments the molecules in a vacuum chamber. The molecular ions are sorted by mass/charge (M/z) using a magnetic field.
- The observed spectrum is "M/z vs. intensity."
- The fragmentation pattern gives the makeup of the molecule.
- Interpretation requires **isotope masses**, not **atomic weights**.

CHROMATOGRAPHY

- Solubility and surface-interactions separate a mixture.
- The mobile phase carries the sample, which interacts with the stationary phase.
- The greater the interaction between a sample component and stationary phase, the longer the material stays on the column, giving a separation over time.

paper chromatography: liquid-solvent carries sample along a paper strip

column chromatography: sample passes through a high-surface-area matrix

instrumental separation methods; HPLC (High Performance Liquid Chromatography): sample carried by a liquid mobile phase, interacts with a solid column

gas chromatography (GC): vaporized sample is carried by a flow of inert gas through a porous-packed solid or coated column

THERMODYNAMICS

The study of the heat and work associated with a physical or chemical process.

Key Thermodynamic Variables

- **Enthalpy (H):**
ΔH = heat absorbed or produced by a process under constant pressure (normal lab conditions).
$\Delta H < 0$ for exothermic, $\Delta H > 0$ for endothermic
Enthalpies of Formation, ΔH_f^0:
$\Delta H = \Sigma$ product $\Delta H_f^0 - \Sigma$ reactant ΔH_f^0
- **Entropy (S):**
ΔS = change in thermodynamic disorder for a process
Standard Entropy, S^0:
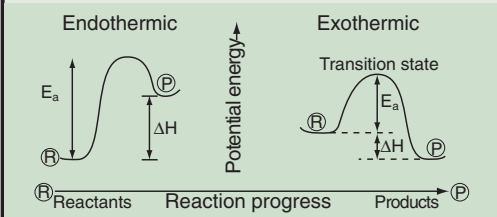$\Delta S = \Sigma$ prod $S^0 - \Sigma$ react S^0
- **Gibbs Free Energy (G):**
$\Delta G = \Delta H - T\Delta S$. ΔG is the capacity of the system to perform work. $\Delta G = 0$ at equilibrium, $\Delta G < 0$ for spontaneous (large K_{eq}), for $\Delta G > 0$, the reverse process is spontaneous.
Endergonic: $\Delta G > 0$; **Exergonic:** $\Delta G < 0$. $\Delta G = -RT \ln(K_{eq})$
Free energy of formation, ΔG_f^0:
$\Delta G = \Sigma$ product $\Delta G_f^0 - \Sigma$ reactant ΔG_f^0

Endothermic   Exothermic

KINETICS: RATE OF CHEMICAL REACTION

For a generic reaction, $A+B \Rightarrow C$, the reaction rate is defined as the rate of producing C (or consuming A or B); the rate law describes the mathematical dependence of the rate on [A].

FIRST-ORDER:
- **Rate = k_1[A]**
One species is involved in the rate determining step.
"ln [A] vs. time" is linear, the slope is the rate constant k_1.
- **Half-Life** ($t_{1/2}$) characterizes the process. [A] decays exponentially with time; $[A] = [A]_0\, e^{-kt}$.
  Examples: radioactive decay, unimolecular decomposition, SN1, E1 (carbocation), molecular rearrangement

SECOND ORDER:
- **Rate = k_2[A]^2 or k_2[A][B]**
Two species in the rate determining step.
Examples: SN2, E2, acid-base

MULTIPLE-STEP REACTION:
Complicated rate-law; focus on rate determining step. The intermediate formed at this step can be modeled using **transition-state-theory**. The **steady-state approximation** works for reactions with unstable intermediates.

TEMPERATURE AND RATE CONSTANT (k)
Arrhenius Law: $k = A\, e^{-E_a/RT}$
- **E_a**: activation energy
- Plot of "ln(k) vs. 1/T" is linear;
  slope is $-E_a/R$, intercept is ln(A)
- **T**: temperature in Kelvin (not °C)!
- **catalyst**: decreases E_a and accelerates the reaction