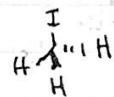
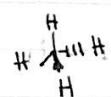


30 Mar 2020

> Chemical Intuition of org & inorg chemical react

Olivia
Danielle
shampoo
cake
genetics

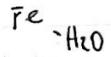
methane iodomethane



- nontoxic
- flammable
- very toxic
- nonflammable



- yellow
- stable in H₂O



- blue
- unstable in H₂O

> Where's e⁻, how they flow

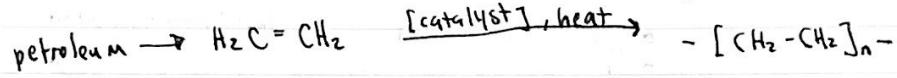
organic chem - C-containing compound

inorganic chem - transition metal & main group compound

materials chem - extended solid, materials

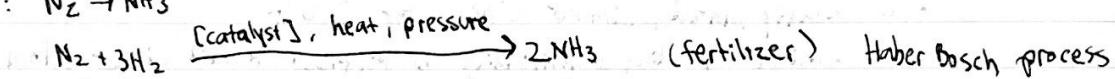
> O chem: Plastic -

> polymer - large molecules composed of many repeating subunits



polyethylene

> Inorganic: N₂ → NH₃



> Materials: Silicon → element we know how to make most pure - "Aragadro project"

- Semiconductor, transistor effect

1 Apr 2020

Saturated Alkenes Hydrocarbons (Alkenes)

<< Versatility of Carbon

- small → easy to form multiple bonds
- 4 valence e⁻ → var geometry (linear, trigonal, tetrahedral)
- intermediate e⁻ negativity → covalent bond w/ elements

<< Hydrocarbons

> compounds of carbon & hydrogen

> energy source - gasoline

> chemical feedstock - plastic, pharmaceuticals

> saturated (alkane) - only single bond ex: ethane

> unsaturated (alkenes) - w/ double bond ethylene

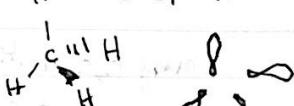
(alkynes) - w/ triple bond acetylene



H C: sp³ tetrahedral

→ Bonding: VB theory & hybridization

- σ bond formed by overlap of hybridized orbital



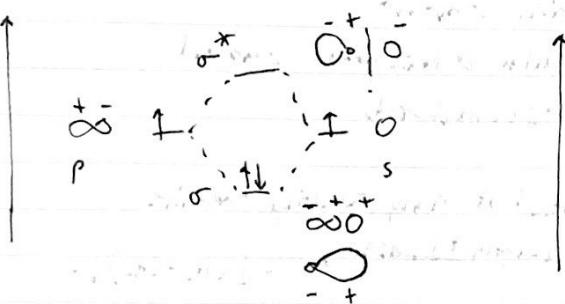
H: s orbital

MO Theory

- orbital overlap
 - bonding - in phase
 - antibonding - out of phase
- Bonding - in phase
- stabilizing
- constructive interference

→ Organic Molecules

C-H

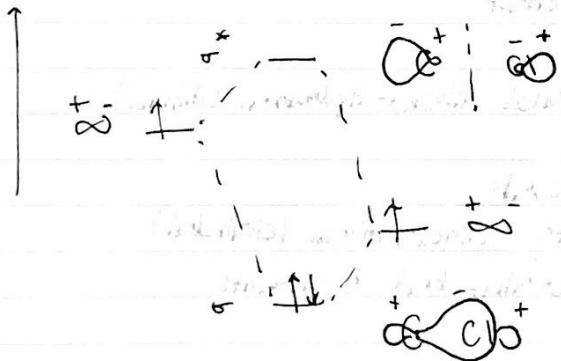


C-C



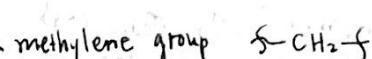
- remember change in phase
- e⁻ equally shared, similar e⁻ neg. for C & H
- neither bonding & antibonding is polarized toward either atom

C-X, where X is more e⁻ neg. - e.g. halide, oxygen



Linear Alkanes

- straight chain
- C_nH_{2n+2}

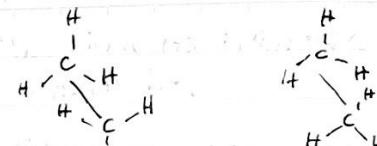


- many representations
- naming - memorize

→ Conformation Analysis

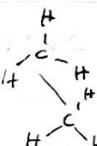
- C-C bond rotate easily in linear alkanes.
- use Newman projection to visualize
- staggered (more stable by 12 kJ/mol (99%))

↓
staggered, eclipsed, gauche



staggered $\xrightarrow[60^\circ]{\text{rotate}}$

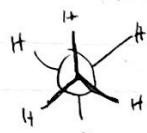
more stable



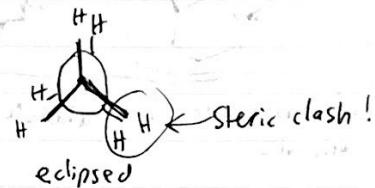
eclipsed

↑
has more

steric clash
between hydrogens

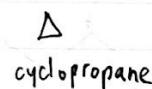


staggered



eclipsed

↔ Cyclic Alkanes



(less stable)

ring strain - poor overlap of orbitals, less stable

→ Chair Conformation

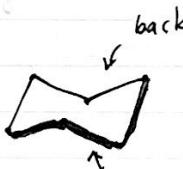
- lowest energy

- three sets of parallel lines

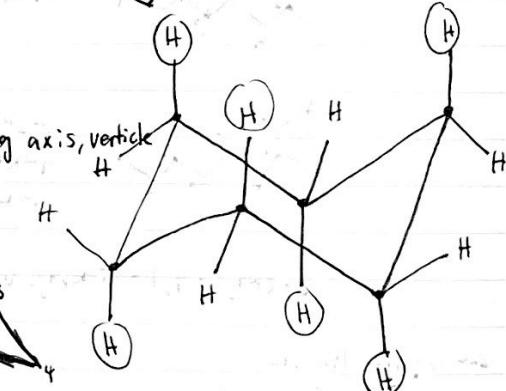
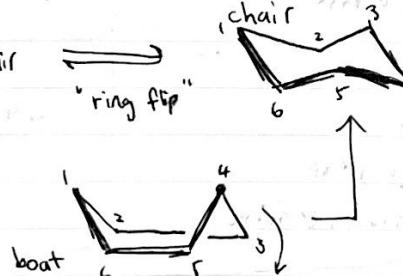
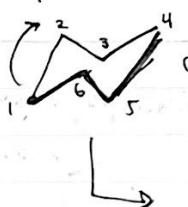
- two sets of inequivalent hydrogens

- axial - up & down, pointing along ring axis, vertical

- equatorial - points along ring equator



- cyclohexane is Dynamic



- after ring flip, all axial H becomes equatorial H

- large substituents prefer to be equatorial to prevent steric interference

- $-C(CH_3)_3$ can have some axial, but most equatorial

- $-C(CH_3)_3$ equatorial almost always

- conformation affects reactivity

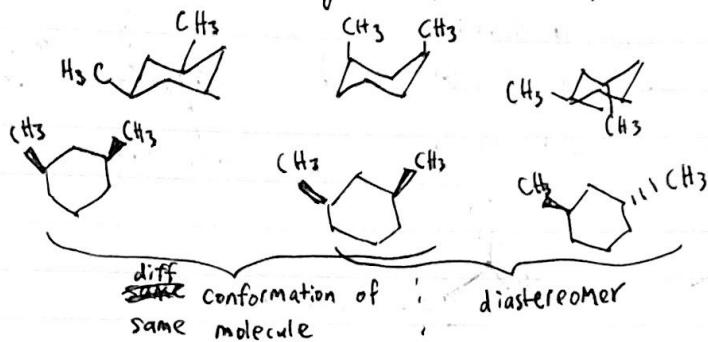
- strict orbital overlap requirement

3 April 2020

Nomenclature & Isomerism

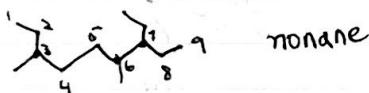
CHEM165

> conformation: diff spacial arrangements of molecule that can freely convert via single bond rotation (eg. staggered vs eclipsed in chair flips)

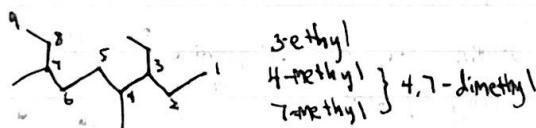


Branched Alkane Naming

1. Find longest cont. carbon chain
2. Name alkyl groups
3. Number alkyl groups
4. Assign prefixes
5. Alphabetize & combine



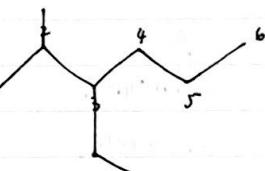
nonane



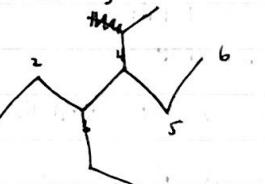
3-ethyl
4-methyl
7-methyl } 4,7-dimethyl

3-ethyl-4,7-dimethylnonane

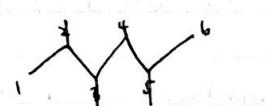
3-ethyl-2-methylhexane



3,4-diethylhexane



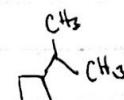
2,3,5-trimethylhexane



Cyclic Alkane

1. Find parent cycloalkene
2. Name, number the alkyl group
3. Assign prefix, alphabetize, combine

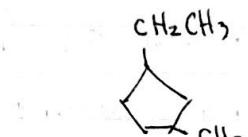
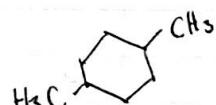
* If alkyl group has more carbon, it should be named as a branched alkane



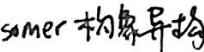
1-isobutylcyclobutane

propyl

1,4-dimethylcyclohexane

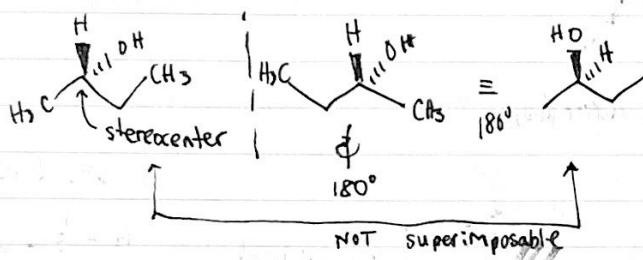


1-ethyl-3-methylcyclopentane

conformational isomer 

Isomers

- > constitutional isomers - same formula, diff. connectivity
- > stereoisomers - same formula, connectivity, diff space arrangement
- > enantiomers - non-superimposable mirror image
- > diastereomer
- > chirality - a molecule that is not identical to its mirror image : (chiral, have handedness)
- > C w/ 4 diff groups (chiral center / stereocenter)



Properties of enantiomer

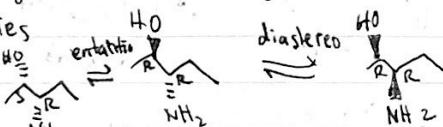
- same chem & phys properties in achiral env.
- bio systems is ~~not~~ chiral
- > racemic - 50/50 mix of enantiomer
- > R & S config
 - 1. Order atoms by priority (atomic #)
 - e.g. I > Cl > C > H
 - 2. If first atom is the same, consider the second
 - 3. Assign priorities 1 → 4 (1 = highest)
 - 4. clockwise = R ; counterclockwise = S
 - rotate
 - rotate

6 April 2020

> Diastereomer - same connectivity & NOT mirror image

> diff phys. chem. properties

e.g. 1 + chiral center
diff @ some centers



e.g. cis-trans isomer for alkenes

> separation

> can't separate by crystallization

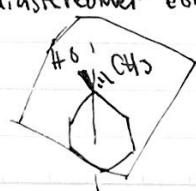
(~~not~~ same solubility)

diastereomers + chiral compound → diastereomer compound

(diff solubility)

> enantiomers - config are diff at all chiral centers

> molecules w/ internal mirror planes are not chiral



same molecular formula

 N

isomers

nonisomers

same connectivity?



stereoisomers

constitutional

isomer

enantiomers

diastereomer

对映异构体

非对映异构体

chiral

achiral

configurational

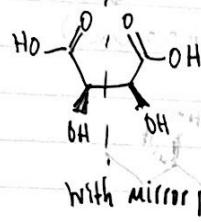
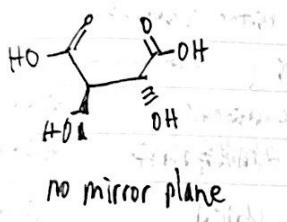
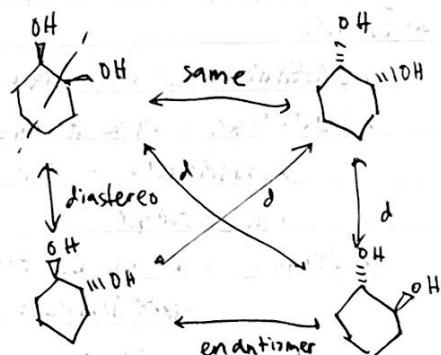
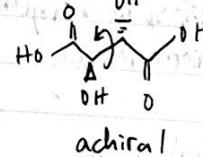
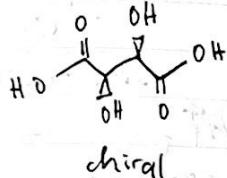
cis-trans

diastereomer

diastereomer

Chirality and Stereometry

→ Determine chirality with mirror plane



Unsaturated Hydrocarbon

- Alkene - with double bond

- Alkyne - with triple bond

- No free rotation @ multi bond

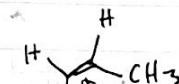
- Cis (same side), trans (diff side) isomers [diastereomers], classifies disubstituted alkenes

→ E, Z notation

- split double bond,

- rank the atoms by atomic #

- diff side: E; same side: Z



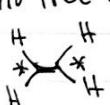
trigonal planar

sp, linear



Valence Bond Theory

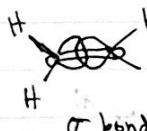
- No free rotation @ multi bond



C - sp² - trigonal planar

3 × sp²

1 × p



σ bond



π bond

- Degree of "s-character": sp³ < sp² < sp

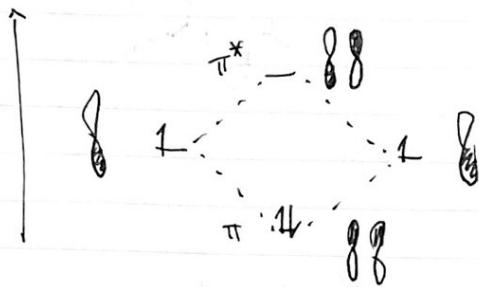
- help remember e⁻ neg trend & pKa trends

- enough to describe isolated multi bond:



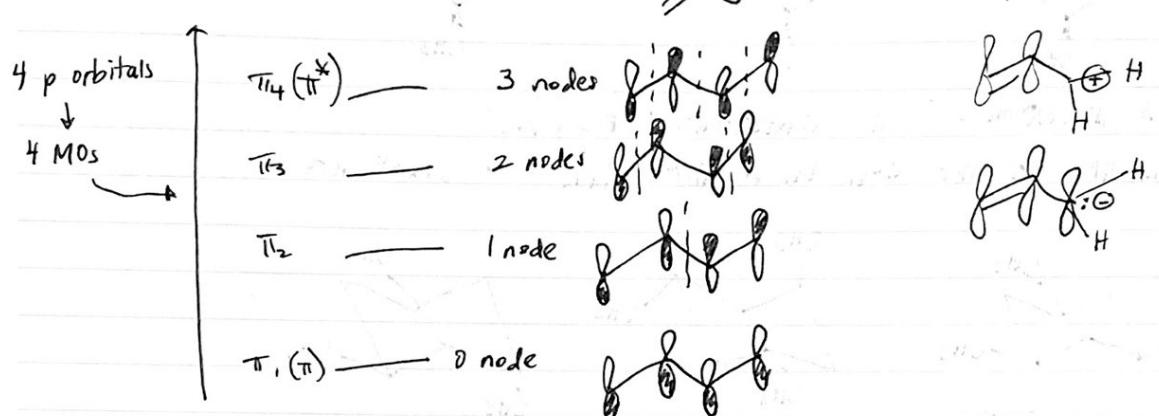
« MO Theory

→ π system w/ $2 \times p$ orbitals



- $2 \text{ AO} \rightarrow 2 \text{ MO}$
- lowest energy orbital has no nodes
- Higher E orbital increase nodes by 1

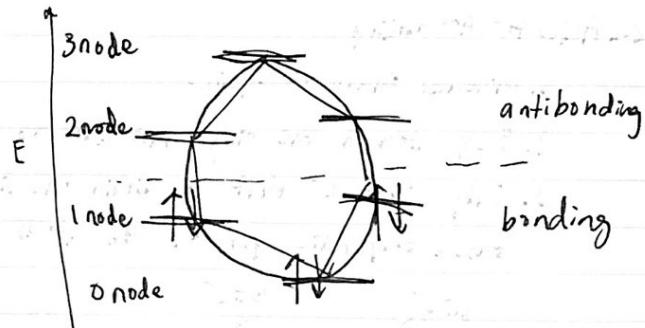
→ π system w/ $4 \times p$ orbitals :



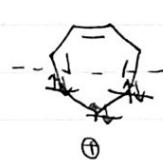
→ Cyclic Conjugated π systems
• Frost Circles

1. place cyclic compound inside a circle with a vertex pointing down

2. vertices of molecule = energy of MO



→ tropylum ion $6\pi e^-$ → cyclooctatetraene $8\pi e^-$



anti bonding
nonbonding
bonding



benzene

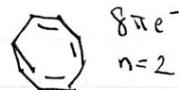
« Aromaticity

→ Aromaticity: planar, $(4n+2)\pi e^-$, bonding orbital only, stable

→ Anti-aromaticity: planar, $4n\pi e^-$, antibonding/nonbonding, destabilized

$\boxed{1} \quad 4\pi e^-$
 $n=1$

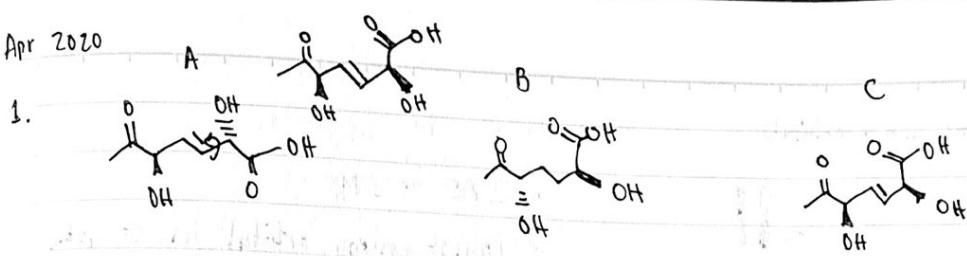
* cyclooctatetraene is not planar
(not arom/antirom)



$8\pi e^-$
 $n=2$

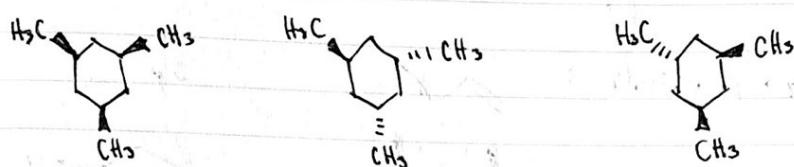
8 Apr 2020

CHEM 165



AB diastereomers ; AC same ; BC diastomer

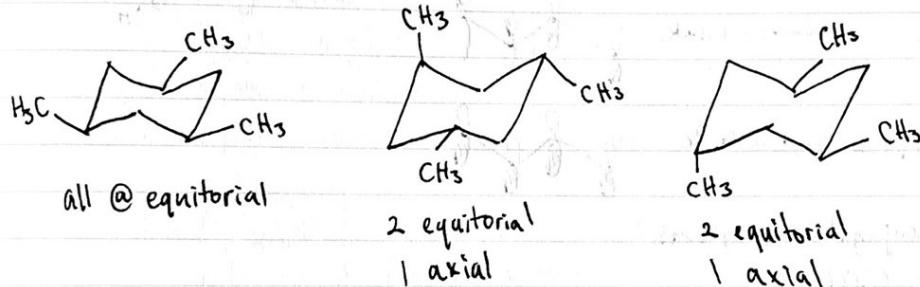
2.



AB diastereomers ; AC diastereomers ; BC same

All ABC are not chiral due to mirror plane : no enantiomers

3.



Rules for Aromaticity

1. molecules must be cyclic
2. Every atom in the ring must have an available p orbital
3. Only count e⁻ that are within one single ring, or that are part of a fused polycyclic system! All atoms must be sp² hybridized.



4. Molecule must be planar

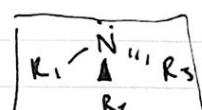
Functional Groups

• Alkane \rightarrow CH₄

• Alkene \rightarrow C=H

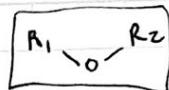
• Alkyne \rightarrow C≡H

• Amine \rightarrow NH₂



e.g. amino acid

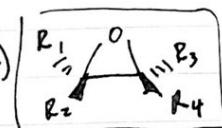
• ether



e.g. diethyl ether

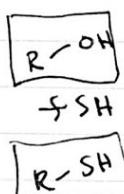
• epoxide

(special cyclic ether)



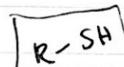
• Alcohol \rightarrow OH

e.g. ethanol



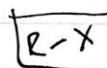
• Thiol

\rightarrow SH



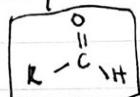
e.g. tert-butylthiol
rotten eggs

• Alkyl Halide \rightarrow X



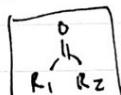
e.g. CFC, chlorofluorocarbons

• aldehyde



e.g. cinnamaldehyde

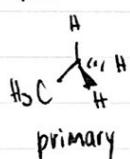
• ketone



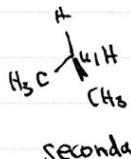
e.g. acetone

Nomenclature

• alkane & amine: # of C attached the C or N



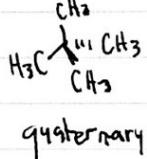
primary



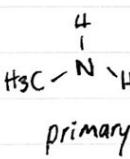
secondary



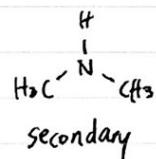
tertiary



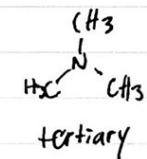
quaternary



primary

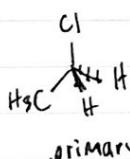


secondary

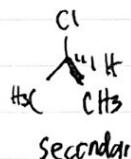


tertiary

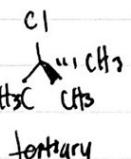
• alkyl halide & alcohol: # of C attached to the C bonded to the functional group



primary

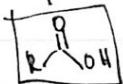


secondary



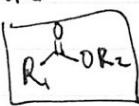
tertiary

• carboxylic acid



e.g. amino acid
acetic acid

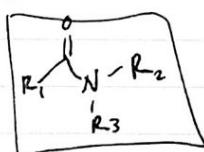
• ester



e.g. fat

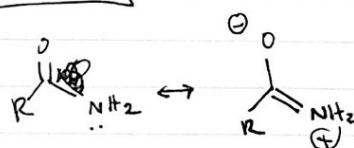
• smells like fruit

• amide

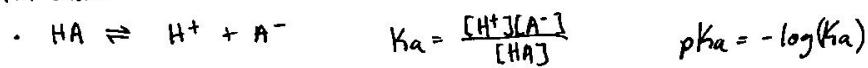


e.g. peptide, protein

• N in amide is sp² hybridized



<< pKa Scale



- low $\text{p}K_a$ = high K_a = high acidity
- be aware if $\text{p}K_a$ is for protonated/neutral species
- how stable are e^- on conjugate base?
- if e^- on A^- are very stable, then HA is more acidic

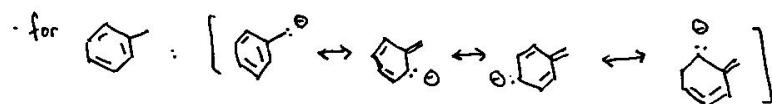
<< $\text{p}K_a$ trends & e^- stabilization

→ Element Effect

- atomic size: larger atoms stabilize additional e^- better (in a group \uparrow)
- e^- neg: within a row, more e^- neg atoms stabilize additional e^- better (in a family \leftrightarrow)
- atomic size $>$ e^- neg within a group

→ Resonance Effect (π bond)

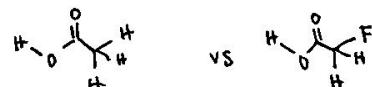
- e^- on conjugate base are more stable if they can be delocalized by resonance



- aromatic group have more resonance than double bond

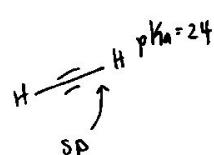
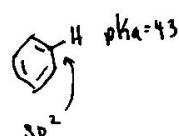
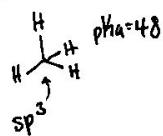
→ Inductive Effect (σ bond)

- additional e^- more stable if near an e^- neg atom (e^- -withdrawing group)
- work through single bond



→ Hybridization Effect

- for a given element, e^- are more stable if the atom has more s-character



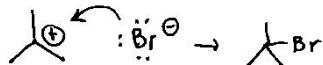
- C_6H_5^- is not resonance stabilized because sp^2 orbital is \perp to π system

<< Curved Arrow Notation

- keeps track of where e^- pairs are in reaction - "arrow pushing"
- each curved arrow represents movement of an e^- pair.
- source \rightarrow destination ($A^+ + :B^- \rightarrow A-B$)
- charge is conserved
- can't give any atom > 8 valence e^-

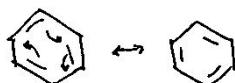
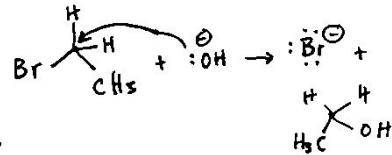
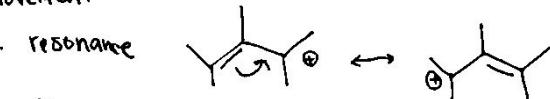
• receiving atom has open octet (6 valence e^-)

• receiving atom has an e^- pair displaced

 \rightarrow Fundamental Rxn Step

• Bond Movement

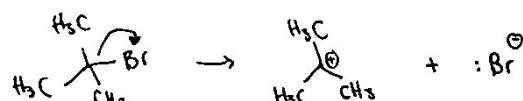
• e.g. resonance



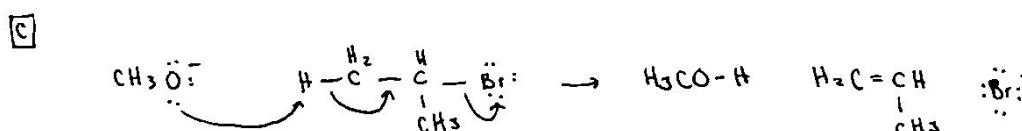
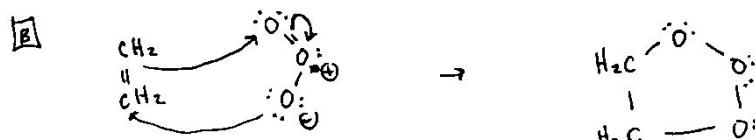
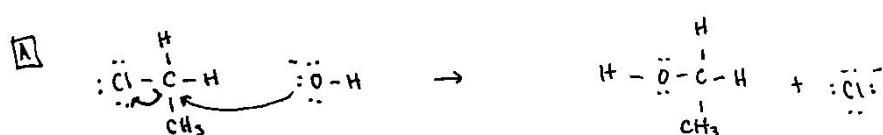
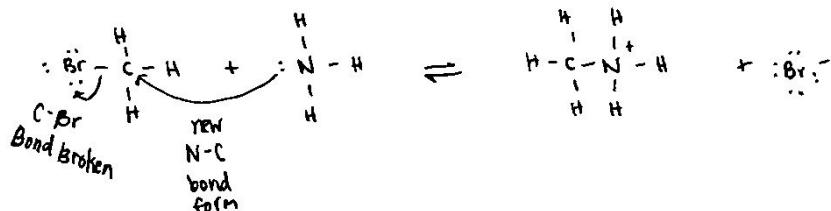
• Bond Making

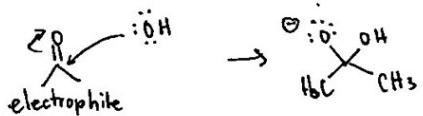
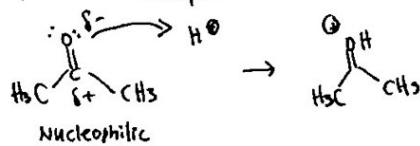
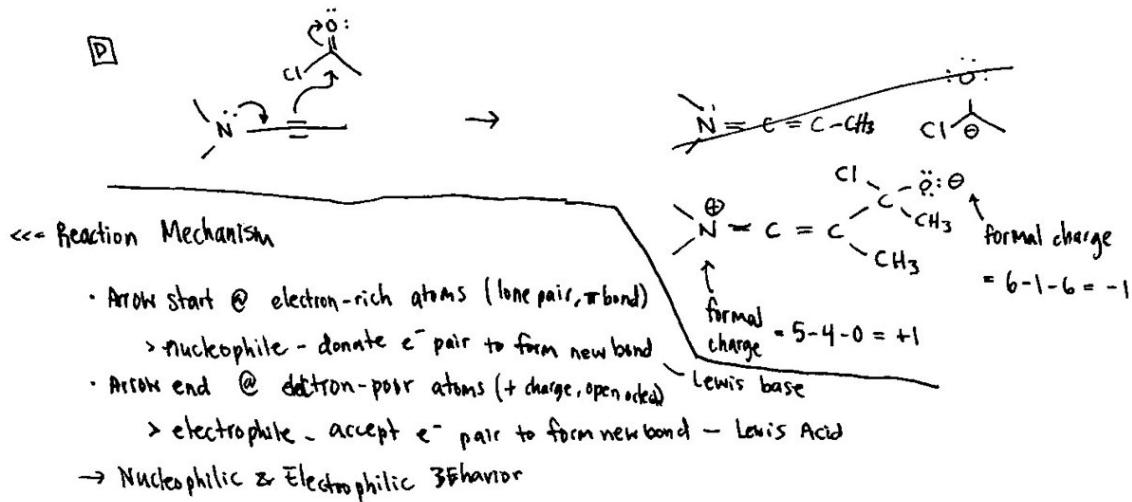


• Bond Breaking



* If arrow starts at a bond, the bond is broken.

 \rightarrow Illustrate Rxn Mechanism



<< Alkene Addition Rxn

- Reagents add across a double bond to form 2 single bonds

- electrophilic

- alkenes are weak nucleophilic

- intermediate of carbocation is formed

- incomplete octet

- high energy

- sp^2 , trigonal planar

- more stable carbocation is formed

→ stability of carbocations

- adjacent alkyl groups stabilize carbocation

- alkyl group are e^- -donating

methyl	primary C	secondary C	tertiary C
least stable			most stable

- more alkyl group = more stabilize

- adjacent double bond stabilize through resonance



- Nucleophile can attack at either end of double bond

- multiple types of products can form

- adjacent lone pairs stabilize carbocations through resonance

- N, O, Cl donates lone pairs to empty p orbital

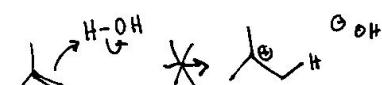
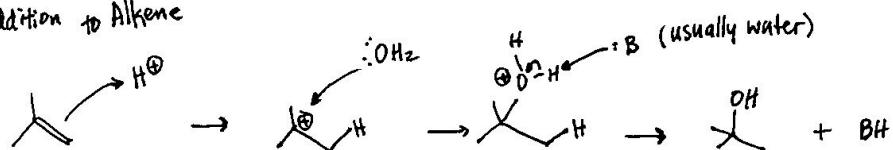
- most powerful effect - all atoms have octet

→ halide rxn

- Markovnikov's Rule - in the addition of HX to an alkene, H attaches to C with fewer alkyl group, X attaches to C with more alkyl group.

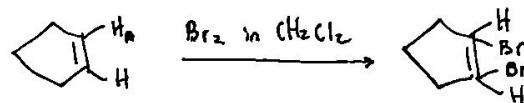
- If same amount of substitution, mixture of product forms

→ H_2O addition to Alkene

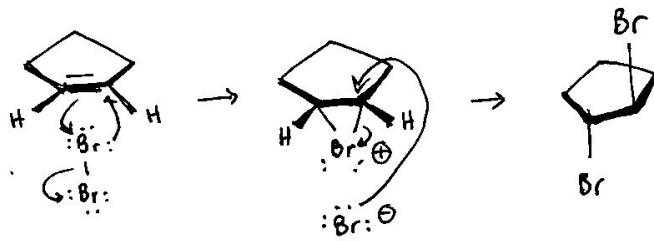


(water is not strong enough electrophile to react w/ double bond)

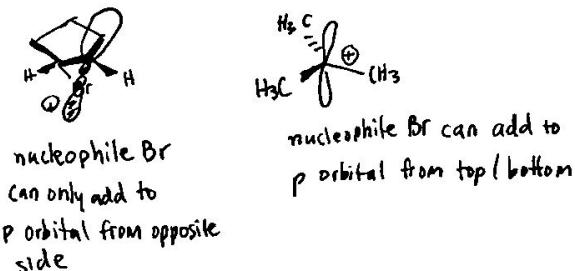
→ Halogen addition to Alkene



- does not involve carbocation
- electrophile w/ lone pairs add in a concerted manner to form a three-membered ring intermediate

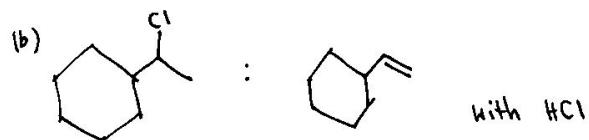
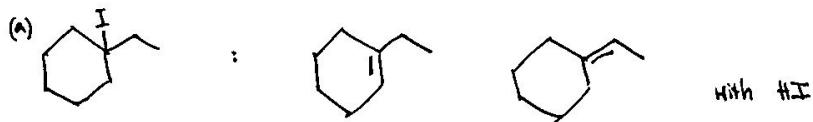


- Br^- attacks the ring to form dibromide product from the opposite side
- trans config of Br
- Br^\ominus lone pair has to overlap with the $\sigma_{c-\text{C}}$ antibonding orbital



- industrial important - precursor to PVC

EX1 What alkene to start with to get:

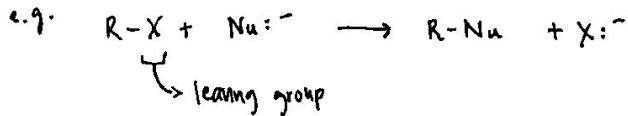


<< Substitution Reaction

- sub & elim rxn are competing

> nucleophilic substitution - nucleophile donates an e^- pair to an electrophile to displace a leaving group.

↳ usually alkyl halide

→ S_N2 Rxn

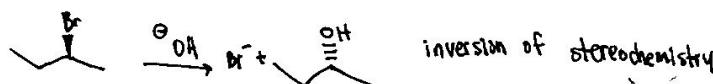
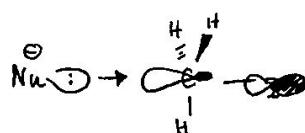
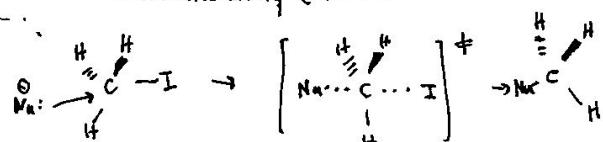
- concerted rxn → single step, w/ inversion of stereochemistry (umbrella flip)

- pentacoordinate transition state

- "backside attack"

- orbital overlap requirement

- lone pair of nucleophile must overlap w/ σ_{c-x}^* antibonding orbital



→ Rate Determining Factor

- sterics of electrophile (big)

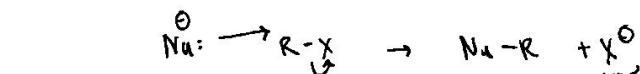
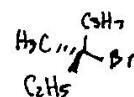
- more sterically hindered → slower

- leaving group ability → can stabilize e^- !

- most stable leaving group → faster

> leaving group - Molecular fragment that departs w/ a pair of e^- when bond is broken

eg. tertiary alkyl halide difficult to react



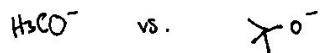
- nucleophilicity

weaker base,
faster rxn

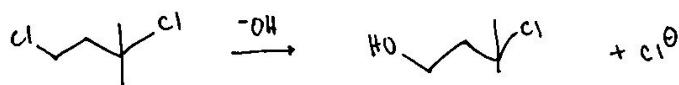
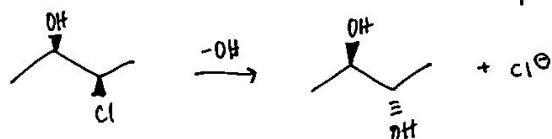
- nucleophilicity parallels basicity

• exception: nucleophilicity decreases as steric bulk increases

• MeO^- better nucleophile than tBuO^- despite similar basicity



ExII



17 Apr 2020

Substitution & Elimination Reactions

CHEM 165

<< Elimination Reaction

> loss of two groups from adjacent carbons to form a double bond

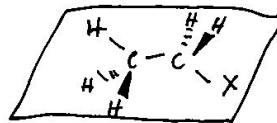
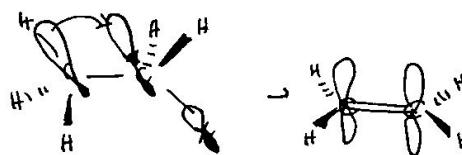


→ E₂ Rxn Mechanism

- concerted mechanism
- promoted by strong bases

• H and X must be in same plane and 180° from each other (antiperiplanar)

• σ_{H-X} must overlap w/ σ^{*}_{H-X}

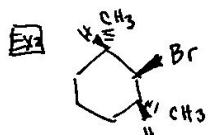
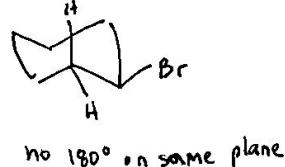
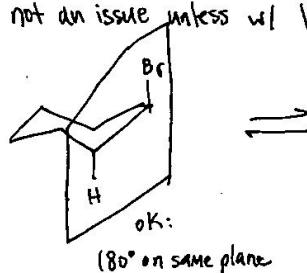
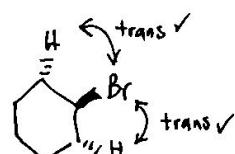


* Cyclohexane: Make sure antiperiplanar requirement met!

• Must be a C-H bond trans to leaving group

• leaving group must be in axial position

• not an issue unless w/ large group that prevents ring flip



can't undergo E₂ elimination: no trans C-H bond.

<< Competing Rxns

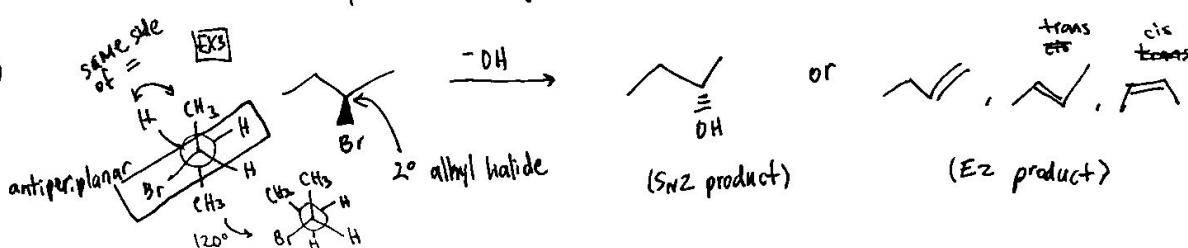
• S_N2 & E₂ rxn are competing

• rate of S_N2 rxn more sensitive to electrophile sterics

• S_N2 faster than E₂ for 1° alkyl halide

• E₂ faster than S_N2 for 3° alkyl halide

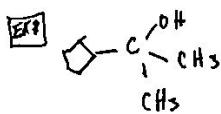
• 2° alkyl halide undergo both rxns



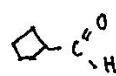
<< Oxidation State of Carbon

- for bond less e⁻neg element / neg charge : -1 $\text{HC}\equiv\text{C}^{\ominus} (-1)$
- another carbon : 0
- to more e⁻neg element / pos. charge : +1 $\begin{array}{c} \text{O} \\ || \\ \text{C} \\ | \\ \text{CH}_3 \end{array} (+1)$

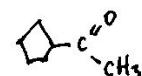
. oxidation state is the sum of all values



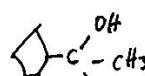
$$(3)(0) + (1)(1) = \boxed{+1}$$



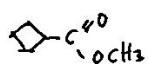
$$(1)(0) + (1)(-1) + 2(1) = \boxed{+1}$$



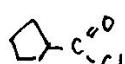
$$\boxed{+2}$$



$$\boxed{+1}$$



$$\boxed{+3}$$



$$\boxed{+3}$$

→ Reduction & Oxidation

• look at organic molecule being transformed

• determine which C is undergoing a change

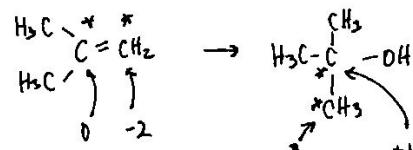
• calc. oxidation state

• ox # (product) > ox # (reactant) → oxidation

• ... < ... → reduction

• ... = ... → none

Ex:



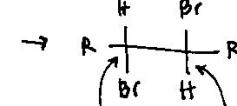
$$\text{ox #: } \boxed{-2}$$

$$\text{ox #: } \boxed{-2}$$

NO redox



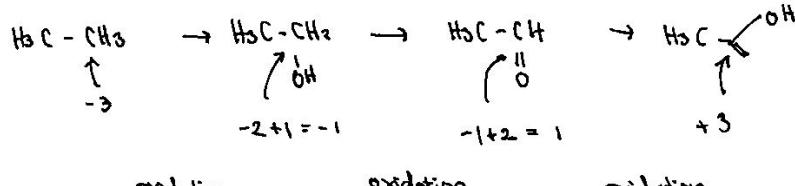
$$\text{ox #: } \boxed{-2}$$



$$< \text{ox #: } \boxed{0}$$

oxidation ($2e^-$)

Ex:

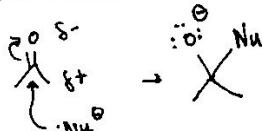


oxidation

oxidation

oxidation

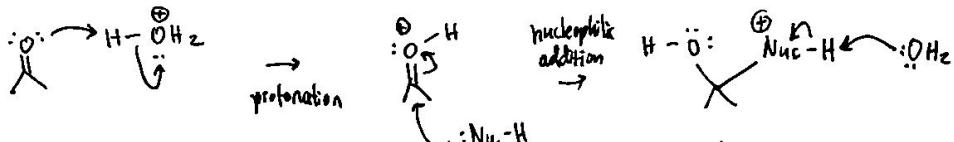
<< Nucleophilic Addition



<< Mechanism of Nucleophilic Rearrangement

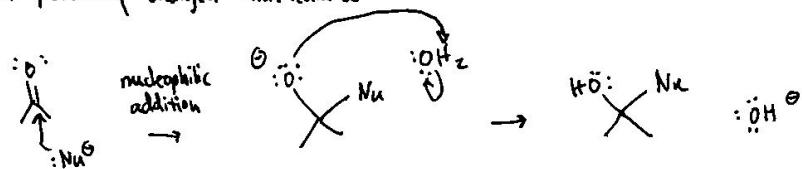
→ Acidic Condition

- carbonyl is protonated, be more electrophilic
- nucleophile is neutral
- no neg charged intermediates



→ Basic Condition

- nucleophile can be neg charged, attacks directly the carbonyl
- no positively charged intermediates

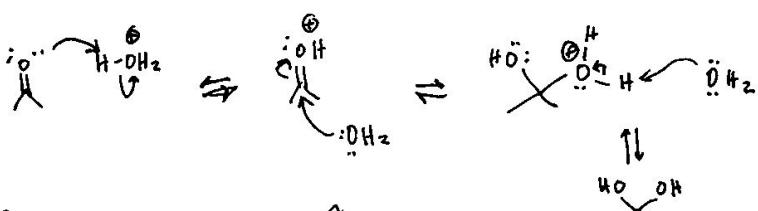


<< Case Studies

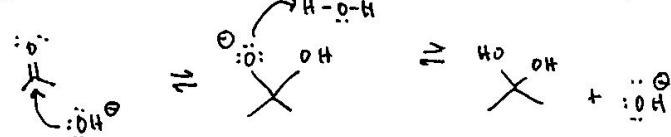
→ Addition of H_2O

- carbonyl hydrates formed : stable in soln, not stable to isolate (revert to carbonyl)

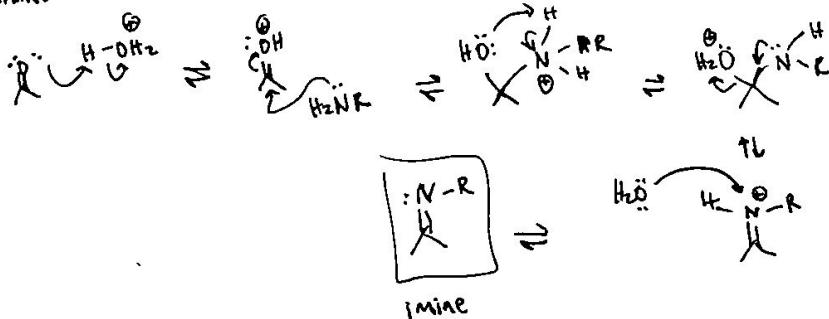
→ Acid



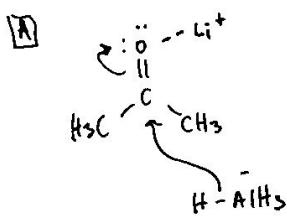
→ Base



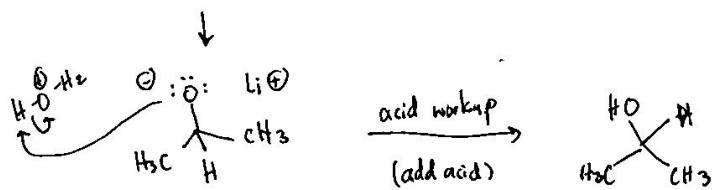
→ Addition of Amines



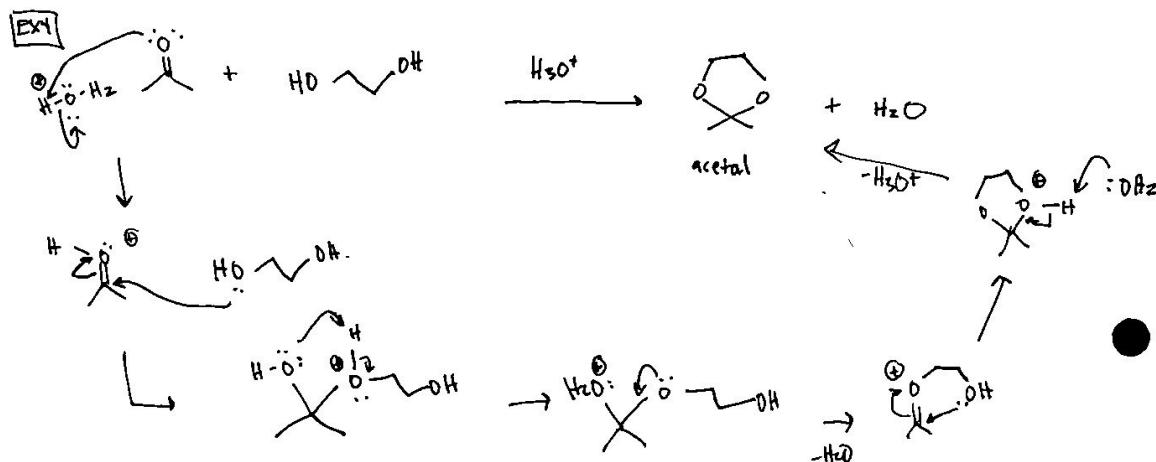
→ Addition of Hydride & Grignards



- add LiAlH_4
- add $\text{H}_2\text{O}^\ominus$
- reduction of carbonyl



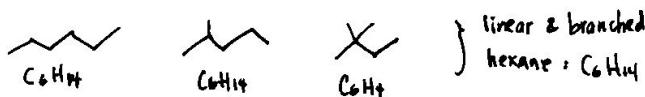
- reduction of carbonyl



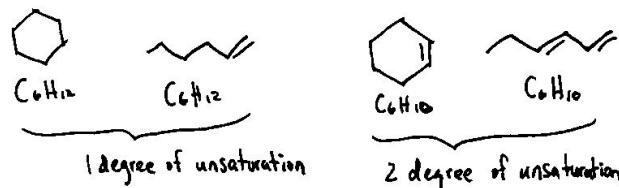
<< Degree of Unsaturation

→ Molecular formula

- mass spectroscopy - provide molecular weight
- elemental analysis (% C, % H, % N, etc)
- give info of structure (multiple bond, ring)
- e.g. alkane $C_nH_{(2n+2)}$



- e.g. ring & multiple bond reduce H by 2 : $C_nH_{(2n-2)}$



→ Degree of Unsaturation

- ignore O, S

$$\text{Degree of Unsaturation} = \frac{2C + 2 + N - H - X}{2}$$

$$\text{e.g. } \text{DOU} = \frac{2 \times 6 + 0 - 6 - 0}{2} = 4 \left\{ \begin{array}{l} 3\pi \text{ bond} \\ 1 \text{ ring} \end{array} \right.$$

$$\text{e.g. } \text{DOU} = \frac{2 \times 2 + 0 - 4 - 0}{2} = 1 \rightarrow 1\pi \text{ bond from } C=O$$

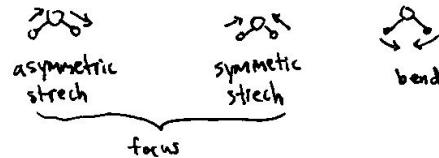
$$\text{e.g. } H-C\equiv C-H \text{ DOU} = \frac{2 \times 2 + 0 - 2 - 0}{2} = 2 \rightarrow 2\pi \text{ bonds from } C\equiv C$$

<< Infrared Spectroscopy

- atoms in constant motion : bond vibration - oscillatory stretching & bending

> IR spectroscopy (vibrational spec.) - probes bond vibrations

- sensitive to functional groups



• simple harmonic oscillator model

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

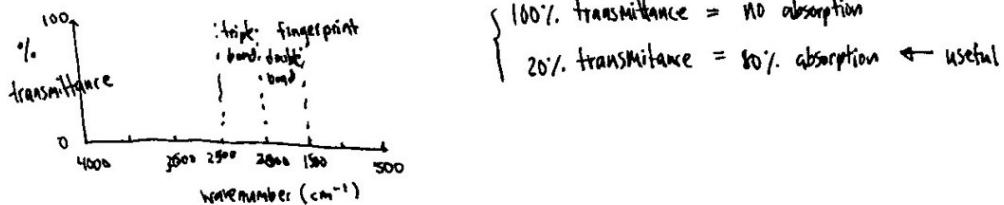
ν - vibrational freq in Hz
k - force constant (stiffness of spring/bond)
 μ - reduced mass

$$\mu = \frac{m_x m_y}{m_x + m_y}$$

! Factors Affecting Vibrational Frequency

- bond strength: strong bond, $k \uparrow, \nu \uparrow$
- mass of x, y: heavy atoms, $\mu \uparrow, \nu \downarrow$

- molecules absorb infrared light if freq of light exactly matches freq of bond vibration
- $4000 - 400 \text{ cm}^{-1}$ (wave number $\tilde{\nu}$ in $\text{cm}^{-1} = \frac{\nu(\text{s}^{-1})}{c(\text{m/s})}$) $c = \lambda\nu \rightarrow \nu = \frac{c}{\lambda}$
- identifies functional groups



- Fingerprint region ($500 - 1500 \text{ cm}^{-1}$) - hard to get useful info (low energy)
 - C-C, C-N, C-O
- Double bonds ($1650 - 1800 \text{ cm}^{-1}$)
 - C=C, C=N, C=O
- Triple bonds ($2100 - 2260 \text{ cm}^{-1}$)
 - C≡C, C≡N
- C-H stretch ($2850 - 3100 \text{ cm}^{-1}$)
 - C-H
- O-H stretch ($3200 - 3400 \text{ cm}^{-1}$)
 - O-H, broad peaks
- N-H stretch ($3300 - 3500 \text{ cm}^{-1}$)
- C-H bond: sp^2 & sp^3
 - sp^2 C-H stronger than sp^3 C-H
 - sp^2 C-H > 3000
 - sp^3 C-H < 3000

« Nuclear Magnetic Resonance (NMR) Spectroscopy \longrightarrow radio frequency (low energy)

• IR - identify functional group, not structure & connectivity

• NMR - more about connectivity & structure

• map of location of hydrogen

→ Mechanism

• electric moving charge, generate magnetic field

• nuclear spin

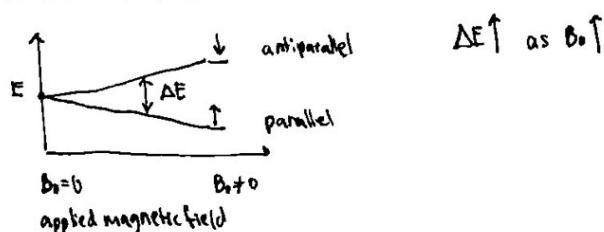
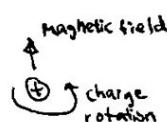
• if no external field, random spin; with external field, spin align parallel/antiparallel

• NMR probes energy diff on parallel vs. antiparallel

(lower E) (higher E)

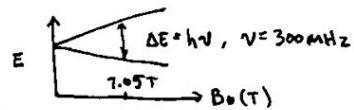
• diff atomic nuclei behave diff, element specific

• common: ^1H NMR



<< NMR Magnets

- use MHz describe magnet strength
- Isolated proton in 7.05 Tesla magnet absorb light with frequency of 300MHz



<< Chemical Shift

- Neighboring atoms & e^- alter magnetic field around proton so $B_{\text{effective}} \neq B_{\text{applied}}$
- Depending on the chem env. the peak can be shifted by 10s to 1000s of Hz

$$\text{chemical shift } (\delta) \text{ (ppm)} = \frac{\text{freq. of sample (Hz)} - \text{freq. of ref (Hz)}}{\text{spectrometer freq (Hz)}} \times 10^6$$

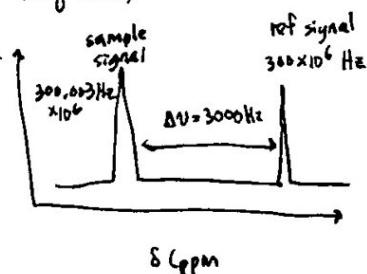
<< Structural Info of NMR (^1H)

- # of peaks ~ # of types of proton
- peak integration ~ # of diff types of proton
- peak location - final group & local chem env.
- peak splitting - # of neighboring proton

→ Chemical shift & peak location

NMR peak shift depending on chem env.

- e^- around proton form local magnetic field that oppose applied magnetic field



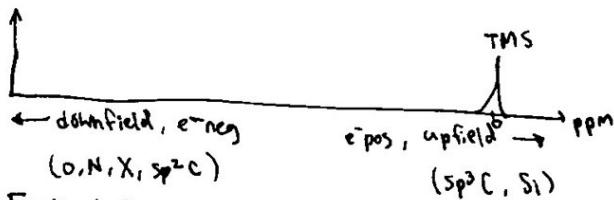
$$\frac{3000 \text{ Hz}}{300 \times 10^6 \text{ Hz}} \times 10^6 = 10 \text{ ppm}$$

- effective magnetic field will be weaker than applied B_0 due to shielding

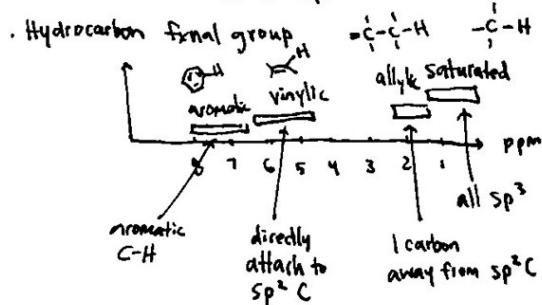
$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}}$$

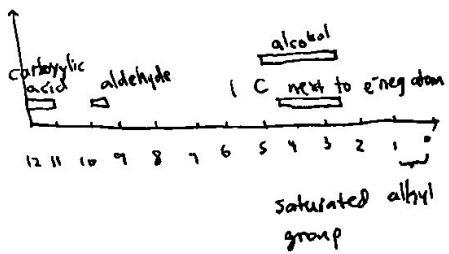
→ Rules

- If proton next to e^- neg atom, less e^- density around proton, deshielded, downfield
- If proton next to e^- pos atom, e^- shield proton, upfield



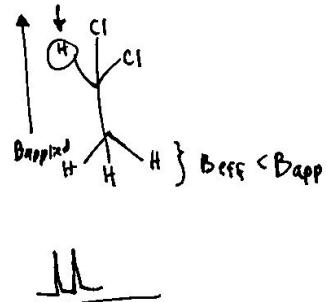
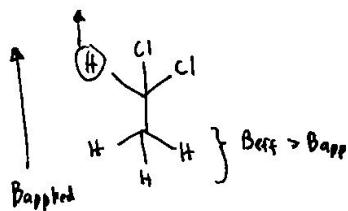
→ Chemical Shifts & Functional Groups





→ Peak Splitting

- NMR peaks are split by nearby protons
 - magnetic field from one proton affects that of neighboring protons, leading to peak splitting
 - spin-spin splitting / coupling



- chemically equivalent protons don't show spin-spin split
 - a proton with n equivalent protons is split into multiplet of $n+1$ peaks (≤ 2 C atoms apart)

<< Polymer Structure & Property

- structure of polymer affect property

→ linear polymer

- held together by weak van der Waals / H-bonding

- heating cause melting - weak interaction

→ Branched polymer

- less dense, softer, less heat resistant

→ Crosslinked polymer

- covalent bond

- strong, heat resistant

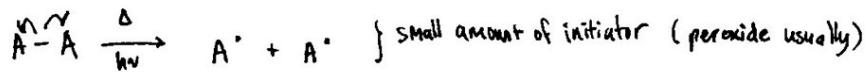
<< Addition Polymerization

→ Monomers join without net loss of atoms

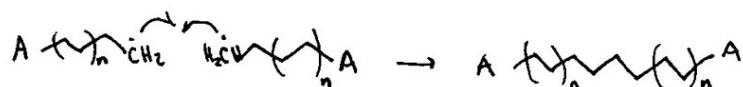
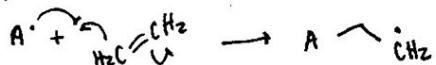
• free radical rxn { initiation
(chain rxn) propagation
 termination

→ Initiation

- molecule break by heat/light



→ Propagation

EXII Synthesis of PVC : polyvinyl chloride

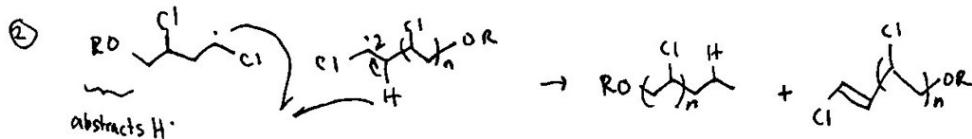
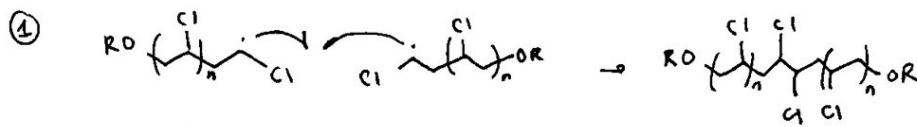
→ Initiation



→ Propagation



→ Termination



<< Condensation Polymerization

→ small molecule (e.g. H₂O) is split off as monomers are added to polymer

• e.g. PET (polyethylene terephthalate)

<< Synthetic Polymers : Polyethylene

• formed by ~~addition~~ → ~~(W)~~

• low-density polyethylene (LDPE) - heavily branched

• poor packing, low density, highly branched
• soft

• high-density polyethylene (HDPE)

• linear, packed efficiently
• hard

• structure & packing of polymer affect macro property

<< Synthetic Polymers : Polyamide

• formed by condensation

→ Nylon 66

• fabric, carpet, molded part
• high mechanical strength, rigidity, good stability under heat
• H-bonding gives strong fiber

→ Kevlar

• bulletproof

• alkyl group replaced by flat aromatic group, connecting monomer

} ff bond → sheet (planar)
planar → stacking

• sheet stack together well by π-π stack

<< Biological Polymers Overview

Carbohydrate

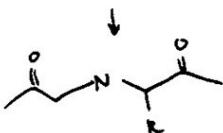
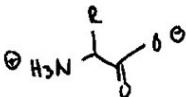
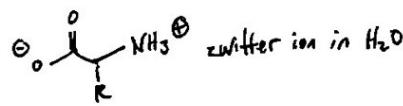
Protein

Nucleic Acid

<< Biological Polymers

→ Protein

- polymer made of amino acid chain
- formed by condensation



peptide bond

→ Protein Structure

→ Secondary Structure

- α helix
- β sheets } H-bonding
- just with peptide backbone
- unlike synthetic polymers, protein has rich side chain diversity

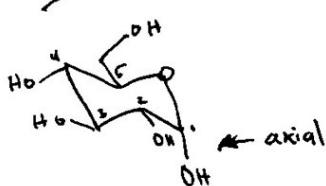
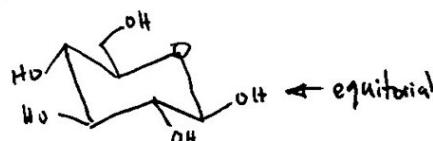
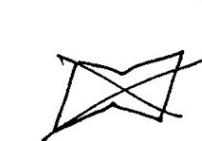
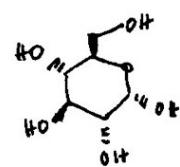
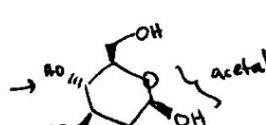
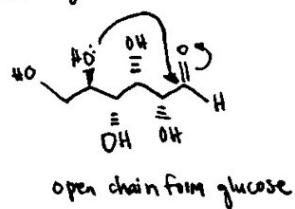
→ Tertiary & Quaternary Structure

- 3D folding of chains

→ Carbohydrate

- monomer: glucose

- two ring form in solution, (open-chain form intermediate)



→ starch (amylose) vs cellulose

- cellulose harder to break than starch
- glucose monomers are different isomers!
- diff packing pattern
- axial OH → α pack → bent linkage → starch
- equatorial OH → β pack → linear linkage → cellulose
 - (H-bond between sheets)
 - insoluble
 - hard to hydrate

Intro to Coordination Chemistry

- > Coordination Compound - a central metal ion surrounded by 1(+) ion/molecule
- > ligands - ions/molecules bound to the metal usually transition metal, group 3-12
- group # = valence e^-
- Diversity of Inorganic Coordination compound
 - hemoglobin - protein transport O_2 , with 4 iron complex
 - iron porphyrin complex
 - cisplatin - chemotherapy drug
 - bind to DNA to prevent replication
 - catalyst making HDPE
- Geometry - Many Coord #
- Color - metalion, oxidation state, ligand
- Magnetism - diamagnetic & paramagnetic

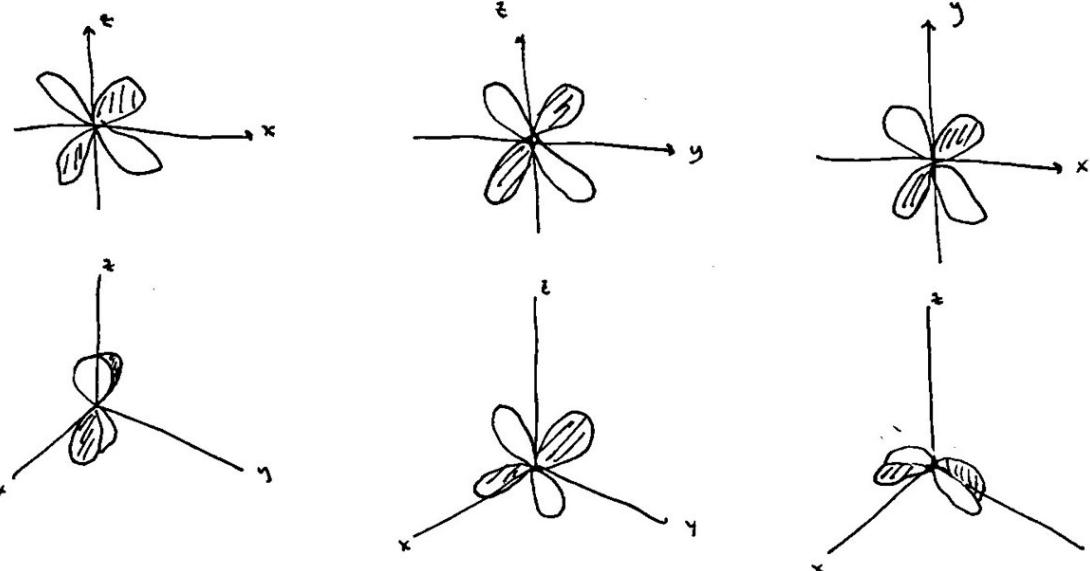
} examples

} d orbital

d Orbitals

· d_{yz} , d_{xy} , d_{zx} lie between axis

· d_{z^2} , $d_{x^2-y^2}$ lie on axis



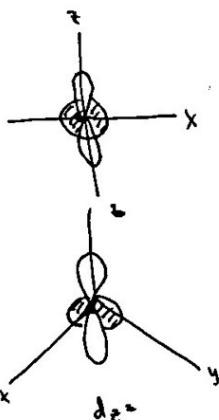
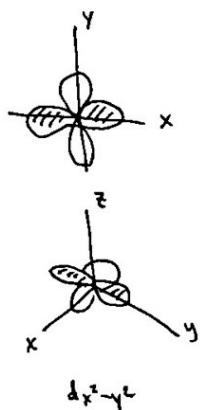
d_{xz}

d_{yz}

d_{xy}

. phase change important!

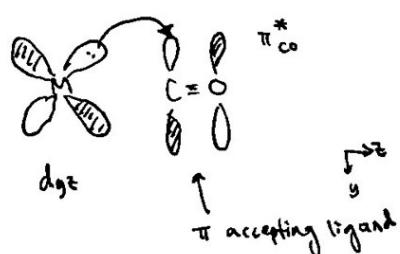
$\rightarrow d_{x^2-y^2} \text{ & } d_{z^2}$



<< Lewis Acid & Base

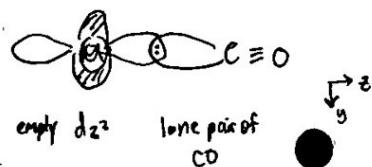
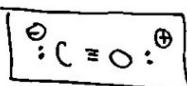
\rightarrow Lewis acid

- e^- acceptor
- w/ empty orbital
- metal cation (e.g.)
- * have exceptions : CO

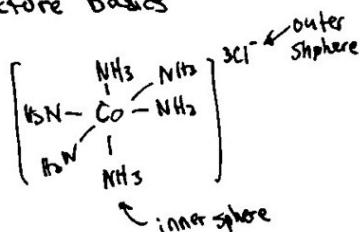


\rightarrow Lewis base

- e^- pair donor
- have filled orbital / lone pairs
- ligand (e.g.)
- * exception : CO :



<< Structure Basics



> outer sphere - not directly bound to metal

> inner sphere - directly bound to metal

> coordination number - # of ligand directly bound to metal

• depend on size of metal

• size of ligand

• electronic interaction of M & L

<< Geometry

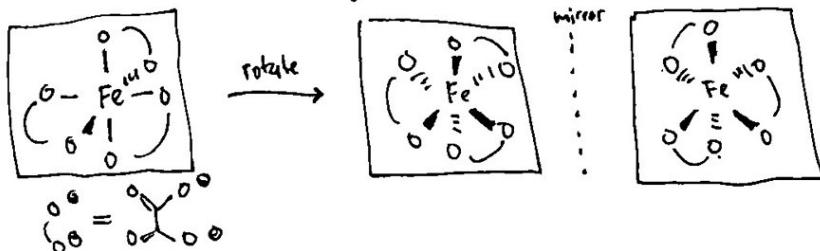
• have isomers, cis & trans

> trans - 180°

> cis - 90°

sometimes diastereomers : diff property

• complex w/ 2(+) bidentate ligands can have enantiomers \rightarrow same property in nonchiral envr

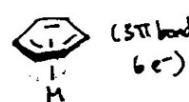
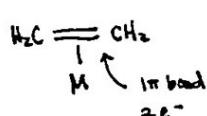
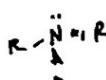
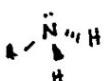


Common Ligand Type

 $\rightarrow L$ Type

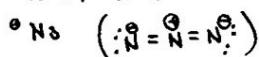
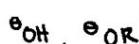
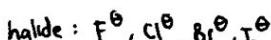
- neutral molecule that has lone pair / π bond to donate.

e.g.

 $\rightarrow X$ type

- anionic molecule with lone pairs that can donate to metal

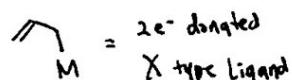
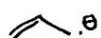
e.g.

Mononucleardianionic "X₂"

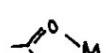
$$1\sigma + 1\pi = 4e^\ddagger \text{ donated}$$

triaxionic "X₃"

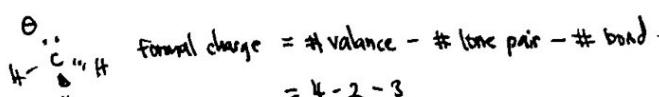
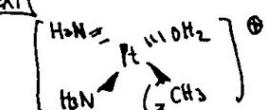
$$1\sigma + 2\pi = 6e^\ddagger \text{ donated}$$

 \rightarrow Combination of L & X typeAllyl anion "LX"

X type

2e⁻ donated

LX type

4e⁻ donatedEX1

X type ligand

↳ Metal Oxidation State

> metal oxidation state = (total molecular charge) - \sum (ligand charge)

- # d e⁻ = group # - oxidation state

e.g. $[\text{Cr}(\text{CN})_6]^{4-}$, Mos = $-4 - \sum (-1) = +2$

$$\# \text{d } e^- = 6 - 2 = 4$$

↳ Electron Counting

> 18 e⁻ rule : s² p⁶ d¹⁰ * exceptions!

→ Total e⁻ count

- SUM of

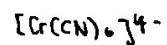
- # d e⁻ of metal, taking oxidation state into account

- # e⁻ provided by each ligand

- each lone pair & π bond counts as 2 e⁻

- usually $\leq 18 e^-$, rarely $> 18 e^-$

EX2



$\text{Mos} = +2 \rightarrow \text{Cr(II)}$

$\# \text{d } e^- = 6 - 2 = 4$

$\# \text{total } e^- = 4 + 6(2) = 16$



↑ Donated 2e⁻

EX3



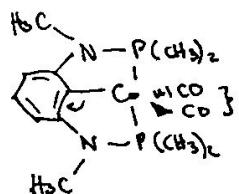
$\text{Mos} = 1 - (-1) = 2 \rightarrow \text{Pt(II)}$

$\# \text{d } e^- = 10 - 2 = 8$

$\# \text{total } e^- = 8 + 2 + 4 + 2 = 16$

↑ 1 H₂O ↑ 2 NH₃ ↑ CH₃

EX4



$\text{Mos} = 0 - (-1) = 1$

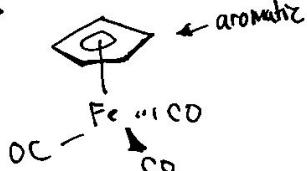
$\# \text{d } e^- = 9 - 1 = 8$

$\# \text{total } e^- = 8 + 4 + 4 + 2 = 18$

↑ 2 CO ↑ 2 PR₃ ↑ 1 e⁻



EX5



$\text{Mos} = 0 - (-1) = 1 \quad \text{Fe(I)}$

$\# \text{d } e^- = 8 - 1 = 7$

$\# \text{total } e^- = 7 + 6 + 6 = 19$

↑ 8 CO ↑ C_P



6 May 2020

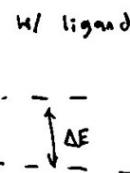
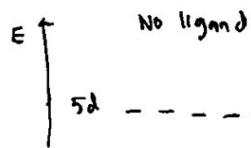
Electron Counting

CHEM 165

⇒ Crystal Field Theory

→ Energy of d orbital w/ ligand

- In absence of ligand, 5x d orbital are degenerate
- in presence of ligand, E of d orbital will split



} d orbital splitting diagram

{ magnitude?
pattern?
color & magnetism?

→ Crystal Field Theory

- ligands are treated as point charge

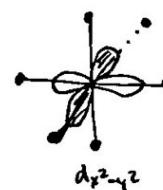


metal cation M^{n+}

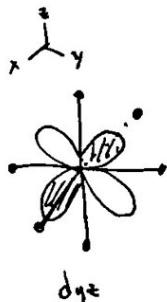
metal cation w/
spherical distribution
of neg charge

→ e^- in d orbital ↑ E
due to e^-e^- repulsion

d_{xy} d_{z^2} d_{yz}



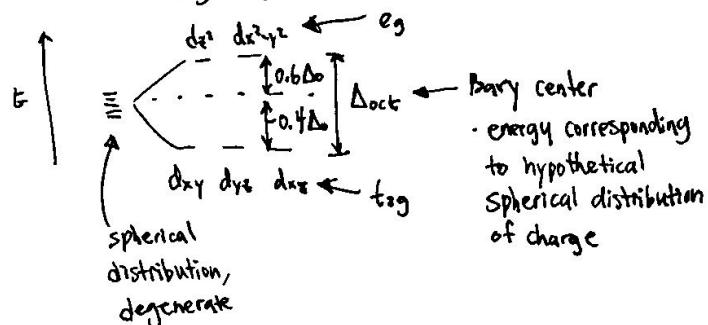
lobes of these
point directly at
ligand, ↑ E



<< Color of Transition Metal Ions

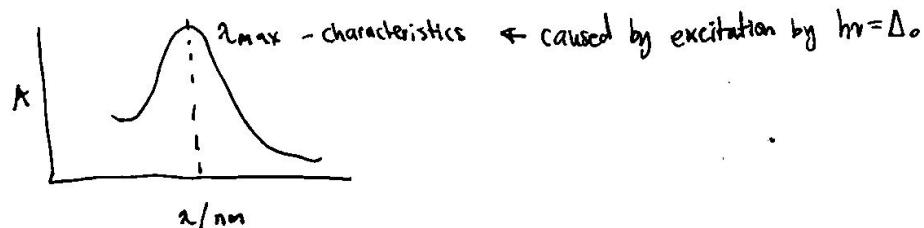
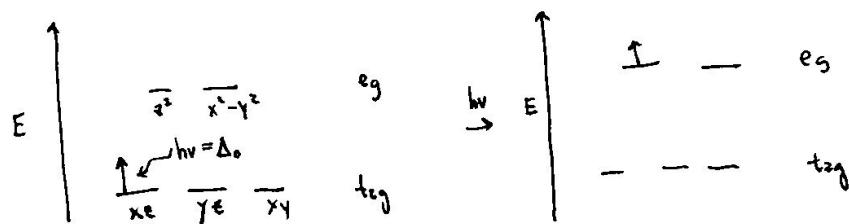
- Cr^{3+} - emerald & ruby
- Co^{2+} - cobalt blue, violet
- Mn^{3+} - purple
- Cu^{2+} - teal purple
- color depends on metal identity & local chem envir

→ d orbital splitting diagram



- e_g, t_{2g} = symmetry label
- e - doubly degenerate
- t - triply degenerate
- g - symmetric

→ UV-Vis Spectrum

[Ex] $\text{Ti(OH}_3\text{)}_6^{3+}$ for Ti(III)

- only work for $d^1 - d^3$ metals - need $d \rightarrow d$ transitions
- λ_{max} give direct experimental measurement of Δ_o
- Δ_o depends strongly on ligand envir and metal identity.

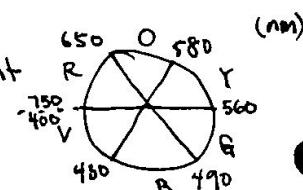
- Typical value of Δ_o is 1-4 eV

- Correspond to visible spectrum \Rightarrow

→ Color Theory

- If a compound absorb a light, we see its complement

- R O Y G B I V \rightarrow increasing energy



$\ll \Delta$

I ⁻	Br ⁻	Cl ⁻	F ⁻	HO ⁻	H ₂ O	NH ₃	ethylenediamine	CN ⁻ , CO
weak field ligands							strong field ligands	increasing Δ

> spectrochemical series - series of ligands shown above

• keeping metal center constant, Δ increase along series

→ Rationalizing Δ trend

• σ donor - strong σ -donating ability, larger Δ \uparrow

• π donor - stronger π -donating ability, smaller Δ \downarrow

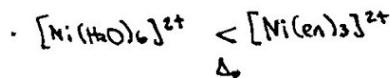
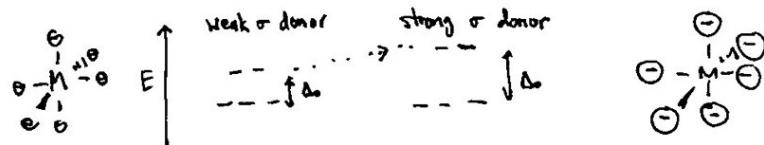
• π acceptors - stronger π -donating ability, larger Δ \uparrow

→ σ donor

• σ -donating ability \propto basicity

• strong base = strong σ -donating ability

• $e^- - e^-$ repulsion between Δ orbital & lone pairs of strong σ -donor $\rightarrow \Delta \uparrow$

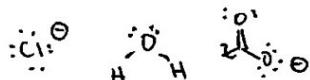


Δ

→ π donor

> π donor - ligand w/ 1+ e^- lone pair as π donor in addition to σ -donors

e.g. Cl⁻, H₂O, ROH, RCOO⁻



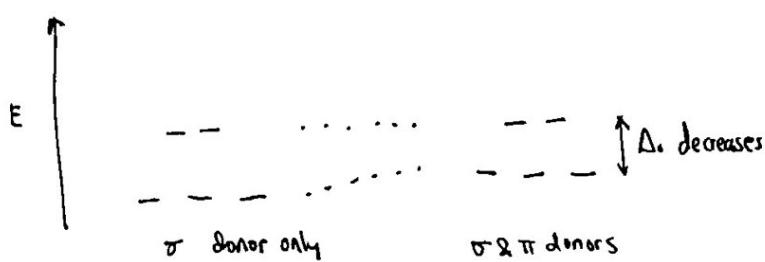
• π bonding lone pairs interact w/ dxz, dyz, dxy

• electrostatic repulsion destabilizes these orbitals

• lead to smaller Δ

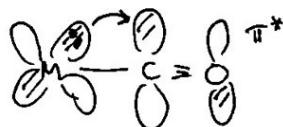
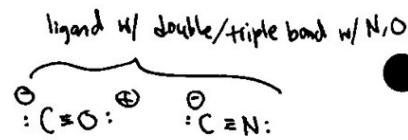


• a "partial" π donor
but not fully π bond

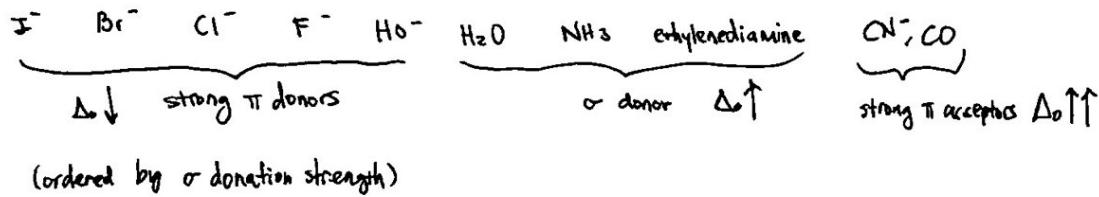


→ π acceptor

- > π acceptors - ligand w/ low lying π^* orbitals
 - empty orbitals, double bond, triple bond
 - e.g. CO , CN^- , pyridine
 - empty π^* accept e⁻ from dce. dng, dyes
 - stabilize the orbital, $\uparrow \Delta_o$.



→ Grouping of Spectrochemical Series



→ Metal

- complex w/ similar ligand envir., Δ_o depend on metal

→ Oxidation State

- $\uparrow \text{OS}$, $\uparrow \Delta_o$

- $\downarrow \text{M-L bond length}$, $\uparrow \text{e}^-\text{e}^-$ repulsion between d orbital & ligand, $\uparrow \Delta_o$

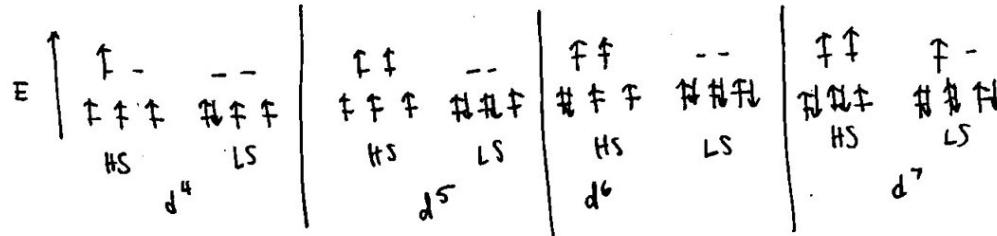
→ $3d$ vs $4d/5d$ (1st row vs 2nd/3rd row transition metal)

- $4d/5d$, $\uparrow \Delta_o$

- $4d/5d$ has d orbitals extend farther than $3d$, interact with ligand more, $\uparrow \text{e}^-\text{e}^-$ repulsion, $\uparrow \Delta_o$

\leftarrow High Spin & Low Spin e^- Config

- d^1-d^3, d^8-d^{10} has only one possible config
- d^4-d^7 has two possibility



\rightarrow Factors Influencing HS & LS

- If $\Delta_o > P$, low spin
- If $\Delta_o < P$, high spin

$\rightarrow \Delta_o$ - energy penalty for populating eg set

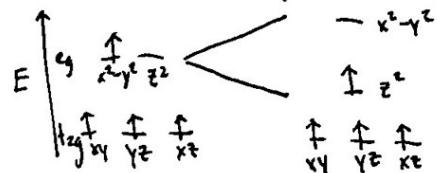
- Δ_o is energy diff between eg & t_{2g} set
- large Δ_o favor pairing of e^- : don't populate eg set

$\rightarrow P$ - pairing energy; energy penalty for pairing e^-

- Coulombic repulsion - e^- in same orbital repel
- exchange energy \downarrow favors unpaired e^-

\leftarrow Jahn-Teller Distortion

- When there is an unequal population of e^- in degenerate orbitals, the molecule will distort to remove degeneracy
- distortion occurs to lead to a net energetic stabilization



not distorted

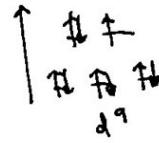
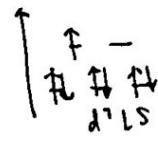
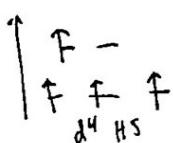


distorted

- elongate along z
- compress along x & y
(or viceversa)

- strong JT Distortion if eg set involved

d^4 HS, d^7 LS, d^9



« Other Geometries (4-coord-complex)

→ Predicting Geometry

1. Count Δe^-

- d^0, d^1, d^2, d^{10} always tetrahedral → no energetic diff, tetrahedral sterically preferred.

2. Consider energetic factor for d^3-d^9

• d-orbital splitting (Δ_o)

- $\uparrow \Delta_o$, squared planar

• Coloumbic repulsion

• Exchange Energy

• Sterics

$\Delta > P + \text{sterics}$

Square planar, LS

$\Delta < P + \text{sterics}$

Tetrahedral, HS

2.1 Tetrahedral HS

- $\downarrow \Delta$, 1st row TM, weak-field ligand

2.2 Square planar LS

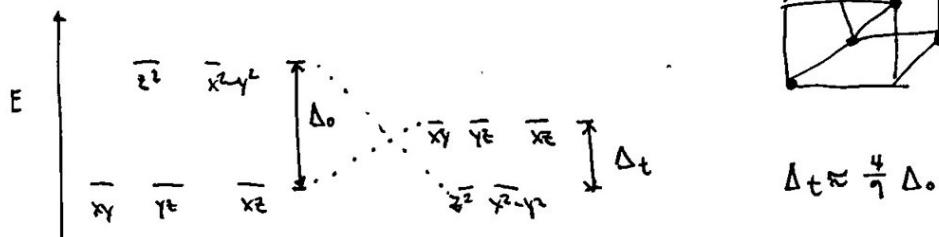
- $\uparrow \Delta$, 1st row TM + strong-field ligand

- $\uparrow \Delta$, 2nd/3rd row TM

→ Tetrahedral (HS)

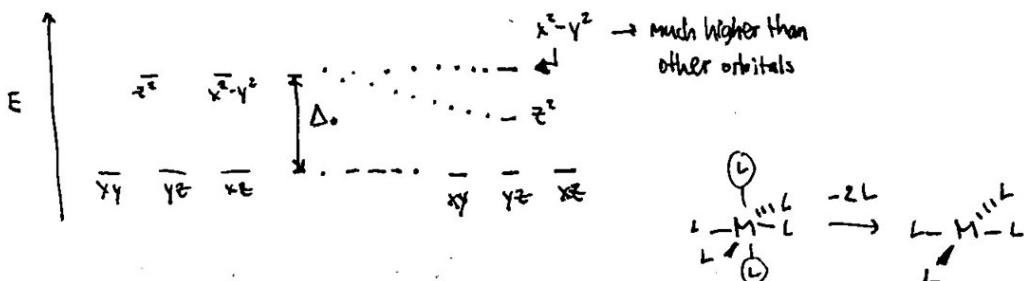
- Comparing to octahedral, tetrahedral has ligand in between x,y,z axis

- ligands interact more strongly with d_{x^2}, d_{xy}, d_{yz}



- poor spatial overlap between d_{x^2}, d_{yz}, d_{zx} orbitals & ligands
- less e^-e^- rep., $\downarrow \Delta$
- always HS

→ Square planar (LS)

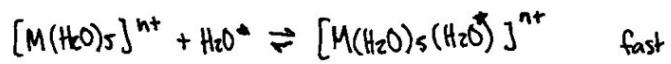
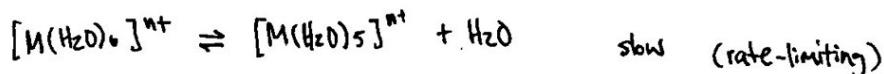


13 May 2020

Ligand Substitution

CHEM 165

<< Mechanism of Ligand Substitution



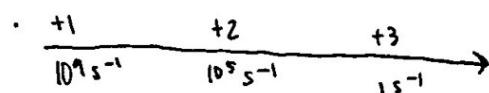
<< Rate of Ligand Substitution

→ labile - relatively fast ligand sub ($K > 1\text{s}^{-1}$)→ inert - relatively slow ligand sub ($K < 1\text{s}^{-1}$)

→ Effect of Metal charge

• Main group metal

- ↑ positive charge, ↓ slower ligand sub 4-5 order



• TM

- similar to main group metal

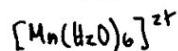
- extreme change explained by d orbital population

- 2nd/3rd row TM are inert {

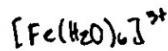
- low spin

- M-L bond strength higher

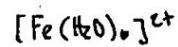
→ d orbital population

normally

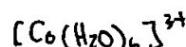
MOS = 2

 $d\text{e}^- = 5$ $\uparrow \uparrow$ $\uparrow \uparrow \uparrow$ $d^5 \text{ HS}$ 

MOS = 3

 $d\text{e}^- = 5$ $\uparrow \uparrow$ $\uparrow \uparrow \uparrow$ $d^6 \text{ HS}$ specialty

MOS = 2

 $d\text{e}^- = 6$ $\uparrow \uparrow$ $\uparrow \downarrow \uparrow$ $d^6 \text{ HS}$ 

MOS = 3+

 $d\text{e}^- = 6$ $--$ $\uparrow \downarrow \uparrow$ $d^6 \text{ LS}$

E

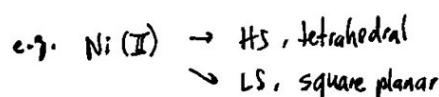
• more e^- in eg set → faster ligand sub• e^- in d orbital, e^- -ligand repulsion.

<< Intro to Organometallic Chemistry

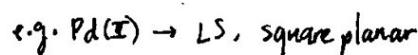
- > study of compound containing metal carbon (M-C) bond
 - can also contain M-H, M-P, M-N, M-O
 - can form challenging C-C, C-N, C-O bond
 - has control over stereochemistry

<< Reactivity of Transition Metal

- 1st row TM
 - often HS, sometimes LS
 - 1e⁻ radical chemistry often occurs



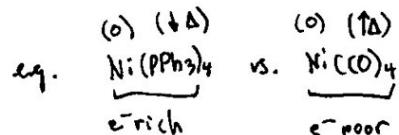
- 2nd / 3rd row TM
 - always LS
 - 2 e⁻ chemistry predominates - well behaved



<< Electron Rich/Poor Metal Centers

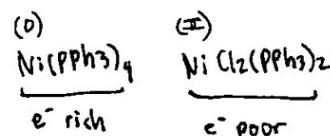
→ Electron rich

- low oxidation state → readily oxidized
- bound to strong σ-donor (↓Δ)



→ Electron-poor

- high oxidation state → readily reduced
- bound to weak σ-donor > (↑Δ)
- bound to strong π acceptor

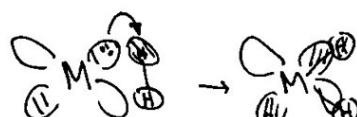


influence rate of rxn

<< Oxidative Addition



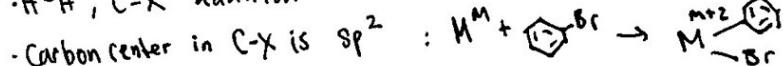
- effective charge $\left\{ \begin{array}{l} \text{MOS} \uparrow +2 \\ \text{de}^- \downarrow -2 \\ \text{tot e}^- \uparrow +2 \quad (\text{lost 2 de}^-, \text{gain 2 bonds}) \\ \text{coord \#} \uparrow +2 \end{array} \right.$



require:
tot e⁻ ≤ 16
can be oxidized by 2
coord # ≤ 4

→ Types of Bonds

- H-H, C-X addition



<< Reductive Elimination



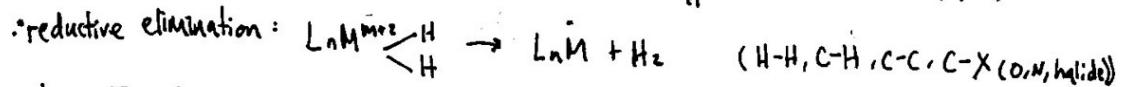
- effective change $\left\{ \begin{array}{l} \text{MOS} \downarrow -2 \\ \text{de}^- \uparrow +2 \\ \text{tot e}^- \uparrow +2 \\ \text{coord \#} \downarrow -2 \end{array} \right.$

→ Types of Bonds

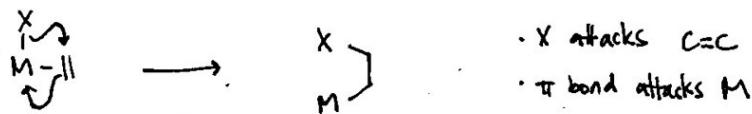
- H-H, C-H, C-C, C-X (X = O, N, halide)

- carbon center is sp²

--> Review: Oxidative Addition & Reductive Elimination



--> Migratory Insertion



• Requires $\begin{cases} X\text{-type ligand} \\ \text{unsaturated L-type ligand} \end{cases}$ - alhene, alkyne.

- MOS - no change
- tot e⁻ - ↓ - 2
- coord # - ↓ - 1

--> B-Elimination

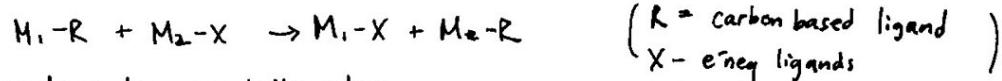


• B-hydride elimination is common

- MOS - no change
- tot e⁻ - ↑ + 2
- coord # - ↑ + 1

--> Transmetalation

→ two metal centers swap ligands

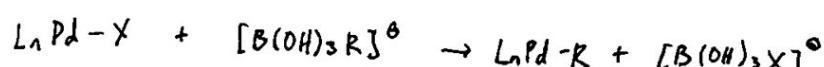


• reaction driven by e⁻ negativity values

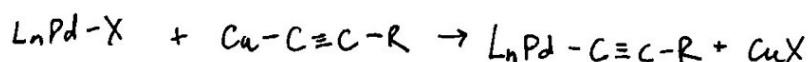
• X-type: prefer more e⁻ pos. metal/semimetal (M₁) ← B, Cu, Sn

• L-type: prefer more e⁻ neg metal (M₂) ← Rh, Pd, Ir, Pt

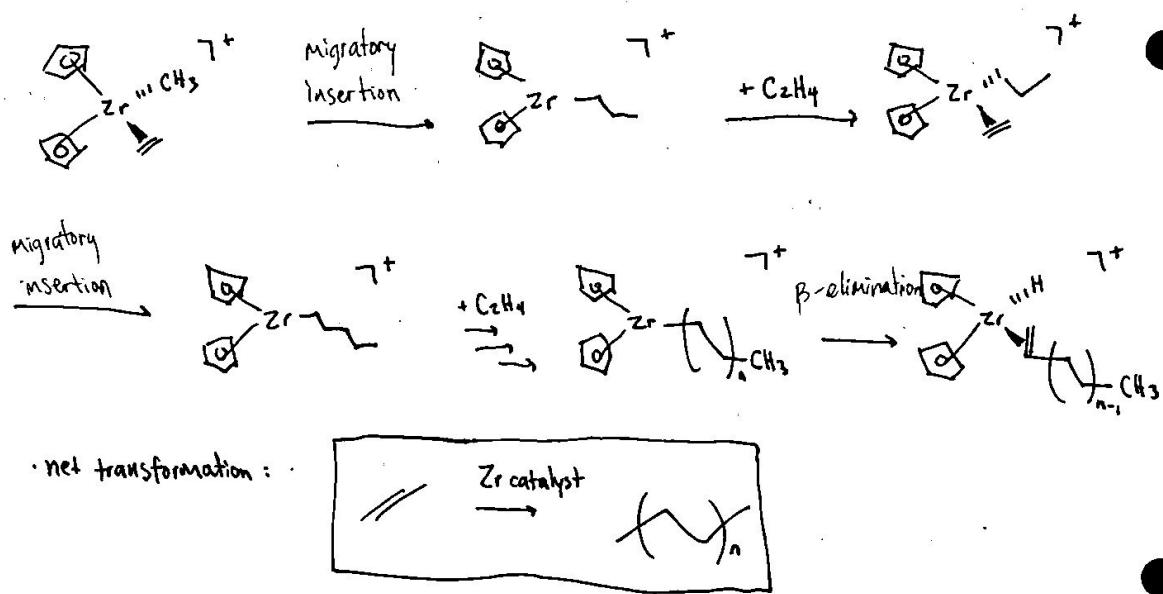
→ Aryl & Aryl Boron



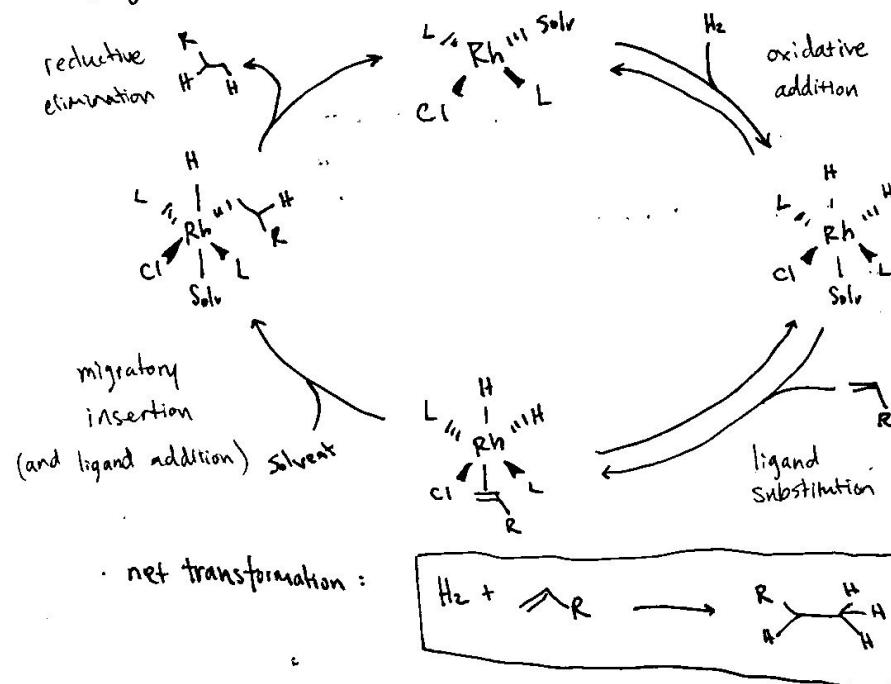
→ Copper



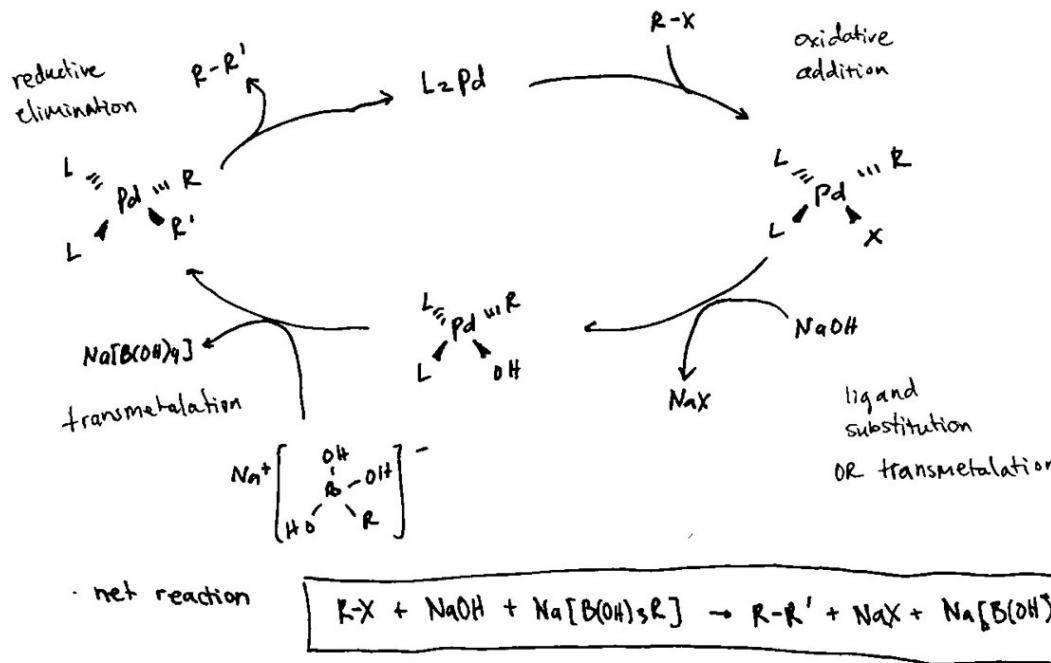
<< Polymerization



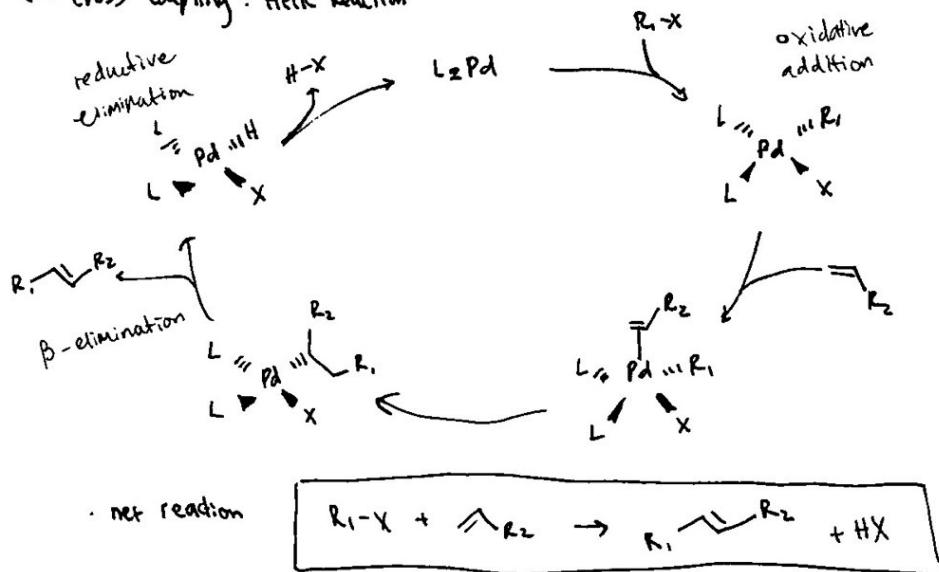
<< Hydrogenation



<< Cross-Coupling : Suzuki Reaction



<< Cross-Coupling : Heck Reaction

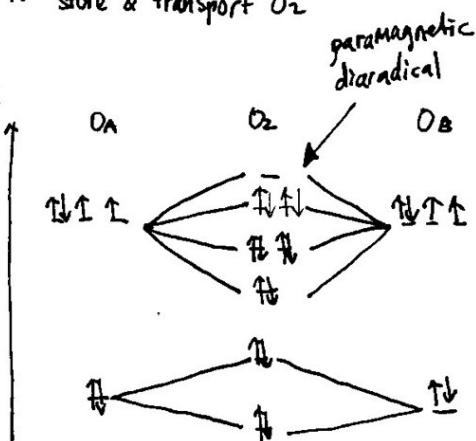


<< History of O₂

- Early Earth is anaerobic - evolution of photosynthesis - $\uparrow [O_2]$
- The Great Oxygenation Event ~ 2.3 billion yrs ago
- anaerobic respiration ~ 2 ATP/glucose
- aerobic respiration ~ 38 ATP/glucose
- O₂ has poor solubility in water - need ways to store & transport O₂

<< O₂ as Strong Oxidant

- O₂ is a strong oxidant { paramagnetic } D.O. = 2
diamagnetic } O₂
 > superoxide - O₂¹⁻
 • paramagnetic
 • radical (O₂^{•-}) } B.V. = 1.5
- > peroxide - O₂²⁻
 • diamagnetic
 • all e⁻ paired } D.O. = 1

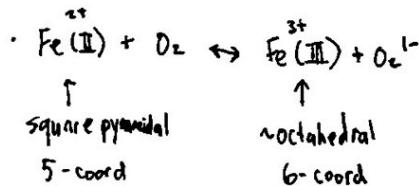


- O₂ carriers have metal centers that can reversibly bind & reduce O₂ to form O₂¹⁻ or O₂²⁻
- O₂ bond order decreases as O₂ is reduced

bond order = $\frac{\text{#e}^- \text{ bonding} - \text{#e}^- \text{ antibonding}}{2}$

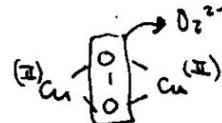
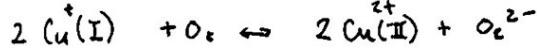
<< Hemoglobin

- protein contains iron porphyrin \rightarrow 1 x Fe(II) center binds O₂ to form Fe(III)-superoxide (heme)



<< Hemocyanin

- protein contains copper \rightarrow 2 x Cu(I) center bind O₂ to form 2 x Cu(II) with bridging peroxide
- deoxyhemocyanin + O₂ \leftrightarrow oxyhemocyanin

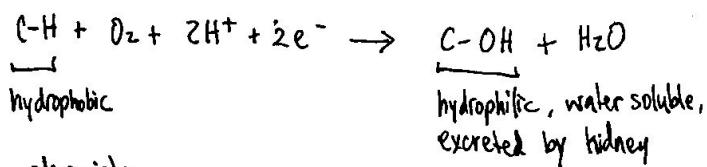


Determining O₂ Binding Mechanism

- characterization techniques to probe MOs and O-O bond order
 - Use IR (vibrational) spectroscopy to know O-O bond order
 - stretching frequency is lower for weaker bonds
 - $\nu = 760$; $\downarrow \nu$; Oz^{2-} ; $Bo=1$
 - $\nu = 1100$; $-\nu$; Oz^{1-} ; $Bo=1.5$
 - $\nu = 1550$; $\uparrow \nu$; Oz ; $Bo=2$

cis O₂ Activation & Oxygenase

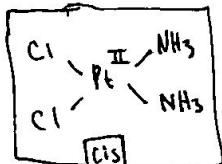
- Organisms use O₂ as oxidant to oxidize organic substance
 - break/build complex molecule
 - fundamental component of metabolic pathway
 - e.g. Cytochrome P450
 - liver → 75% drugs metabolized!
 - structure similar to hemoglobin
 - breaks O-O bond and transfer one oxygen to an organic substrate
 - other O forms H₂O



Medicinal Bioinorganic chemistry

- metals used as probes & drugs

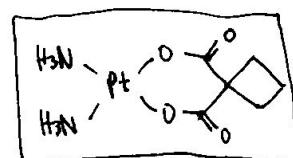
→ Cisplatin



- treat cancer - in cis config
 - cross-links DNA
 - need 2 labile Cl { trans \otimes
chelating ligand \otimes - not undergo ligand sub
 - bind to pairs of GG / GA.

→ Carboplatin

- reduce toxicity → increase stability
 - Method 1 - slow ligand sub using chelating ligands
 - replace Cl with chelating ligands



→ Method 2 - slow ligand sub using \uparrow Pt MOS ($\text{Pt(II)} \rightarrow \text{Pt(IV)}$)

- Cancer cells typically more reducing environment (consume lots of O₂)

<< Intro to Material Chemistry

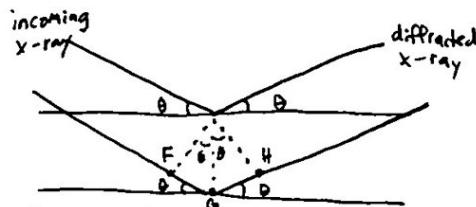
- > material chemistry - chemistry of extended solid
- > crystalline solid - periodic arrangement of atoms exhibiting long-range order
- > amorphous solid - no long-range order
- X-ray crystallography
 - > technique where X-rays are used to determine atomic structure of a crystal
 - sample can be single crystal or powder
 - can be used for small molecule or extended solid

<< Crystals & Unit Cell

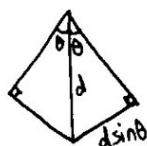
- > unit cell - smallest repeating portion of a crystal lattice
- contains all structural info about crystal
- repeat infinitely along all 3 dimensions
- unit cells are parallelepipeds defined by 3 edges & 3 angles
 - a, b, c - lengths of three cell edges
 - α - \angle between b and c
 - β - \angle between a and c
 - γ - \angle between a and b
 - they don't necessarily have to be the same.

<< Bragg's Law

- X-rays are scattered by e⁻ density with a crystal



- periodic arrangement of atoms lead to constructive interference when Bragg condition is met:
- 2nd x-ray has to travel an extra distance $F \rightarrow G \rightarrow H$
- x-ray will be in phase only if this extra distance = $n\lambda$



$$2d \sin \theta = n\lambda$$

Bragg's Law

<<Types of Crystalline Solids

- > Molecular - discrete molecules held together by weak van der Waals / H-bonding force
 - e.g. H_2O , ferrocene
- > Ionic - cation & anion held together by electrostatic force
 - e.g. NaCl , BaO
- > Covalent - 2,3-D network held together by strong covalent bond
 - e.g. boron nitride (2D), diamond (3D)
- > Metallic - 3D packing of metal atoms held together by metal metal bonds
 - e.g. Fe , Cu , CuZn

<<Ionic Solid

- structure of ionic solid predicted by looking at ionic radii of cation & anion

- $\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{r_+}{r_-}$ (cation generally smaller than anion)

→ Radius Ratio Rules

• Cesium halide

- large cation ; cation 8-coord

(Cs^+ radius 1.81\AA)

- $\frac{r_+}{r_-} \geq 0.732$

• Sodium chloride

- Medium cation ; cation octahedral (6-coord)

Na^+ radius 1.16\AA

- $0.414 \leq \frac{r_+}{r_-} < 0.732$

• Zinc blende

- small cation ; cation tetrahedral (4-coord)

Zn^{2+} radius 0.88\AA

- $0.225 \leq \frac{r_+}{r_-} < 0.414$

→ Deriving the Rules

> limiting radius ratio - min allowable ratio of $\frac{r_+}{r_-}$ for structure to be stable

cation typically smaller than anion : $\frac{r_+}{r_-} < 1$



unstable

repulsive force only
Since anions touching each other, but cation is too small to interact.



stability limit

anions touching each other and cations



stable
anions only touch cation

<< Large Cation: Cesium Halide

- Cl^- at vertices of cube

- Cs^+ at center, 8-coord

→ Derive limiting radius ratio

- assume unit-cell has length one.

- size so that cation, anion on same plane

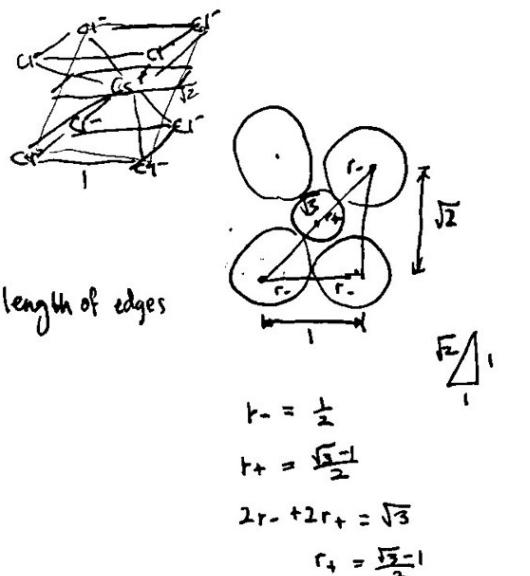
- use pythagorean theorem to calculate the length of edges

- calculate r_+ , r_- , $\frac{r_+}{r_-}$

$$r_- = 0.5$$

$$r_+ = \frac{\sqrt{3}-1}{2}$$

$$\boxed{\frac{r_+}{r_-} = 0.732}$$



<< Medium Cation: Sodium chloride (Rock Salt)

- Cl^- at vertices of cube and center of each face

- "face-centered cube"

- Na^+ at octahedral sites inbetween Cl^-

→ Derive ratio

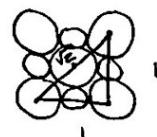
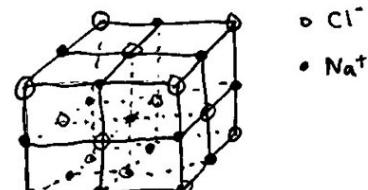
$$4r_+ = \sqrt{2}$$

$$r_+ = \frac{\sqrt{2}}{4}$$

$$2r_- + 2r_+ = 1$$

$$r_+ = \frac{1 - 2\frac{\sqrt{2}}{4}}{2} = \frac{1 - \frac{\sqrt{2}}{2}}{2}$$

$$\boxed{\frac{r_+}{r_-} = 0.414}$$



<< Small Cation: Zinc Blende

- S^{2-} at vertices of cube and center of each face

- "face-centered cube"

- Zn^{2+} occupy tetrahedral sites

→ Divide the unit-cell to 8 pieces

- top half: Zn at front left, back right

- bottom half: Zn at front right, back left

→ Derive ratio

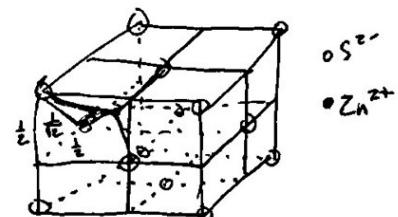
$$2r_- = \frac{1}{2}$$

$$r_- = \frac{1}{2}\sqrt{2}$$

$$(r_+ + r_-)^2 = \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\sqrt{2}\right)^2$$

$$(r_+ + r_-)^2 = \frac{3}{16}$$

$$r_+ = \frac{\sqrt{3}}{4} - \frac{1}{2}\sqrt{2}$$



$$\boxed{\frac{r_+}{r_-} = 0.265}$$

Structure of Metals

primitive cubic	body-centered cubic	close-packed		
		face-centered cubic (fcc)	hexagonal (hcp)	
packing efficiency	52%	68%	74%.	
Example				

→ Primitive Cubic

→ packing efficiency - fraction of space occupied by atoms

• efficiency = 52%.

• unit cell edge = 1

$$\cdot V = 1^3 = 1$$

$$\cdot \text{radius of atom} = \frac{1}{2}$$

• each unit cell has 1 full atom :

$$\left. \begin{array}{l} \\ \\ \end{array} \right\} V = \frac{4}{3}\pi r^3 = 0.52$$



→ Body-Centered Cubic

• each unit cell has 2 full atom

• efficiency = 68%.

→ favored at $\uparrow T$
(greater atomic vibration)

→ Close-Packed

• most efficient way to pack spheres

• 6 neighbors, Δ spaces in between

} single layer



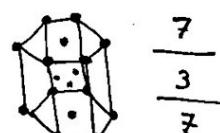
• second layer atoms sit in the valleys created by 1st layer

• diff 3rd layer

→ hexagonal (ABA) (\neq hcp)

• 3rd layer exactly on top of 1st layer.

• have holes in between



→ face-centered cubic (ABC) (fcc)

• 3rd layer sit in valleys created by 2nd layer

• favored at $\downarrow T, \uparrow P$



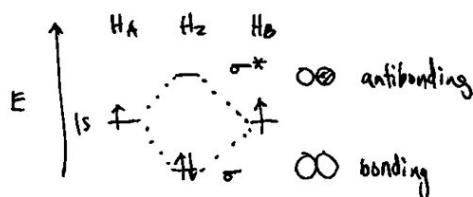
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<< Bonding in Metal

→ Drude Model - Sea of e^-

- a fixed array of \oplus metal ion surrounded by a sea of e^-
- malleability of metal
- if metal deformed, ions simply move to new place, delocalized e^- adjust to maintain
- conductivity of metal
- delocalized e^- easily respond to applied field

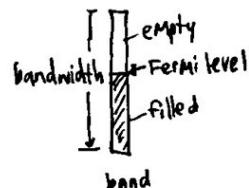
→ AO & MO theory



- n AO \rightarrow n MO
- 1 mol metal AO \rightarrow 1 mol metal MO

→ Bands

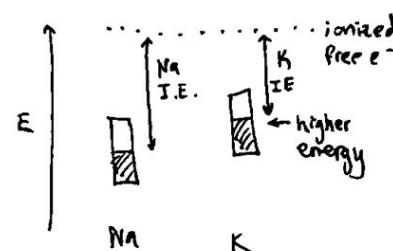
- too many MOs, making energy "less discrete"
- > band - distribution of MO over some range of energy
- can't distinguish one MO from the other since they're close in energy
- metals are characterized by partially filled band, no energy gap between filled & unfilled
- > Fermi Energy - at 0K, the energy of top occupied orbital.
- > Fermi level - at $T > 0K$, 50% probability of finding e^- at that energy.
- Conductivity - e^- at Fermi level can easily move into unoccupied orbitals, allowing net motion of charge



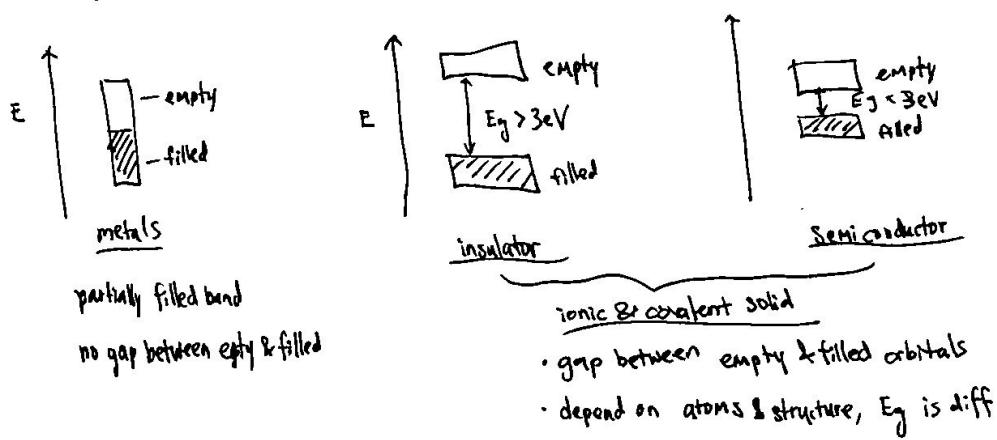
→ Predicting Fermi Energy of Metal

- \uparrow Fermi Energy = \downarrow Ionization energy
- periodic trend
 - ↓ group, ↓ ioniz. E, ↑ Fermi E
 - → row, ↑ ioniz. E, ↓ Fermi E

\uparrow \leftarrow e_{neg} \uparrow
ioniz. E \downarrow
Fermi E \uparrow



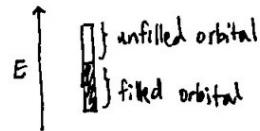
→ band Diagrams



<< Band Diagram of Metals, Ionic Solid, Covalent Solid

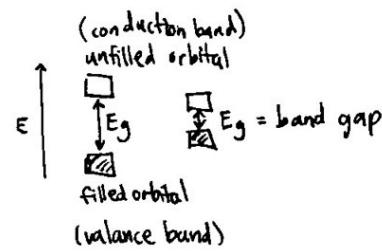
→ Metal

- partially filled band
- no gap between filled/unfilled
- conductors



→ Ionic & Covalent Solid

- gap between filled/unfilled
- can be insulator/semiconductor → size of gap



→ Insulator

- large band gap ($> 3\text{ eV}$, outside visible light)
- not conductive - energetically prohibited to populate conduction band

→ Semiconductor

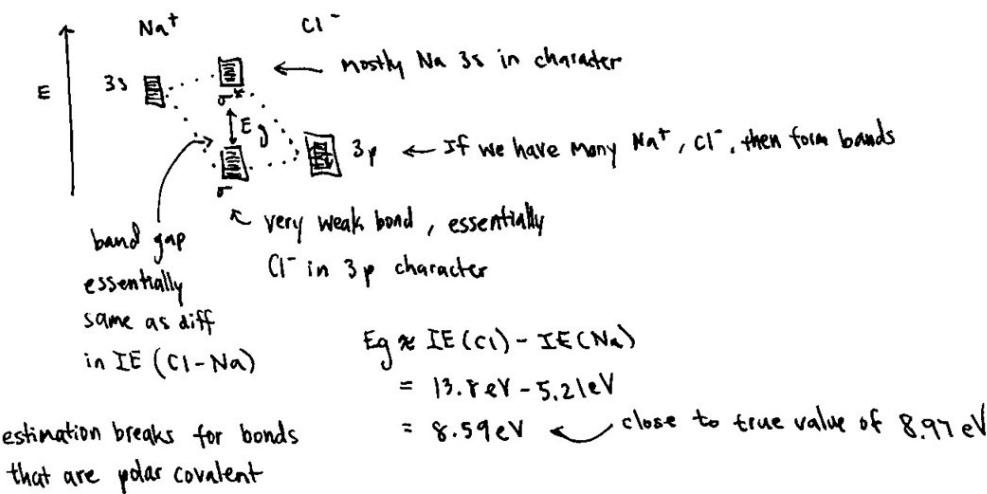
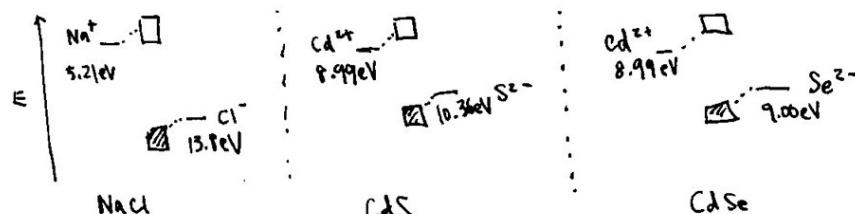
- band gap $< 3\text{ eV}$
- e^- excited into conduction by heat ($\uparrow T$) or light ($h\nu$)

<< Band Gap Prediction

→ Ionic Solid

- use ionization energy (IE) for rough trend

e.g. NaCl

estimation breaks for bonds
that are polar covalentestimate: 8.59 eV real: 8.97 eV

1.37 eV

1.7 eV

0.01 eV

1.5 eV

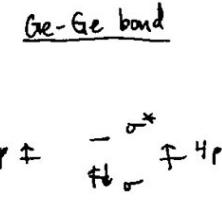
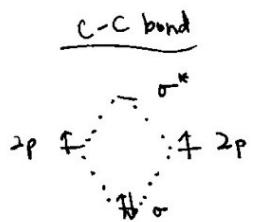
estimate deviates when energy diff is small (polar covalent)

<< Band Gap Prediction

→ Covalent Solid

- use orbital overlap & bond strength to estimate

- Main group element : orbital overlap decreases going down a group



↑ orbital overlap
↑ bond strength
↑ band gap

make these bands
to estimate band
gap

↓ orbital overlap
↓ bond strength
↓ band gap

∴ diamond is colorless due to its ↑ band gap, out of visible light range

<< Doping Semiconductors & Insulators

→ doping - introduction of impurity into a solid

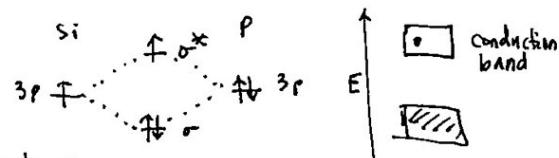
- physical property of semicond & insulator changed by doping

→ n-doping (negative-doping)

- n-type semiconductor

• doping w/ atoms that supply e⁻ to

conduction band (more e⁻ than no doping) } conduct e⁻

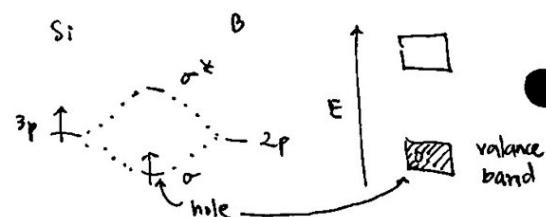


→ p-doping (positive-doping)

- p-type semiconductor

• doping w/ atoms that remove e⁻ from
valence band (less e⁻ than no doping)

• conduct holes



• doping works w/ ionic solid

- both cation & anion can be replaced

• n-type - replace w/ more valence e⁻

• p-type - replace w/ fewer valence e⁻

• doping materials w/ large band gap

• indium oxide (In₂O₃) doped with tin (Sn) → (ITO)

- n-type

• band gap > 3.5 eV

• transparent due to ↑ E_g, but highly conductive

• used in touchscreens

3 June 2020

Electronic Structure of Solid

CHM165

<< p-n junction

→ p-n junction - putting - p-doped & n-doped side by side

• p-n junction direct flow of charges

: important for solar cells

→ Solar Cells

• When light hits semiconductor, e^- excited to conduction band, & leaving hole in valance band

• If no driving force to separate excited e^- and hole pair, they would just recombine (point less!)

• p-n junction creates an internal electric field that drives charge separation.

p type n type

$e^- \rightarrow$
 $\leftarrow \text{hole}^{\oplus}$

