

Chemistry Final Review

Chemical Kinetics

Mole Fractions: unit of amount of a constituent divided by the total amount of all substituents

$$\chi_A = \frac{n_A}{n_A + n_B}, \chi_B = \frac{n_B}{n_A + n_B}, \chi_A + \chi_B = 1$$

$$\chi_{\text{solution}} \approx 1$$

Concentration: Experimentally measured

- Pressure for a gas: $P_A = \frac{n_A}{V} RT$
- Absorbance of a solution: $\text{Absorbance} = \epsilon lc$

Reaction Rate

The **rate** or velocity v of reaction is defined as a **positive** quantity

- $A + 2B \rightarrow C$
- $v = -\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{d[C]}{dt}$, **stoichiometry** is important
- Rates of chemical reactions must be determined **experimentally**

For a general reaction:

$$v = \frac{1}{n_1} \frac{d[P_1]}{dt} = \frac{1}{n_2} \frac{d[P_2]}{dt} = \dots = -\frac{1}{m_1} \frac{d[R_1]}{dt} = -\frac{1}{m_2} \frac{d[R_2]}{dt}$$

- P : products
- R : reactants

Reaction rate is **the slope of a tangent** drawn to the graph of **concentration as a function of time** divided by the **relevant stoichiometric coefficient**

- Average rate: $v_{mean} = \frac{c_2 - c_1}{t_2 - t_1}$
- Instantaneous rate: $v = \frac{dc}{dt}$

Factors affecting reaction rate

- Nature of reactants and products
- Concentrations of reactants and products
- Temperature (often rate doubles for $10^\circ C$ rise in temperature)
- Catalyst / Inhibitor

Rate Law

Find the rate: $v = f(\text{concentration}, \text{temperature})$

Rate laws can be written as a simple power law

$$v = -\frac{d[A]}{dt} = k[A]^a[B]^b[C]^c$$

- k : rate constant
- a, b, c : order of the reaction
- **Order of reaction \neq Stoichiometric coefficient**

Rate Constant

The rate constant usually depends on temperature and may also depend on concentration

The units of k must be consistent with the rate units which are usually expressed as concentration over time \rightarrow depend on the *reaction order*

- a th order in A , b th order in B , c th order in C
- Overall order of reaction: $n = a + b + c + \dots$
- The units of k are $L^{n-1}mol^{1-n}s^{-1} = M^{1-n}s^{-1}$

Determining the Order of a Reaction

- Examine **initial rate** ($t = 0$)

- Zeroth Order:
 - Concentration vs. Time: Linear
 - Rate vs. Time: Constant
- First Order
 - Initial Rate vs. Initial Concentration: Linear
- Second Order
 - Initial Rate vs. Initial Concentration: Quadratic
 - Initial Rate vs. Initial Concentration²: Linear

Determination of rate laws from experimental data

- Determine the order of reaction for each reactant and the overall order
- When comparing concentration and initial rate, look for the same concentrations
- $k = \frac{v}{[A]^a[B]^b[C]^c \dots}$

Pseudo Order of Reaction

- The concentration of one reactant is significantly higher than other reactants, throughout the reaction, the concentration of this reactant will be almost constant
- $v = k[S_2O_8^{2-}][I^-] \approx k'[I^-]$, if persulfate's concentration is 100 times higher than that of iodide ions
- Turned a second-order reaction into a *pseudo* first-order reaction with a *pseudo* first-order rate constant: $k' = k[S_2O_8^{2-}]$

Integrated Rate Laws

- 1st Order IRL ($aA \rightarrow B$)

$$v = -\frac{1}{a} \frac{d[A]}{dt} = k[A] \rightarrow \frac{d[A]}{[A]} = -ak \cdot dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -ak \int_0^t dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \ln[A] - \ln[A]_0 = \ln\left(\frac{[A]}{[A]_0}\right) = -akt$$

$$\ln[A] = \ln[A]_0 - akt \rightarrow [A] = [A]_0 e^{-akt}$$

- 0th Order IRL

$$v = -\frac{1}{a} \frac{d[A]}{dt} = k \rightarrow \int_{[A]_0}^{[A]} d[A] = -ak \int_0^t dt$$

$$[A] = [A]_0 - akt$$

- 2nd Order IRL

$$-\frac{d[A]}{dt} = ak[A]^2 \rightarrow \frac{1}{[A]} = \frac{1}{[A]_0} - akt$$

Half-life of a reactant

- 0th Order: $t_{\frac{1}{2}} = \frac{[A]_0}{2ak}$
- 1st Order: $t_{\frac{1}{2}} = \frac{\ln 2}{ak}$
 - Forms the basis for radiocarbon dating
 - ${}^{14}_6C \rightarrow {}^{14}_7N + \beta^- + \nu$
- 2nd Order: $t_{\frac{1}{2}} = \frac{1}{ak[A]_0}$

Consecutive Reactions

- $A \xrightarrow{k_1} B \xrightarrow{k_2} C$
- $-\frac{d[A]}{dt} = k_1[A], \frac{d[B]}{dt} = k_1[A] - k_2[B], \frac{d[C]}{dt} = k_2[B]$
- If $k_1 \ll k_2$, $[B]$ never gets a chance to build up, then we can treat the system as $A \xrightarrow{k_1} C$
- Steady State: $\frac{d[X]}{dt} = 0$

Parallel Reactions

- $A + B \xrightarrow{k} C + D, A + B \xrightarrow{k^*} E + F$
- $v = -\frac{d[A]}{dt} = k[A][B] + k^*[A][B] = (k + k^*)[A][B] = k_{sum}[A][B]$
- The most rapid path determines the predominate path

Equilibrium

- $A \rightleftharpoons B$
- At equilibrium, $k_f[A] = k_r[B] \rightarrow \frac{[B]}{[A]} = \frac{k_f}{k_b} = K_{eq}$

Reaction Mechanism

- Most reactions occur by a series of steps
- A reaction mechanism is a step-by-step description of a reaction
- The rate law can be determined from the reaction mechanism
- **Rate determining step** and **Steady state approximation**

Temperature Dependence of Reaction Rates

- Arrhenius Equation: The rate constant is a function of temperature

$$\ln k = \ln A - \frac{E_a}{RT} \leftrightarrow k = Ae^{-\frac{E_a}{RT}}$$

- A : pre-exponential factor (same unit as k), E_a : activation energy

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Interpretation of Arrhenius Law

- Assumptions
 - Molecules or atoms must collide to react (A)
 - The collision must provide enough energy (E_a)
- Three questions (Gas phase reaction of O_2 molecules at $300K$)
 - Speed of the molecule
 - $v_{rms} = \sqrt{\frac{3RT}{M}} = 484m/s$
 - $\bar{c} = 630m/s$
 - Cross section
 - $\sigma \approx 1.8 \times 10^{-19}m^2/molecule$
 - Concentration
 - $[O_2] = \frac{PN_A}{RT} = 2.45 \times 10^{25}molecules/m^3$
 - $\bar{c}\sigma[O_2] = 2.8 \times 10^9 collisions \cdot s^{-1}$

- Rate of collision: $\frac{\bar{c}\sigma[O_2]^2}{2} = 3.4 \times 10^{34} \text{ collisions} \cdot m^{-3} \cdot s^{-1}$
- $v = k[O_2] = Ae^{-\frac{E_a}{RT}}[O_2]^2 = \frac{\bar{c}\sigma[O_2]^2}{2}e^{-\frac{E_a}{RT}}$
- $A = \frac{\bar{c}\sigma}{2}$
- Collision Theory
 - Fraction of molecules f that collide with a kinetic energy that is no less than $E_{min} \approx E_a$ for a reaction is given by the shaded areas under each curve
 - $f \approx e^{-\frac{E_{min}}{RT}}$
 - Boltzmann distribution
 - A is roughly constant
 - P is fudge factor: effective collision factor

Elementary Reactions

- The rate law of an elementary reaction can be determined without an experiment
- Unimolecular: $v = k[A]$
- Bimolecular: $v = k[A]^2$ or $v = k[A][B]$
- Termolecular (**very slow**): $v = k[A][B][C]$, $v = k[A]^2[B]$, $v = k[A][B]^2$, or $v = k[A][B][C]$

Steady State Approximation

- List rate laws for each step of reaction
- Identify the intermediate and find the expression the rate of change
- Find the concentration of the intermediate in terms of concentration of reactants, products, and rate constants
- Substitute the concentration of the intermediate to the proper rate expression
- Final rate law must not include intermediates

Catalysis

- Accelerates or decelerates the reaction but undergoes no net chemical change
- Provide new pathway with a lower activation energy
- Enzymes
 - Homogeneous catalysts that catalyze reactions necessary to life
- Substrate
 - Molecules on which the enzymes act to promote biochemical reactions
- Michaelis-Menten mechanism
 - $E + S \rightleftharpoons ES \rightarrow E + Product$
 - Three steps, three rate laws, Steady State Approximation to find the general rate law
 - $v_r = \frac{v_{max}[S]}{K_M + [S]}$
 - $v_{max} = k_3[E]_{total}$
 - $K_M = \frac{k_2 + k_3}{k_1}$
 - when $v = \frac{1}{2}v_{max}$, $K_M = [S]$
- Alternative form of the Michaelis-Menten Equation - Lineweaver-Burke Equation
 - $\frac{1}{v_r} = \frac{K_M}{v_{max}} \frac{1}{[S]} + \frac{1}{v_{max}}$
 - $y = mx + b$
 - $y = \frac{1}{v_r}$
 - $x = \frac{1}{[S]}$
 - $m = \frac{K_M}{v_{max}}$
 - $b = \frac{1}{v_{max}}$

Quantum Chemistry

- Chemistry based on interaction of atoms
 - *electrons are the key in bonding*
- Probe: ***electromagnetic radiation***
 - An oscillating electric field

- Associated perpendicular magnetic field

$$c = \nu\lambda$$

$$E = h\nu = \frac{hc}{\lambda}$$

- Why Quantum Mechanics

- Black Body Radiation

- Different atoms and molecules can emit or absorb energy in discrete quantities only
- The amount of energy is "quantized"

$$\hbar = \frac{h}{2\pi}$$

$$\lambda_{max} \approx \frac{hc}{4.965kT} = \frac{2.9 \times 10^{-3}}{T}m$$

- Photoelectric Effect

- Light exists as small packets of energy now known as photons

- Optical Line Spectra

$$\frac{1}{\lambda} = Z^2 R_H \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

- $R_H : 1.09677 \times 10^7 m^{-1}$
- $n' < n$

- Bohr Model

- $mvr = \frac{nh}{2\pi}$
- e^- travel in perfectly defined orbits around the nucleus
- Energy is quantized
- Excellent at predicting energy of one-electron species
- $R_H = \frac{m_e e^4}{8\epsilon_0^2 h^3 c}$
- $E = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{Z^2}{n^2} \text{ Joules}$
 - $\frac{m_e e^4}{8\epsilon_0^2 h^2} = 2.1795 \times 10^{-18} \text{ Joules}$
 - $E = -\frac{1}{2} \frac{Z^2}{n^2} \text{ Hartree}$
 - Only applies to one electron species

- Atomic units are the best to do quantum mechanics
- Particle/Wave Duality
 - Any small particles of matter may at times display wavelike properties
 - de Broglie Equation

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

- Heisenberg Uncertainty Principle

$$\Delta x \Delta p \geq \frac{h}{4\pi}, \Delta E \Delta t \geq \frac{h}{4\pi}$$

- It is impossible to simultaneously measure both the *position* and *momentum* of a subatomic particle
- Schrodinger Equation (Time-Independent)

$$\hat{H}\Psi = E\Psi$$

- Ψ : wavefunction
 - for confined e^- are standing waves
 - \hat{H} : Hamiltonian operator
- Particle In a Box
 - Probability $\propto \Psi^2$
 - Normalized wavefunction

$$\int_0^l \psi_n(x) \psi_n^*(x) dx = 1$$

- Possible values of $\lambda = \frac{2l}{n}$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = E\psi$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\psi = \sqrt{\frac{l}{2}} \sin\left(\frac{n\pi x}{l}\right)$$

- Energy of a Particle in a Box

$$E_K = \frac{n^2 h^2}{8ml^2}$$

- What is a wavefunction?
 - Electron is described by a wavefunction
 - Phase of the electron's wavefunction changes at each node
 - Probability of finding the electron at a particular point x is proportional to ψ^2
 - Probability of finding the electron at a node is zero

Electrons in Atoms

- Atom: 3D box
 - e^- constrained in 3 dimensions
 - defined by interaction between e^- and nucleus
 - e^- will have both *kinetic* and *potential* energy
- Cartesian coordinates (x, y, z) vs. Spherical coordinates (r, θ, ϕ)
 - θ : angle from z -axis - latitude
 - ϕ : angle from x -axis in xy plane - longitude
- Wavefunctions are called **orbitals**
 - In atomic units

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}}e^{-Zr}$$

- Orbitals are defined by 3 quantum numbers
 - Principal ($n = 1, 2, 3, \dots$)
 - Orbital Angular Momentum ($l = 0, 1, \dots, n - 1$)
 - Magnetic: ($m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l$)
 - $\psi_{n,l,m}$
- For H , all orbitals with same principal value have the same energy (degeneracy)
- Atomic orbitals
 - Same n : same principal shell
 - Same l within n : same subshell

- The # of subshells = n
- s, p, d, f
- Orbitals have 3 parts: Radial part, angular part, constant
- Increased distance from nucleus (exponential decay)
- Presence of radial nodes (oscillatory part)
- Drawing atomic orbitals
 - Each type of subshell (l) has a specific **base shape**
 - Total # of nodes = $n - 1$
 - Total # of angular nodes = l , they are planar
 - Total # of radial nodes = $n - l - 1$, they are spherical
 - Node represents a change of phase in the wavefunction
- Electron spin facts
 - electron spin is quantized
 - 4th quantum number: $m_s = \pm \frac{1}{2}$
 - m_s does not depend on the previous three quantum numbers
 - Electron spin must be taken into consideration when "filling" orbitals
 - Consequence of the union of quantum mechanics and relativity
 - *electrons* are "fermions", all fermions have a half integer spin
- Multi-electron atoms
 - repulsion between electrons
 - higher Z = lower orbital energies
 - shape/size of orbitals is not the same
 - orbitals with same n do not have same energy
 - Helium
 - Need approximations, no analytical solution
 - Perturbation theory
 - modify the Hamiltonian operator
$$E = E^{(0)} + E^{(1)} + \dots \leftrightarrow \hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} + \dots$$
 - Variational method
 - Set and change parameters until a minimum energy is reached

$$E_0 \leq \frac{\int \psi \hat{H} \psi d\tau}{\int \psi^2 d\tau}$$

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- Electronic Configurations
 - Start with ground state
 - Pauli exclusion principle
 - Two electrons in an atom **may not** have the same quantum numbers
 - Aufbau process
 - Building up based on energy ordering of atomic orbitals
 - Hund's rule
 - Electrons in different singly occupied orbitals of the same subshell have the same or parallel spins
 - Higher total spin = lower energy
- Periodic Table
 - Only outer (valence) electrons take part in chemical reactions and bonding
 - Outer-shell electron configuration determines chemistry
 - Periodicity in outer-shell electron configuration shown by periodic table
 - Periodic Trends
 - Ionization energies
 - Energy required to remove an electron from an atom
 - Half-filled and filled shells are stable
 - Across a row increases
 - Down a group decreases
 - Effective charge (Z_{eff})
 - Increases down a group because the screening by inner-shell electrons is not perfect
 - Increases across a row, but less than expected because of screening by other valence electrons
 - Atomic radius

- Along a row, size decreases
 - Greater nuclear charge
 - No screening in same level
- Down a group, size increases
 - Outer electrons are in levels with greater n
- Reactivity
 - Group 1 - alkali metals
 - Group 17 - halogens
- Metallic Character
 - Most metallic, bottom left
 - Least metallic, top right

VBT and MO Theory

- Covalent bonds are molecular orbitals: constituted by atomic orbitals overlapping

Valence Bond Theory

- Atomic orbitals combine and mix: hybridized atomic orbitals
- $1 \times 2s + 3 \times 2p = 4 \times sp^3, 3 \times sp^2 + 1 \times p, 2 \times sp + 2 \times p$
- Same hybridization = same size, shape, energy; not the same geometry
- Total Energy of 4 hybridized orbitals = Total Energy of 4 original atomic orbitals
- Linear combination of atomic orbitals
 - sp^3 : 75% p-character, sp : 50% p-character,...
- Electrons are held farther from the nucleus in the order $sp^3 > sp^2 > sp$
- Geometry
 - sp^3 : Tetrahedral
 - sp^2 : Trigonal planar
 - sp : Linear
- Bonds (molecular orbitals)

- σ bond: $s - s(sp^n)$ bonding, formed by atomic orbitals pointing toward each other, electron density around and between the nuclei
- π bond: $p - p$ bonding, electron density above and below the axis containing the σ bond, parallel but close enough to overlap, **overlap of all 4 lobes**
- Normally, cannot have π bond without a σ bond
- Determining hybridization
 - $0 \times p = sp^3$
 - $1 \times p = sp^2$
 - $2 \times p = sp$
- Conjugation
 - If an atom **can** be **conjugated** to a π -system, it **will** be. Thus that atom will be considered to have at least one (unhybridized) p-orbital

Molecular Orbital Theory

- Molecular orbitals can be bonding (energy of MO < AOs), non-bonding (energy of MO = AOs), or anti-bonding (energy of MO > AOs)

$$\text{Bond Order} = \frac{(\text{bonding } e^-) - (\text{antibonding } e^-)}{2}$$

- Bonding: In phase; Anti-bonding: Out of phase
- e^- filled into MOs as they are in AOs, low energy first, no more than 2 per orbital, opposite spin
- σ bonds are composed of AOs that point toward each other; π bonds are composed of AOs that are parallel to each other; p orbitals can form σ bonds in MO theory
- As Z increases, the energy levels between $2s$ and $2p$ are farther apart
 - B : $2s$ and $2p$ orbitals can mix
 - Ne : $2s$ and $2p$ orbitals cannot mix
 - Energy levels of the elements will change
- Magnetism
 - Diamagnetic: No unpaired electrons, lightly repelled by a magnetic field
 - Paramagnetic: Has unpaired electrons, attracted to a magnetic field

- HOMO: Highest Occupied Molecular Orbital; LUMO: Lowest Unoccupied Molecular Orbital
- π -Delocalization
 - Conjugated system (all atoms in the chain must have a p -orbital in the same plane)
 - Butadiene: four $2p$ AOs combine to form 4 Ψ MOs
 - Allylic system: allylic cation, radical, and anion are all stabilized due to delocalization
 - Delocalization requires the p -orbitals to be contiguous and coplanar
 - **Allene**: is not conjugated because p -orbitals are not co-planar
- Resonance
 - Charge delocalized is more stable than charge localized
 - Curved arrows to indicate electrons movement
 - Reason
 - Polarity of carbonyl
 - Electronegativity
 - Charge on C , O from resonance
 - Missing an octet is worse than placing $+$ charge on a more electronegative atom
 - The only time we use charge separation in resonance structures is to demonstrate such polarity and certain bond characters; we do not use charge separation in a simple alkene nor a simple benzene ring
 - Formal charges
 - To minimize the number of formal charges
 - To minimize the number of atoms lacking an octet
 - No second row atom should have a formal charge other than 0, +1, or -1
- What drives conjugation
 - Small energetic cost in promoting an orbital from sp^3 to p , but there is a large energetic payback through conjugation
- Inductive effects
 - Depends on electronegativity, draws e^- density

- O, N : donate to the e^- density more than draw from it
- F : draws from e^- density more than donate to it

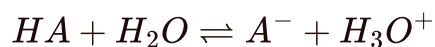
Acid-Base

Bronsted-Lowry

- Acid: Donates H^+
- Base: Accepts H^+
- Conjugate acid-base pair

Lewis

- Acid: Accepts e^- pair
- Base: Donates e^- pair



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

Dissociation constant

- Strong acids: $K_a \gg 1$, dissociation is nearly complete
- Weak acids: $K_a < 1$, dissociation is incomplete
- Equilibrium constant for water dissociation is $K_w = 10^{-14}$ at $25^\circ C$
- $K_a K_b = K_w$, for any conjugate acid-base pair

$$pH = -\log[H_3O^+], [H_3O^+] = 10^{-pH}$$

$$pOH = -\log[OH^-], [OH^-] = 10^{-pOH}$$

- The smaller the pK_a , the stronger the acid
- The smaller the pK_b , the stronger the base
- The salt of a weak acid gives a basic solution, the salt of a weak base gives an acidic solution

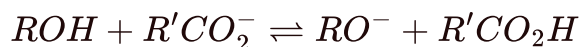
Buffers

- Solutions that are resistant to changes in pH upon addition of water, acid, or base
- Weak acid + its conjugate base in "appreciable amounts"
 - Equimolar of acid + base $\rightarrow pH = pK_a$

$$[H_3O^+] = 10^{-pH} = K_a \frac{[HA]}{[A^-]}$$

Organicky Acid-Base Chemistry

- Conjugate base of a strong acid is a weak base
- Conjugate base of a weak acid is a strong base
- Equilibria will always lie toward the weaker (more stable) acid and base



$$K = \frac{[RO^-][R'CO_2H]}{[ROH][R'CO_2^-]} = \frac{K_a(ROH)}{K_a(R'CO_2H)}$$

- charges are unstable
 - Charge stabilization: negative charge on a conjugate base; positive charge on a conjugate acid
- Electronic effects on pK_a
 - More electronegative atoms can hold a negative charge better (basicity decreases as you go to the right in the same row)
 - Basicity goes up as you go up on the Periodic Table: larger atoms can hold a negative charge better since the charge is more spread out in a much larger orbital
 - Resonance: the more stable of a conjugate base, the stronger is the conjugate acid
 - Inductive effects: More electronegative atoms can stabilize a negative charge through one or more σ -bond via "induction"
 - Hybridization and Bonding: negative charge closer to the nucleus is more stable, thus more s -character, more stable
 - Carboanion: $sp^3 < sp^2 < sp$

- Hydrogen bonding: Intramolecular hydrogen bonding is more stable
- Aromaticity: If protonation of a molecule breaks up its aromaticity (6 π electrons), then the resulting compound will be highly acidic. The original molecule will be stable and non-basic

α -amino acid

- amino group: basic
- carboxyl group: acidic
- In steps of dissociation: the most acidic proton dissociates first
- Why is the pK_a of the carboxylic acid of an α -amino acid so much lower than that of acetic acid
 - Inductive effect: positive charge on the ammonium a few bonds away inductively withdraws electron density from the carboxylate and thereby stabilizes the negative charge
- Isoelectric point
 - The pH at which the amino acid exists in solution predominantly as a neutral species

$$pI = \frac{pK_a(1+) + pK_a(1-)}{2}$$

Substitution Reaction Mechanisms

SN2 (Bimolecular nucleophilic substitution)



- Bromomethane is **electrophile**: in the form of a lone pair of electrons to form a new covalent bond. Lewis acids. Electrophilic carbon has a partial positive charge due to the dipole of the polar covalent bond
- I^- is **nucleophile**: donates a pair of electrons to an electrophile to form a new covalent bond. Lewis bases
- Br^- is **leaving group**: leaves from electrophile
- $v = k[CH_3Br][Na^+I^-]$, obey second-order kinetics

- Carbon makes a new bond and breaks an old bond; it remains tetravalent
- Any of iodide's 4 lone pairs can attack
- Carbon is attacked from its "backside" (back lobe of the $C - Br$ bond)
- $C - Br$ bond is broken heterolytically, both electrons goes to Br , as opposed to homolytically
- During transition state, both iodide and bromide are partially bonded to carbon, each has a partial negative charge
- Electrophilic carbon is said to undergo **Walden Inversion**, where the substituents invert about the carbon
- It is concerted as the attack by the nucleophile and the departure of the leaving group occur in concert (simultaneously); there are no intermediates
- The rate of the SN_2 reaction depends on
 - The structure of the electrophile
 - The nucleophilicity of the nucleophile
 - The stability of the leaving group
 - The polarity of the solvent
- Electrophile
 - Methyl structure: $CH_3 - X, v_{relative} = 30$
 - Primary (1°) structure: $CH_3 - CH_2 - X, v_{relative} = 1$
 - Primary electrophiles cannot undergo SN_1 reactions
 - Secondary (2°) structure: $(CH_3)_2 - CH - X, v_{relative} = 0.02$
 - This electrophile can undergo either reaction
 - Tertiary (3°) structure: $(CH_3)_3 - C - X, v_{relative} \approx 0$
 - Tertiary electrophiles do not undergo SN_2 reactions
- Nucleophile
 - More polarizable **lone pairs** are better: polarizability refers to how easily the electron density in an orbital can be reshaped by a local charge or dipole
 - "Hard" orbitals: O, N ; "Soft" orbitals: S, P
 - Conjugate bases are better nucleophiles than their conjugate acids
- Periodic Trends

- Nucleophilicity increases as you go down the Periodic Table due to an increase in polarizability
- Nucleophilicity increases as you go to the left of the Periodic Table due to decreased nuclear charge
- Basicity increases as you go up the Periodic Table due to greater charge density (higher affinity for proton); Basicity increases as you go to the left on the Periodic Table due to lower electronegativity
- Leaving groups
 - Good leaving groups are those that are stable in solution with the pair of electrons they have secured.
 - They must also have weak $C - \text{leaving group}$ bonds
 - Hydride and most carbanions are highly unstable and will not be leaving groups
 - Protonation of the alcohol converted a poor leaving group into a good leaving group
 - Its ability correlates with its stability (the pK_a of its conjugate acid)
- Solvents
 - Good solvents for S_N2 are moderately polar (and aprotic), stabilizes the polar transition state
 - Too polar, solvate the nucleophile too well, hindering it from reaction
 - Highly polar solvents also enhance S_N1 reactions. Such solvents are called **protic** solvents if they contain an (weakly) acidic hydrogen (δ^+ on H). They can dissociate, and can donate a hydrogen bond
- Stereochemistry
 - No stereogenic centers: Achiral product
 - Has stereogenic centers but not at the electrophilic carbon: start with optically pure, produce optically pure
 - Electrophilic center is the only stereogenic center: optically pure gives optically pure
 - Several stereogenic centers (including the reaction center): optically pure gives optically pure

SN1 (Unimolecular Nucleophilic Substitution)

- Rate is dependent on the concentration of the electrophile and **independent** of the concentration of the nucleophile
- Two-step mechanism
 - First, the leaving group leaves, yielding an **intermediate** called a carbocation (rate-limiting step)
 - Second, the nucleophile then attacks the carbocation from either side of the plane
 - If the electrophilic carbon was a stereogenic center, the product is a racemic mixture, the hybridization of the carbon passes from sp^3 to sp^2 and back to sp^3
- Electrophile
 - Methyl and primary carbocations will not form
 - Secondary carbocations will be slow to form
 - Tertiary carbocations will form readily
 - Great stability of the more substituted carbocations is due to an ability of the alkyl groups to donate electron density into the cationic center, namingly **hyperconjugation**
- Nucleophile
 - Nucleophilicity is not very important
 - SN1 reaction is often called solvolysis (nucleophile is often the solvent)
- Leaving group
 - Must be stable
- Solvent
 - Highly polar solvents are best because they stabilize the fully charged carbocation intermediate
 - Protic solvents are better than aprotic solvents, better at solvating anions
 - At secondary centers: protic solvents will enhance SN1 reactions, aprotic solvents will enhance SN2 reactions
 - SN1 will occur in aprotic solvents on tertiary centers
- Stereochemistry

- If center is a stereogenic center: stereoisomers will be produced, enantiomers or diastereomers
- If center is not a stereocenter: only one product will form
- Intramolecular ring closures to form 3 – 6 membered rings is much faster than intermolecular reactions

Other chemicals

- Vinyl/Aromatic halides (sp^2 carbons) do not undergo SN1 or SN2
 - SN2: too hindered
 - SN1: CC bond is unstable
- Allylic/Benzylic carbons can undergo SN1 reactions

Secondary Center Competitions

- Deduce the type of reactions from
 - The optical activity of the product
 - The properties of the solvent

General Guidelines

- Under acidic conditions, try to limit oxygen states to neutral and + (ROH_2^+ , ROH)
- Under basic conditions, try to limit oxygen states to neutral and – (RO^- , ROH)