

3.091
Fall, 2009

Lecture Summary Notes

Prepared by anonymous MIT students

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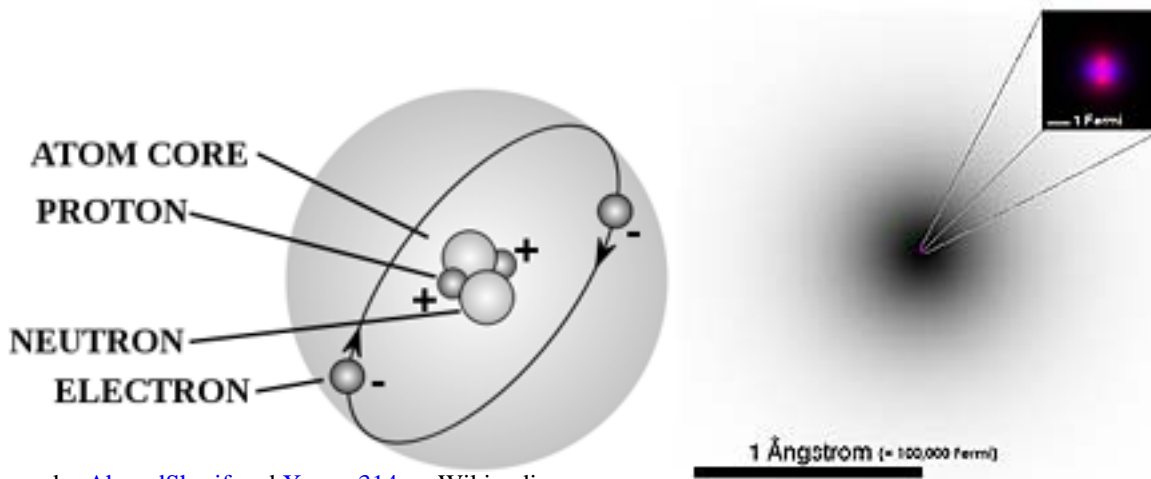
Although these summary notes attempt to cover most of the main topics emphasized during each lecture, they should **not** be considered completely comprehensive. Material covered in assigned readings and/or homework are not necessarily covered by these notes. This document should be used as supplemental study material, in addition to reviewing your own notes and doing the assigned readings and homework questions.

Lecture 1 – Sept 9:

- Intro.

Lecture 2 – Sept 11: PERIODIC TABLE, ATOMIC NOMECLATURE

- History of the Periodic Table
 - Atoms - Dalton (1803) (*nearly got it right*) – pg 14-15
 - Dalton's Atomic Theory
 - Mendeleev (1869) → predicted “missing elements” and their properties
- Structure of the atom
 - Electron (e^-), proton (p^+), neutron (n^0) **see table below**



Images by [AhmadSherif](#) and [Xerxes314](#) on Wikipedia.

- Electrons are tiny ($\sim 1/1830$ the mass of a proton), but their orbital's take up a lot of space, the nucleus is tiny.
- Method of labeling elements: ${}^A_Z X$
 - A= mass # \sim # nucleons (protons + neutrons)
 - Z = proton # (defines chemical properties. An element's “social security identification #”)
 - A, Z are integer numbers
 - ex. ${}^{23}_{11}Na$
- Ions
 - positive (+): e^- deficient = cation (“paws”itive = cat... meow)
 - negative (-): e^- rich = anion (extra ‘n’ = negative)
- Molar masses
 - ‘Relative’ masses of each element determined by mass spectroscopy, average elemental mass amongst its various isotopes
- Faraday's const (**$F = 96,485 \text{ C/mol}$**)
 - “Oil drop experiment” (Millikan) → **$e = 1.6 \times 10^{-19} \text{ C}$**
 - Electrochemistry: $Ag^+ + e^- \rightarrow Ag^0$.
 - Count e^- ($=n_{Ag}$). Weigh Ag. Determine mass per atoms
 - From ‘relative mass’ values, we now know atomic mass of each element
- Avogadro, **$N_{Av} = 6.02 \times 10^{23} \text{ moles}$** :
 - Simply for convenience (easier units than 10^{23} atoms)
 - Defined such that 1 mole of ${}^{12}_6C$ weighs 12g
- **Chemical Reaction Equations**
 1. Write out a balanced equation
 2. convert mass to moles
 3. determine limiting reagent
 4. calculate amount of product
 - ex. $TiCl_{4(g)} + 2 Mg_{(l)} = 2MgCl_{2(l)} + Ti_{(s)}$
- **Isotope calculations** (iso=isotope)
 - $X(m_{iso1}) + (1-X)(m_{iso2}) = m_{avg}$, solve for X. If $X > 0.5$, iso1 is more abundant.

Lecture 3 – Sept 14 – MORE HISTORY

- Structure of atom
 - JJ Thomson (1904): “Plum Pudding”
 - e⁻s distributed uniformly throughout an atom
 - Ernest Rutherford (1911): “Nuclear Model”
 - Conclusion from gold foil expt
 - Majority of mass is found in the nucleus ($r_{\text{nucleus}}/r_{\text{atom}}=1/10,000$)
 - e⁻ orbiting around nucleus
 - Niels Bohr (1913): introduces quantization condition
 - Needed to explain blackbody radiation and atomic spectra
 - Postulated
 - e⁻ follow circular orbits around a nucleus
 - Orbital angular momentum is quantized, hence only certain orbits possible
 - e⁻ in stable orbits do not radiate
 - e⁻ change orbits by radiating or by absorbing radiation

Lecture 4 – Sept 16: BOHR MODEL

- Bohr Model
 - **Developed for H-atom, applicable to any one electron system (e.g. Li³⁺, etc)**
 - Quantized energy states (n=1,2,3...)
 - $r(n) = \frac{a_0 n^2}{Z}$, $E_{\text{electron}} = -K \frac{Z^2}{n^2}$, $v(n) = \frac{hZ}{2\pi m a_0 n}$
 - a₀= Bohr radius = 0.529 Angstroms
 - Z = proton number
 - e = elementary charge
 - m = mass of e⁻
 - h= Planck’s constant
 - n = e⁻ principal quantum number
 - K = a constant = 1.312MJ/mol = 13.6 eV/atom
 - 1eV = 1.6x10⁻¹⁹J

E=0	n=infinity
E ₃ =-KZ ² /9	n=3
E ₂ =-KZ ² /4	n=2
E ₁ =-KZ ²	n=1

- Energy Level diagram
 - E=0 at n=infinity
 - E₁ = ground state energy, when n=1 (e.g. E₁ = -13.6 eV for H)
 - Spectrum from cathode ray tube with known gas
- Stimulated emission
 - Photons: E_{incident} = E_{transition} + E_{scattered}
 - $E_{\text{transition}} = -KZ^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$
- Photons:
 - $E = hv = \frac{hc}{\lambda}$
 - h=Planck’s constant, v = photon freq., λ= wavelength, c=speed of light
- Traveling Particle (in other words, particles with definite mass)
 - $E = \frac{1}{2}mv^2$

Lecture 5 – Sept 18: EMISSIONS SPECTRA, QUANTUM NUMBERS

- Reading: Averill 6.5
- Visible light: 400-700nm = 3.1-1.8eV

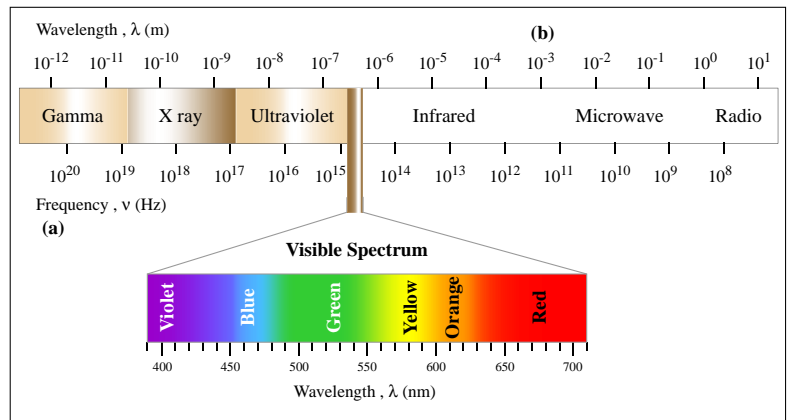


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- Bohr model for hydrogen (1 electron system) resulted in quantized energy level

- Generalized eqn.: $\bar{\nu} = \mathfrak{R}Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$,
- $\bar{\nu} = \frac{1}{\lambda}$ = wave number
- \mathfrak{R} = Rydberg constant = $1.097 \times 10^7 \text{ m}^{-1}$
- Berlin – Franck – Hertz: Hg (mercury vapor) experiment showed quantized energy levels applies to other elements/atoms as well.

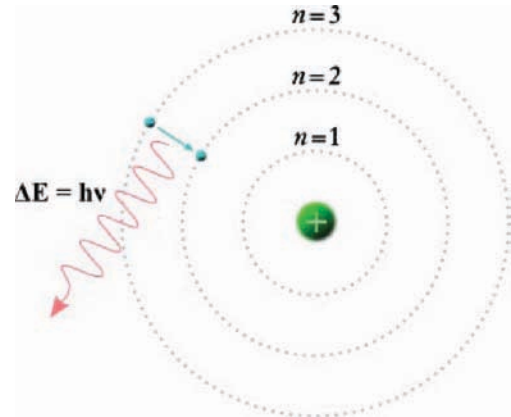


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- Limitations of Bohr model:
 - Fine structure (doublet)
 - Zeeman splitting (under an applied magnetic field (B))
- Sommerfeld proposed 'elliptical shape' to the electron orbitals
 - Quantum numbers: n, l, m, s
- ex. Ag metal beam split by magnetic field (atoms with spin-up e^- go one way, atoms with spin-down e^- go the other way).
- Franck & Hertz Expt.:
 - Gas discharge tube, Hg vapor
 - Demonstrated existence of a threshold energy required to excite electrons in Hg atoms \rightarrow electron energy levels are true to all atoms

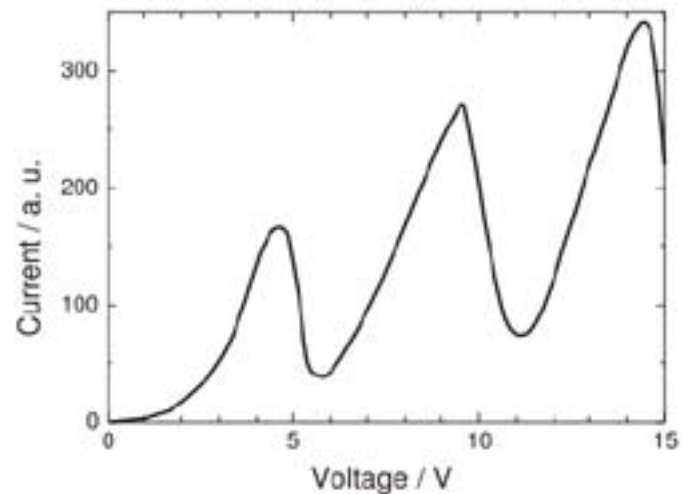
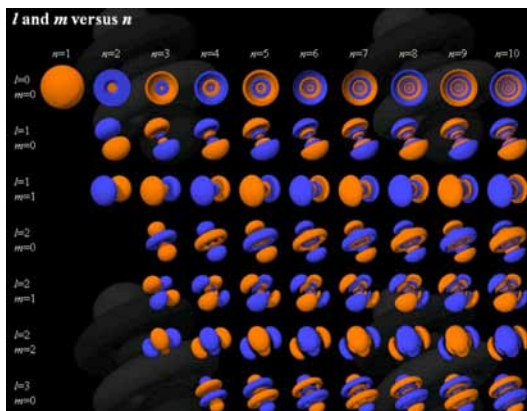


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Lecture 6 – Sept 21: QUANTUM NUMBERS, PARTICLE-WAVE DUALITY

- **Reading: Averill 6.4**
- Quantum numbers defining the ‘state’ of the electron
 - n = principle quantum number $n=1,2,3\dots$, (or K,L,M...)
 - ℓ = angular momentum (“shape”), $\ell = 0..n-1$ (s,p,d,f,g...)
 - m = magnetic quantum number, $m = -\ell..0..\ell$
 - s = spin $+/- 1/2$
- Examples of orbital shapes <http://www.orbitals.com/orb/orbtable.htm> :



Courtesy of David Manthey. Used with permission.
Source: <http://www.orbitals.com/orb/orbtable.htm>

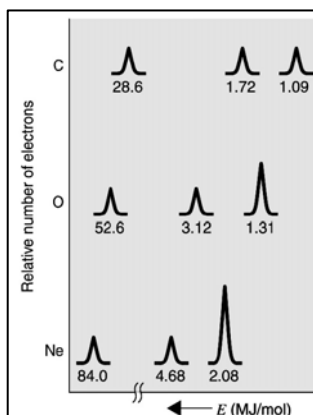
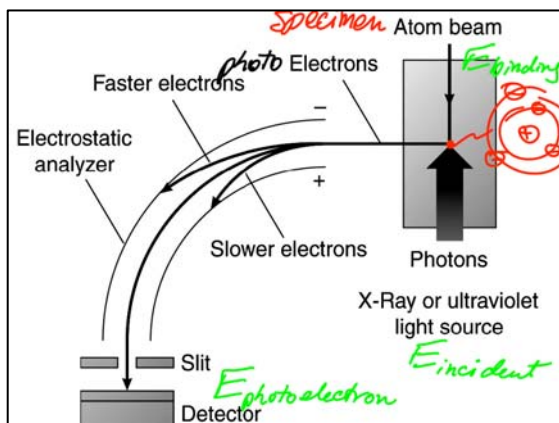
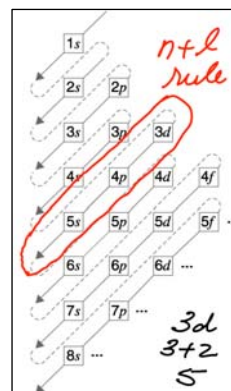
- Aufbau Principle
 1. Pauli exclusion principle: in any atom, each e^- has a unique set of quantum no.’s (n,l,m,s)
 2. e^- fill orbitals from lowest E to highest
 3. Degenerate electrons (same energy level) strive to be unpaired

→ Filling electron states:

 - Ex. Carbon, C: $1s^2 2s^2 2p^2$
- de Broglie – an electron can act as a wave
 - He asked: “if photons can behave as particles, can electrons behave as a wave?”
 - Geometric constraint: $2\pi r = n\lambda$, $n=1,2,3\dots$ (circular wave path)
 - Wavelength of an electron: $\lambda_e = h/p = h/mv \rightarrow mvr = nh/2\pi$!
 - p =momentum = mv
 - Demonstration of diffraction of electron ‘beam’ using a crystal lattice
 - **Particle-wave duality confirmed!**
- Heisenberg – uncertainty principle
 - $(\Delta p_x)(\Delta x) \geq h/2\pi$
 - You can’t know the exact position and momentum of a particle at the same time
 - Deterministic models (billiard balls) turn into probabilistic models
 - Einstein: “God doesn’t play dice with the universe”
 - Bohr: “Einstein, stop telling God what to do!”
- Schrodinger equation (NOT TESTED ON FINAL)
 - $$i\frac{\partial}{\partial t}\Psi(x, t) = -\frac{1}{2m}\nabla^2\Psi(x, t) + V(x)\Psi(x, t).$$
 - It’s a *defining equation* for quantum mechanics
 - Think of it as equivalent to Newton’s equation: $F=ma$
 - Complex equation that allows us to calculate measurable quantities, such as position, momentum, energy of microscopic systems.
 - Well beyond the scope of this class...

Lecture 7 – Sept 23: AUFBAU PRINCIPLE X-RAY PHOTON SPECTROSCOPY

- **Reading** : Averill 8.1-8.2, 12.5, 8.3
- $n+l$ rule for filling orbitals. Fill in ascending n .
 - 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s...
- Measurement of ionization energies ($E_{\text{inc}} = E_{\text{binding}} + E_{\text{kin}}$)
 - Peak height tells # of electrons in shell
 - Energy tells shell (n)



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- Average Valence Electron Energy (AVEE)
 - $<11\text{eV} \rightarrow e^-$ weakly held = metals
 - $>13\text{eV} \rightarrow e^-$ tightly bound = non-metals
 - $>11\text{eV}, <13\text{eV}$ = semi-metals
- Noble gases \rightarrow filled valence shell \rightarrow energy well = extremely stable
- Electron transfer to achieve valence shell filling
 - Ion pair production
 - $\text{Na} \rightarrow \text{Na}^+ + e^-$
 - $\text{Cl} + e^- \rightarrow \text{Cl}^-$
 - Agglomerate without limit due to coulombic attraction \rightarrow Crystal!

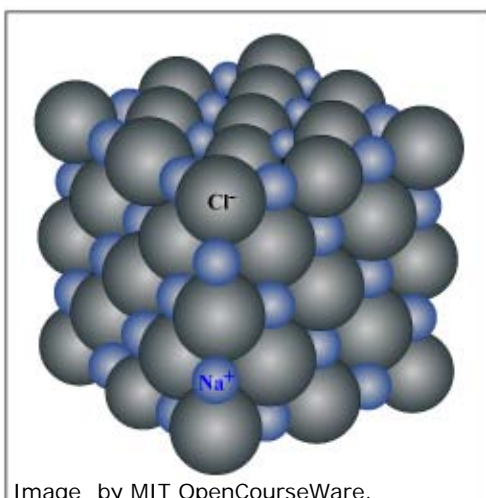
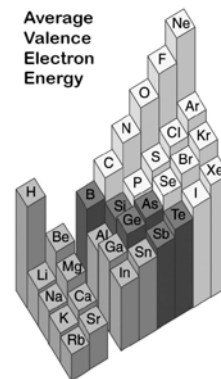


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Lecture 8 – Sept 25 :

- **Reading : Averill 8.3-8.6, 8.8, 9.2**
- **Energetics of pair attraction**
 - → energy gained upon converting a gas of ion pairs, to a crystal array
 - $E_{attr} = \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r}, E_{rep} = \frac{b}{r^n}, E_{net} = E_{attr} + E_{rep}$
 - $b, n = \text{constants}, n \sim 6-12$
 - **Madelung constant, M** → energy related term of a crystal, based on atomic geometry
 - Generally, an infinite sum
 - For a material with +1 and -1 charged species
 - Energy per mole of ions:
 - $E_{lattice} = \frac{-M \cdot z^+ \cdot z^- \cdot N_{AV} \cdot e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$ (sum of all ion interactions)
 - $n = \text{Born exponent}, n \sim 6-12$
 - If $M > 1$ → a solid will form
 - If $M < 1$ → material will remain as a gas
- **Transparent materials:**
 - If $E_{hv, incident} < \Delta E_{trans}$, visible light doesn't have enough energy to promote electron excitation → the photon passes straight through material
- **Hess's Law: energy change in a chemical rxn is path independent**
 - Energy is a *State Function*
 - i.e. $\text{Na}(s) + 1/2\text{Cl}_2(g) \rightarrow \text{NaCl}(s)$
 - a) convert reactants to their independent gaseous forms (steps 1,2)
 - b) remove/add electrons (steps 3,4)
 - c) crystallize (step 5)

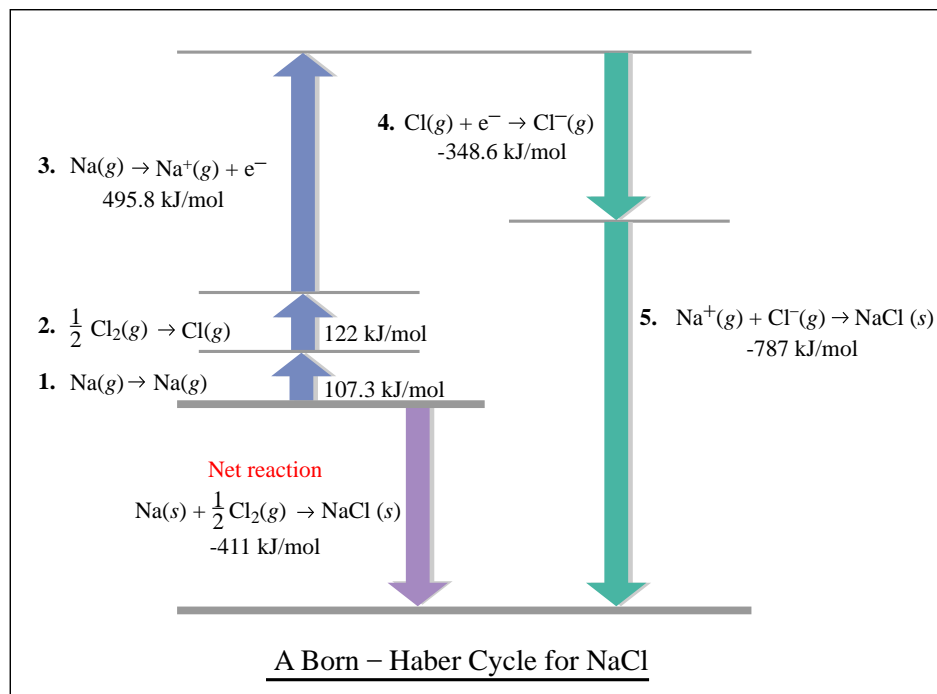


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Lecture 9 – Sept 28 :

- **Reading : Averill 7.3, 8.9**
- Problems with ionic-bonding for diatomic molecules: $H_2, N_2, O_2 \rightarrow$ can't be ionic
- G.N. Lewis (1916) – shell filling by **electron sharing**
 - Lewis Dot notation
 - Cooperative use of valence e^- 's to achieve octet stability = **covalent bonds**
- Ionic Bond = e^- transfer
- Covalent Bond = e^- sharing (directional)

	1A(1)	2A(2)	3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Period 2	• Li •	• Be •	• B •	• C •	• N •	• O •	• F •	• Ne •
Period 3	• Na •	• Mg •	• Al •	• Si •	• P •	• S •	• Cl •	• Ar •

Image by MIT OpenCourseWare.

- Carbon \rightarrow only has 2 unpaired (bonding) electrons in p-orbital
 - s-orbitals 'merge' with p-orbitals \rightarrow **sp^3 hybridized**
 - Results in 4 unpaired e^- , ready to bond

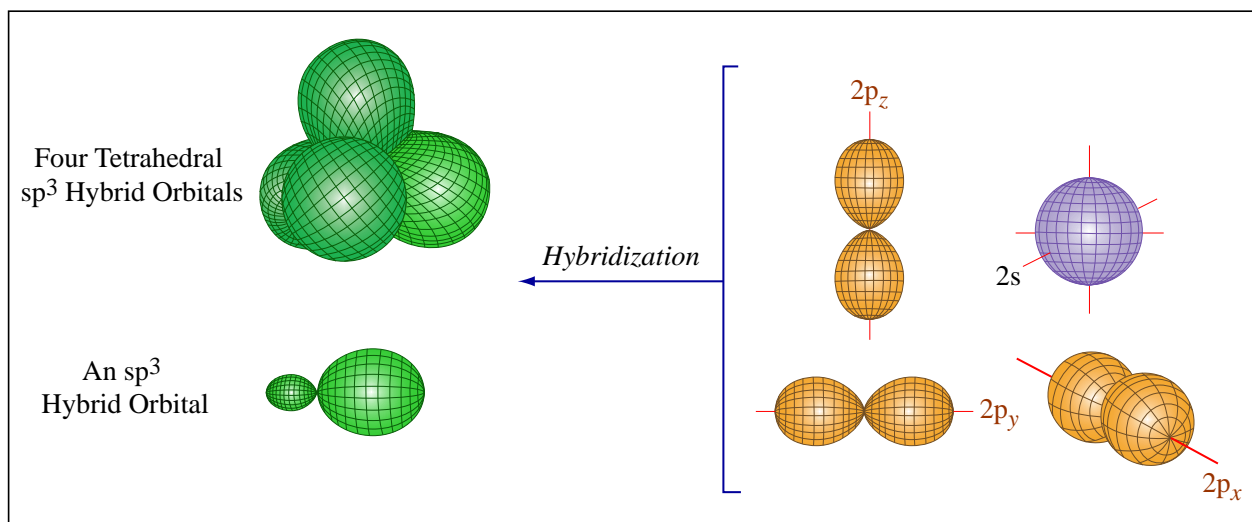


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- Energy of heteronuclear bonds :
 - $E_{A-B} = \sqrt{E_{AA} \cdot E_{BB}} + 96.3 \cdot (\chi_A - \chi_B)^2$ (in kJ/mol)
- % ionic character = $\left\{ 1 - \exp\left(-\frac{1}{4}(\Delta\chi)^2\right) \right\} \cdot 100\%$
- Polar bonding \rightarrow can lead to a polar molecule – but only if there's asymmetry

Lecture 10 – Sept 30 : LCAO-MO

- **Reading : Averill 9.2, 9.3, 9.4**
- **LCAO-MO (Linear Combination of Atomic Orbitals – Molecular Orbitals)**
 - Orbitals split into a bonding (lower) and anti-bonding (higher) orbitals. Electrons fill from lowest energy up.
- **Types of bonds:**
 - σ = no nodal plane separates nuclei
 - eg. $s + s$, $p_z + p_z$, $s + p$
 - π = a nodal plane separates nuclei
 - eg. $p_y + p_y$, $p_x + p_x$
 - don't need to worry about d or f orbitals

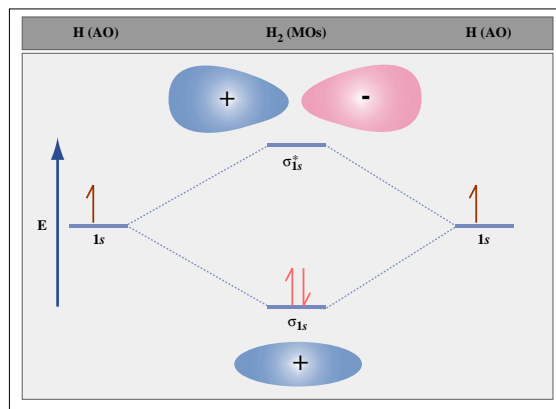
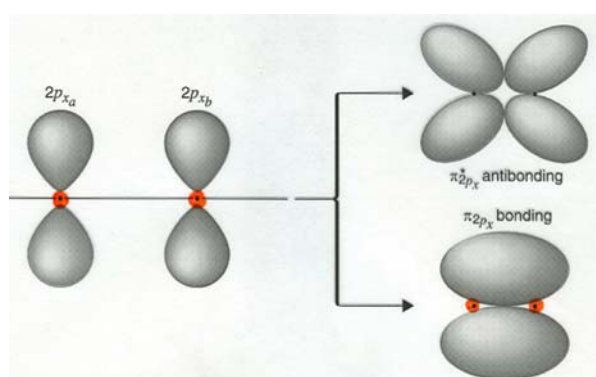
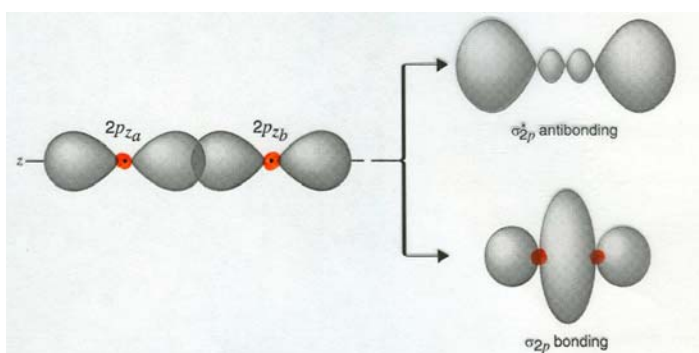


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- **Paramagnetism:** from unpaired electrons in MO
 - eg. liquid oxygen is paramagnetic – can be held by a magnetic field

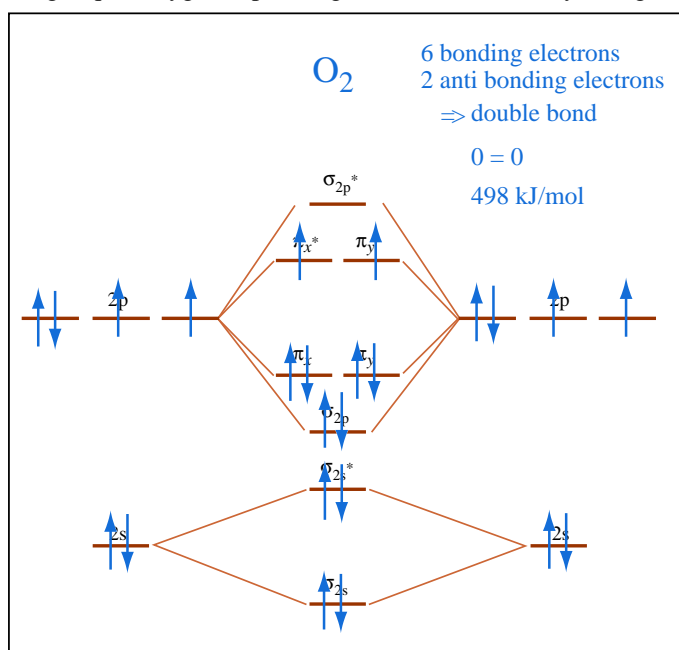


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Lecture 11 – Oct 2 : HYBRIDIZED ORBITALS AND BONDING, SHAPES OF MOLECULES

- **Reading : Averill 9.1, Shackelford 2.5**
- Hybridized bonding in molecules
 - i.e. C_2H_4 (C=C double bond has one σ -bond, and one π_x -bond), and C-H bonds are from sp^2 hybridized orbital in C.

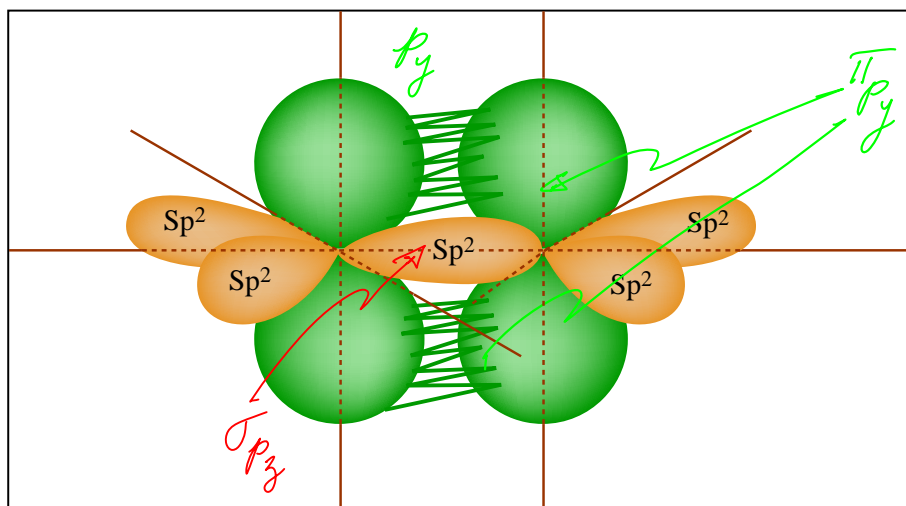


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- VSEPR (Valence Shell Electron Pair Repulsion)
 - Electron Pair Geometry vs. Molecular Geometry

Overview of molecular geometries					
Electron pairs	2	3	4	5	6
Electron pairs geometry					
	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Molecular geometry: Zero lone pairs	$B-A-B$				
	Linear AB_2	Trigonal planar AB_3	Tetrahedral AB_4	Trigonal bipyramidal AB_5	Octahedral AB_6
Molecular geometry: One lone pair					
		Bent (V-shaped) AB_2	Trigonal pyramidal AB_3	Seesaw AB_4	Square pyramidal AB_5
Molecular geometry: Two lone pairs					
			Bent (V-shaped) AB_2	T-shaped AB_3	Square planar AB_4
Molecular geometry: Three lone pairs					
				Linear AB_2	

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- Elements that can undergo an expanded octet are: $Al \rightarrow Cl$, $Ga \rightarrow Kr$, $In \rightarrow Xe$, $Tl \rightarrow At$

Lecture 12 – Oct 5 : SECONDARY BONDING

Averill 12.5, 12.6; Shackelford 2-5, 2-4, 15-1, 15-2, 15-5

1. dipole-dipole:

- applies to polar molecules (i.e. HCl)
- $E_{d-d} \sim 5 \text{ kJ/mol}$ (vs. 780kJ/mol for an ionic bond)
- Much weaker!

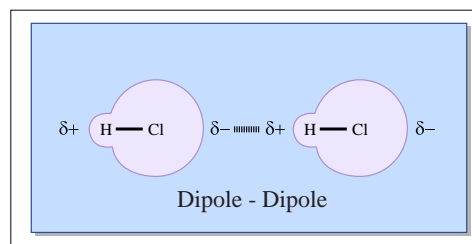


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2. induced dipole – induced dipole

- operative in non-polar species
- explains why non-polar species can exist as a liquid or solid (i.e. N_2 bp = 77k)
- Van der Waals bond or London Dispersion forces
- $E_{vdw} \propto \frac{\alpha^2}{r^6}$
- Force is larger for larger atoms \rightarrow higher bp for larger atoms

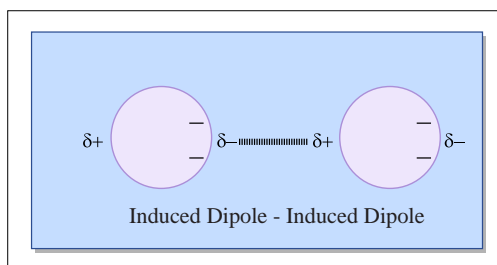
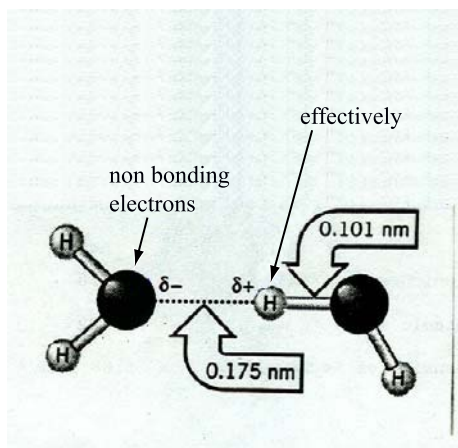


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3. Hydrogen Bonding

- Between exposed proton side of H, and e^- on other atom
- Only applies between H+ F, O, or N. (i.e. HCl does not have a “H-bonding”)
- i.e. (H-F) \cdots (H-F)

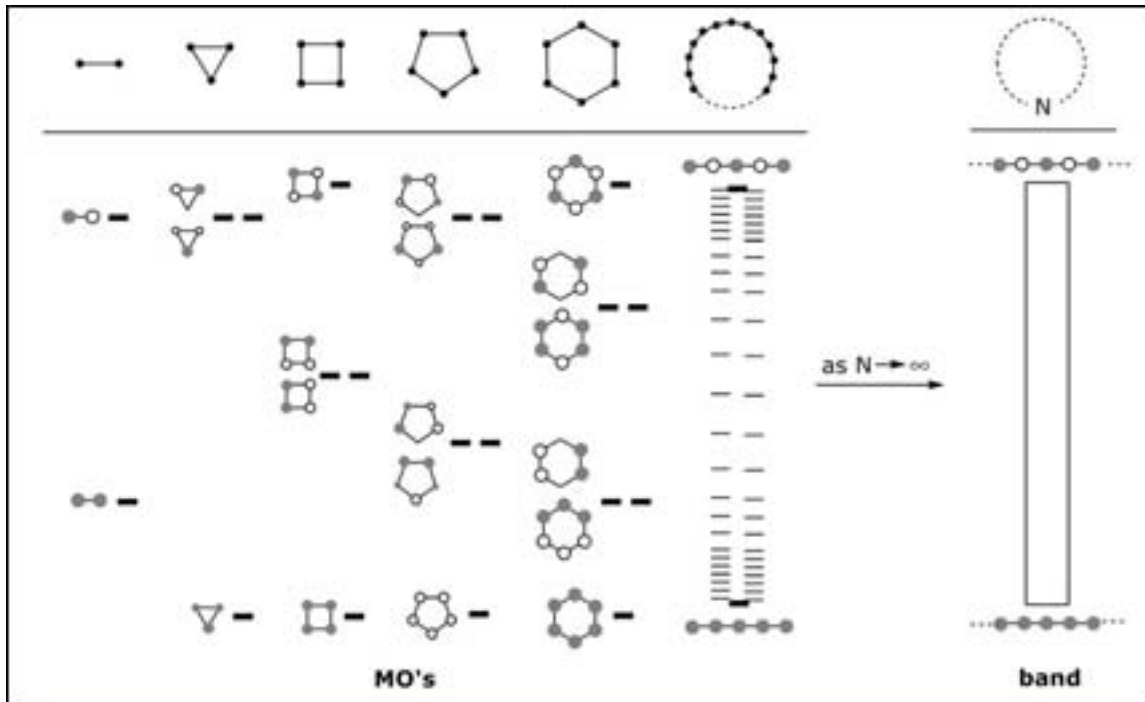


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Lecture 13 – Oct 9: E⁻ BAND STRUCTURE: METALS, CONDUCTORS, INSULATORS

Averill 12.6

- Drude model:
 - “Free e⁻ gas” model → e⁻ in valence shell can move → some success
 - Couldn’t explain insulators vs. metals → needed quantum mechanics!
- Quantum mechanics → LCAO-MO applied to many atoms (solids)
 - Energy levels turn into bands



Courtesy of Daniel Nocera. Used with permission.

- Electrons can only move (e⁻ conduction) if they are in an energy level adjacent to unoccupied states
- Metals ($E_g=0$), Insulators ($E_g>3\text{eV}$), Semiconductors ($1\text{eV}<E_g<3\text{eV}$)

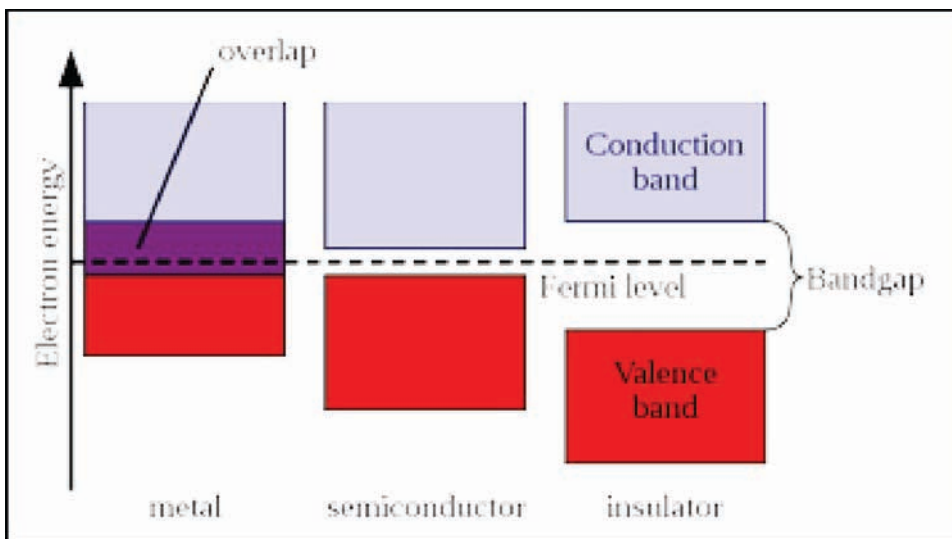


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Lecture 14 – Oct 13: SEMICONDUCTORS

Averill 12.6

- Photo-excitation of e^- from valence band to conduction band
 - Recall: absorption edge plot
- Photo-emission: from an e^- in the valence band falling down to an empty state in the conduction band.
- Thermal excitation
 - $E_{c-} \sim 1/40$ eV at room temperature
 - Maxwell-Boltzmann distribution of e^- energy

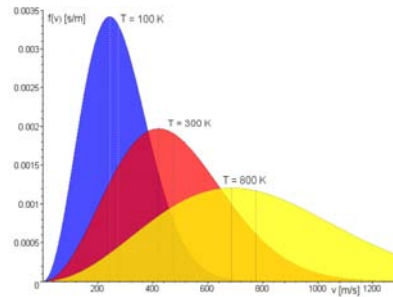
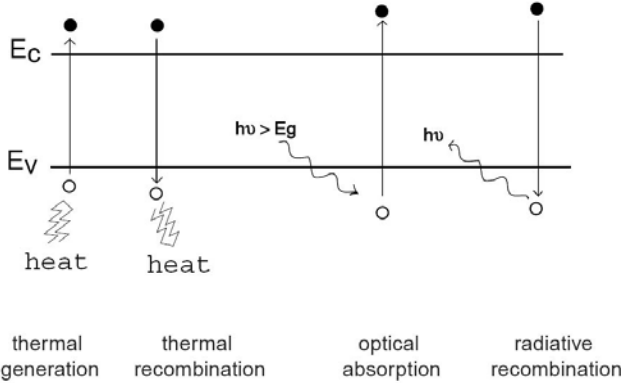
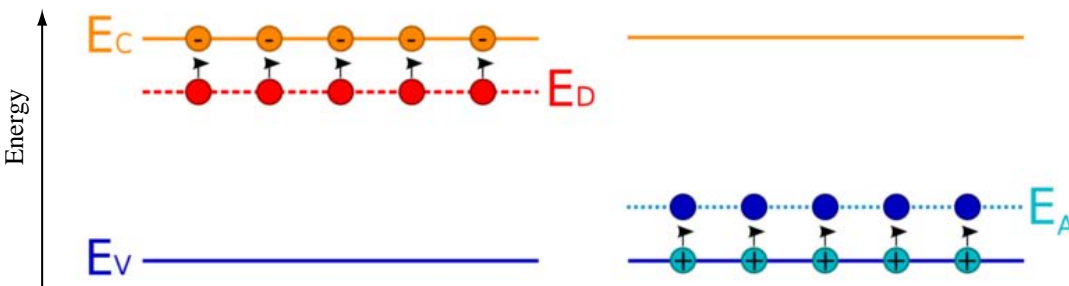


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Courtesy of Jesús del Alamo. Used with permission.

- “Chemoexcitation” = doping of a semiconductor
 - **Intrinsic** = pure Si, Ge, or compound
 - **Extrinsic** = intentional impurity added to inject charge carriers
 - n-type: supervalent (i.e. P) → adds e^- to conduction band
 - p-type: subvalent (i.e. B) → adds h^+ to valence band

Doped semi-conductors

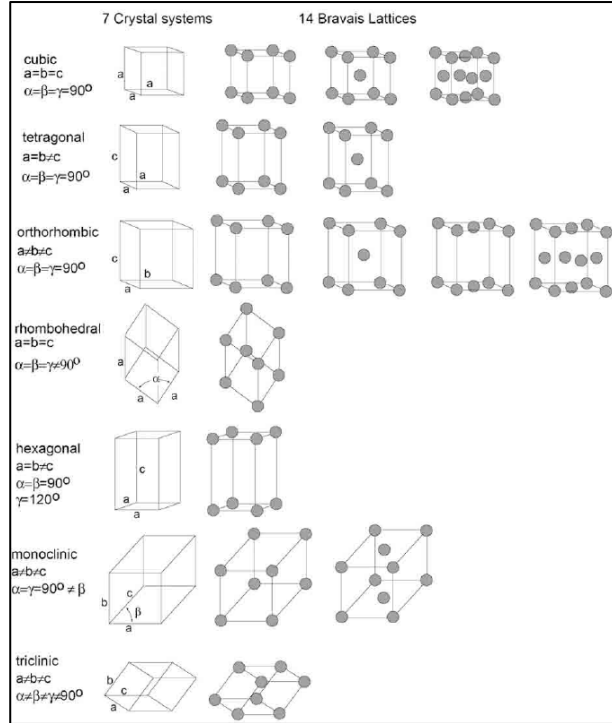


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Lecture 15 – Oct 14: CRYSTALLOGRAPHY

Averill 12.1, 12.2; Shackelford 3-1.

- 7 Crystal systems
 - 7 unique ways to fill space with volume elements
- 14 Bravais lattices
 - Crystal systems, plus lattice sites
 - i.e. sc, fcc, bcc, hcp...
 - Lattice sites are interchangeable – all sites are equivalent
- Basis
 - Atoms or molecules per lattice site
 - i.e. 1 atom, or a molecule
 - i.e. Au atom, or NaCl ion pair, of CH₄ molecule, or C-C pair
- Crystal Structure
 - Bravais lattice & basis
 - i.e. fcc, rocksalt, diamond cubic structure



- Closest Packed structure: 12 nearest neighbors → fcc, and hcp = 74% APD

• Atomic Packing Density, APD:

$$APD = \left(\frac{\text{volume_matter}}{\text{total_volume}} \right) = \frac{\left(\frac{\text{atoms}}{\text{unit_cell}} \right) \cdot V_{\text{atom}}}{V_{\text{cell}}} \cdot 100\%$$

- $V_{\text{atom}} = 4/3 \pi r^3$
- $V_{\text{cell}} = a^3$ (if cubic)
- Calculating lattice constant (a) or atomic radius (r)
 - Molar Volume (V_{molar}) = moles/volume = constant
 - For volume of unit cell, (V_{cell}) (= a^3 for cubic),
 1. (atoms)/(unit volume) = (N_{av}) / (V_{molar}) = (# atoms/cell) / V_{cell}
 → solve for 'a' via V_{cell}
 2. Get a = f(r) based on unit cell geometry (i.e. $a = 4r/\text{sqrt}(3)$ for bcc)
 → solve for 'r'

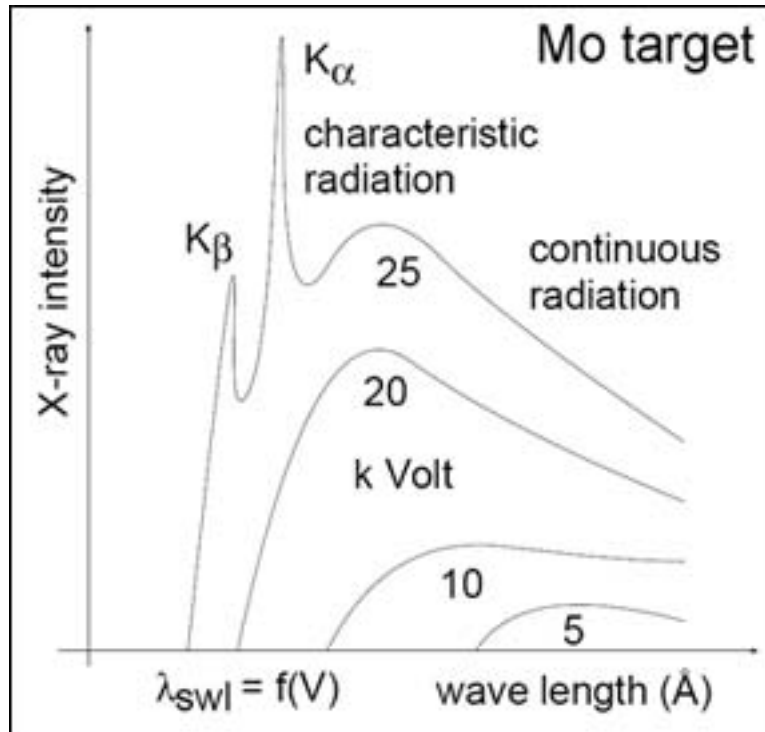
Lecture 16 – Oct 16: MILLER INDICES, X-RAY SPECTRA

Averill 12.1, 12.2; Shackelford 3-2, 3-6

- Miller Indices (ref. handout from class)
 - Point: h,k,l
 - Direction [h k l]
 - Family of directions <h k l>
 - Plane¹: (h k l)
 - Family of planes¹: {h k l}
 - ¹ direction [h k l] is normal to plane (h k l)
 - ¹h,k,l are reciprocal of axial intercepts

- Distance between adjacent planes with miller indices (h k l)
 - $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$
 - a = lattice spacing of unit cell

- X-ray Spectra
 - e⁻ discharge tube (vacuum tube with a large voltage (~35,000V's) applied between two electrodes (cathode and anode (target)))
 - accelerate e⁻ through a vacuum
 - e⁻ 'crash' into anode (target), ejecting bound e⁻ from core shells
 - e⁻ from higher orbitals 'cascade down', releasing high energy photons → x-rays
 - K_α, K_β, L_α, L_β, etc.
 - i.e. K = final shell number of transition (if n=1→K, 2→L, 3→M, 4→N...)
 - i.e. α = Δn of falling electron (1=α, 2=β, 3=γ)
 - Underlying **whale-like shape** from continuous e⁻ deflections → **Bremsstrahlung**
 - Shortest wavelength of Bremsstrahlung curve $\lambda_{swl} = \frac{hc}{eV}$



Lecture 17 – Oct 19: MOSELEY FIT OF X-RAY SPECTRA

Averill pp. 305, 535, 536; Cullity pp. 1E-11E, 19E-22E.

- X-ray spectra data fitted to Rydberg-type equation

$$\bar{\nu} = \mathfrak{R} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \cdot (Z - \sigma)^2$$

- $\bar{\nu} = 1/\lambda =$ inverse frequency
- $\sigma =$ screening factor
 - =1 for K_{α} , and =7.4 for L_{α}
- Results of **Moseley's** work:
 - A plot of $\bar{\nu}$ vs. Z^2 demonstrated a linear relationship
 - Corrected Mendeleev: periodic table should be arranged via Z , and not A (atomic mass number)
 - Placed Lanthanides in periodic table
- Improvements to x-ray spectra apparatus by W. D. Coolidge, MIT alum
 - Lead-shielding
 - Beryllium window
 - Water-cooled anode (target)
 - Heated cathode
 - Better vacuum

Therefore: We can now accurately identify relative amounts of elemental species within a sample!

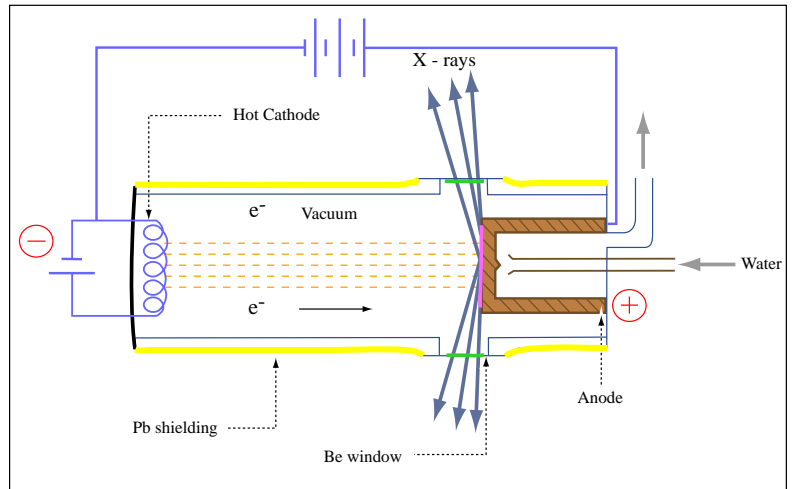


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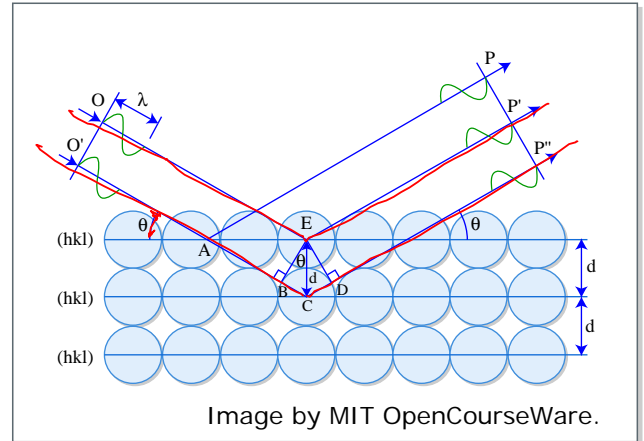
Lecture 18 – Oct 21: PROBING ATOMIC ARRANGEMENT BY X-RAYS, BRAGGS LAW

Shackelford 3-7.

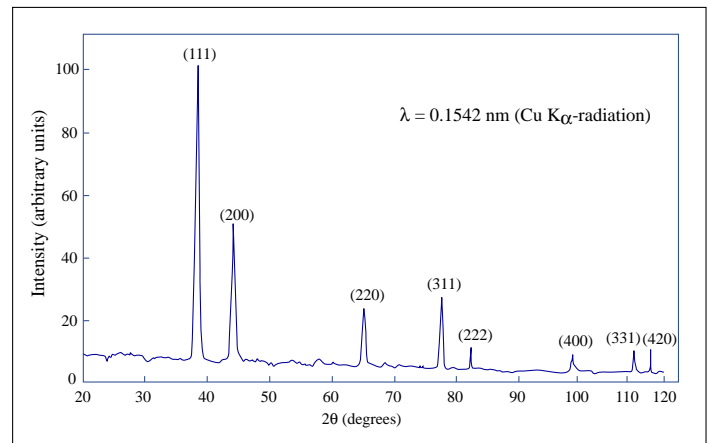
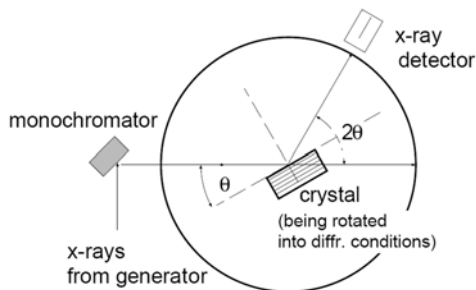
→ See 'lecture notes' for Lecture 18 on steps to determine crystal structure

- **X-Ray Diffraction (XRD) → A means to determine crystal structure!**
 1. Model atoms as mirrors
 2. Apply interference criterion – constructive or destructive
- Parallel monochromatic x-rays (i.e. K_{α} line from a specific target) are sent to sample.
- X-rays reflect off of various planes, constructively or destructively interfering, based on extra distance traveled by ray reflecting off of lower atomic plane.

- $n\lambda = 2d \sin \theta$
 - For 3.091, $n=1$
 - d =interplanar spacing (Lect 16)
- $\frac{\lambda^2}{4a^2} = \frac{\sin^2 \theta}{h^2 + k^2 + l^2} = const$
- Can determine appropriate values of h,k,l , based on θ (handout)
- Can also determine 'a': $a = \frac{\lambda}{\sqrt{2}\sqrt{const}}$
- Determine different crystal types by values of $h^2+k^2+l^2$
 - sc: 1,2,3,4,5,6,8,9 (no 7!)
 - bcc: 2,4,6,8,10,12,14,16 (would appear as 1,2,3,4,5,6,7,8 → there is a 7!)
 - fcc: 3,4,8,11,12... (the first two terms are a $\frac{3}{4}$ ratio, not $\frac{1}{2}$)



- **Two XRD Techniques:**
 1. **Diffractometry** (fixed λ , variable θ)



2. **Laue** (variable λ , fixed θ)
 - Spot pattern → atomic symmetry

Therefore, we can now determine crystal structure!

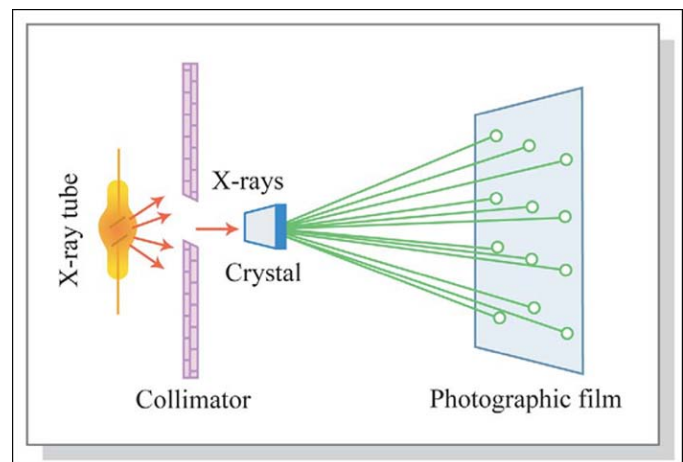


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Lecture 19,20 - Oct 23,26: DEFECTS

o Reading : Averill 12.4; Shackelford 4-1, 4-2, 4-3, 4-4, 5-1.

Point Defects (0-D):

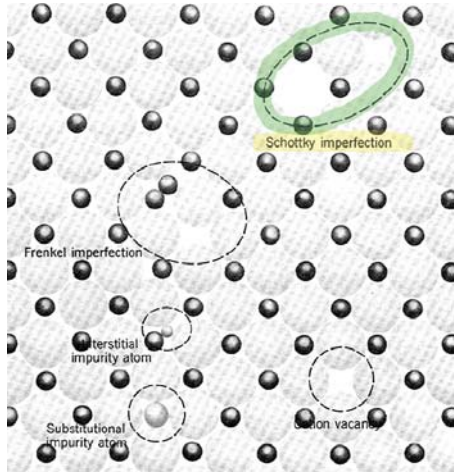
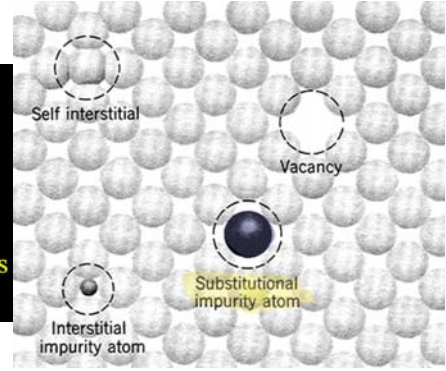
- i) Self interstitial, ii) Interstitial impurity, iii) substitution impurity, iv) vacancy
- Vacancies: i) Schotty, ii) Frenkel, iii) F-center
 - o Should be able to calculate vacancy fraction based on enthalpy of vacancy

**Taxonomy of Defects:
Classify by Dimensionality**

0-dimensional: point defects
1-dimensional: line defects
2-dimensional: interfacial defects
3-dimensional: bulk defects

formation. $f_v = \frac{n_v}{N} = A \cdot \exp\left(-\frac{\Delta H_v}{k_B T}\right)$

- o Also be able to show 'reaction' equation for forming a vacancy.
 (i.e. null $\rightarrow V_{Zr} + 2V_o$)



Line Defect (1-D):

- Edge dislocation – extra half-plane of atoms.
- Crystals deform via. dislocation motion.

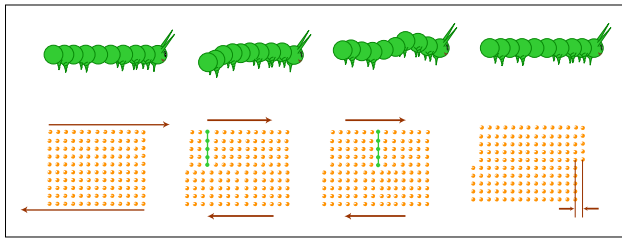
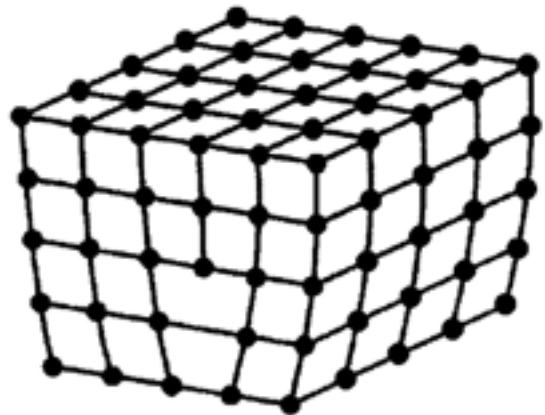


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Interfacial Defects (2-D) - Grain Boundaries, surfaces

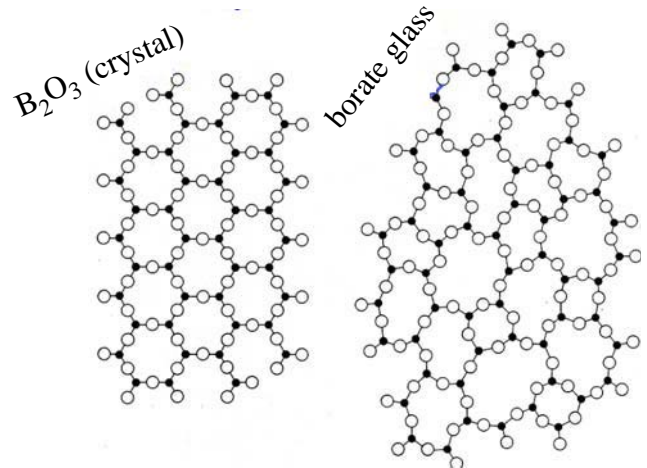
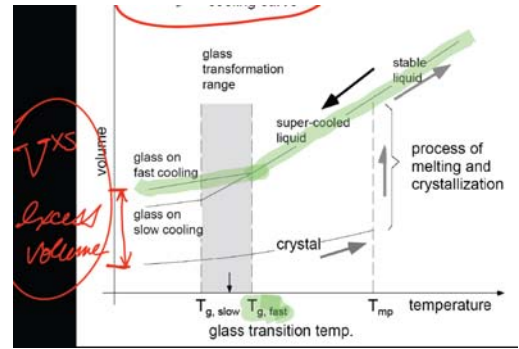
Bulk Defects (3-D) – Amorphous regions in crystal, voids, inclusions, precipitates



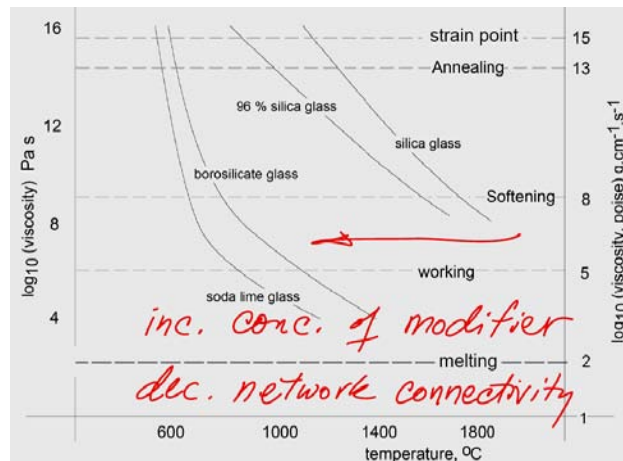
Courtesy of David Roylance. Used with permission.
 Image removed due to copyright restrictions. Please see Fig. 12.16 in Averill, Bruce, and Patricia Eldredge. *Chemistry: Principles, Patterns, and Applications*. San Francisco, CA: Pearson/Benjamin Cummings, 2007. ISBN: 080538039.

Lecture 21 – Oct 30: GLASSES

- Atomistic model of Hooke's law (E vs. r → F vs. r graphs)
- Factors promoting glass formation:
 - (viscosity) x (complexity of xtal structure) x (cooling rate)
 - The larger each of these values, the more likely it is to form a glass instead of a crystal
- Silicate glasses
 - Bridging oxygens, –O–
 - Chemical formula: SiO_2
 - Structural formula: SiO_4^{4-}
- Volume vs. Temperature heating/cooling curves for glasses.
 - Know: excess volume, effect of different cooling rates, T_g , T_m .
- Energy comparison: xstal has lower energy than glass
- Properties of oxide glasses:
 1. Chemically inert
 2. Electrically insulating
 3. Mechanically brittle
 4. Optically transparent
 - → but high melting point → tough to process → add modifiers to lower T_g
- Net work formers: have bridging oxygens, i.e. SiO_2 , B_2O_3 ,
- Network modifiers (lower T_g): ionic bonds → O^{2-} breaks bridging –O– bonds
 - i.e. CaO , Na_2O , Li_2O ...
 - i.e. $\text{CaO} \rightarrow \text{Ca}^{2+} + \text{O}^{2-}$
- Intermediates:
 - A glass that has a cation that makes a different number of oxygen bonds than the majority glass former. It breaks up the network, results in poorer packing, and increases the thermal shock resistance (i.e. Al_2O_3 in a SiO_2 glass)



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Lecture 22,23 – Nov 2, 4: GLASS STRENGTHENING MECHANISMS

- Two assumptions: i) Glasses break by crack formation and propagation, which starts at the surface. ii) Glasses are strong under compression, but fail because their weak under tension. Solution: create internal stresses that place the surface layer under compression, thereby increasing its strength.
 - Thermal treatment → tempering
 - Air jets cool outside of glass faster → larger volume, compressed by slower-cooled internal region → surface under compression yields higher strength
 - $V_{\text{outer}} > V_{\text{bulk}}$
 - Chemical Treatment
 - Ion exchange. A larger ion replaces a smaller ion in the glass (i.e. K^+ (from KCl salt bath) replaced Na^+ from the glass). K^+ is larger → puts a compressive strain on surface region → increases strength

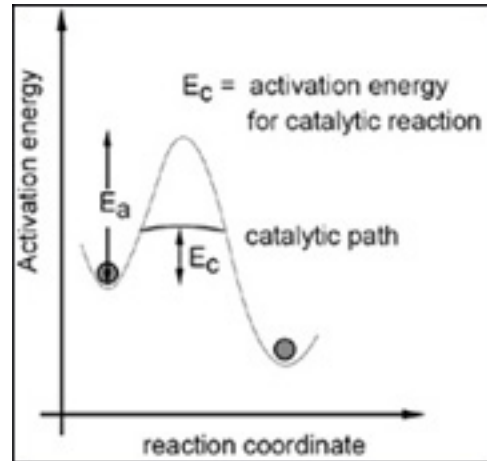
○ **KINETICS:**

- Reaction rates, including nuclear decay.
- Rate of reaction is proportional to concentration of reactant.
- Reaction: $aA + bB \rightarrow cC + dD$
- Rate Equation:

- $r = -\frac{dC}{dt} = kC^n$

- $k = A \exp\left(-\frac{E_a}{k_B T}\right)$

- 'k' is related to Maxwell-Boltzmann distribution of energy → Arrhenius relationship
- Solution depends on value of n (rate of reaction = sum of exponents in reaction equation)
- Solutions to rate equation:
 - $n=1 \rightarrow \ln C = \ln C_o - kt$
 - $n=2 \rightarrow 1/C = 1/C_o + kt$
 - $t_{1/2} = \ln(2) / k$
 - $n=\text{other} \rightarrow \text{plot } \log(r) \text{ vs. } \log(C) \rightarrow \text{slope} = n, \text{ intercept} = \log(k)$



Lecture 24 – Nov 6: DIFFUSION

- Random movement of particles, resulting in a ‘spreading out’ of particles tending towards equal concentration.
- Rate Process “d/dt”
- **Rate at which atoms vibrate. = 10^{13} Hz**
- **Jump Freq = 10^8 Hz → very fast!!**
- Diffusion occurs only if there is a free space to move into (vacancy for self or substitutional diffusion)
- Diffusion (D) is proportional to the concentration of free sites. D also increases with a looser packed atomic structure.
 - i.e. # vacancies, or other defects, such as grain boundaries
- Surface, grain boundary, and volume diffusion occur at different rates → proportional to # of free sites!

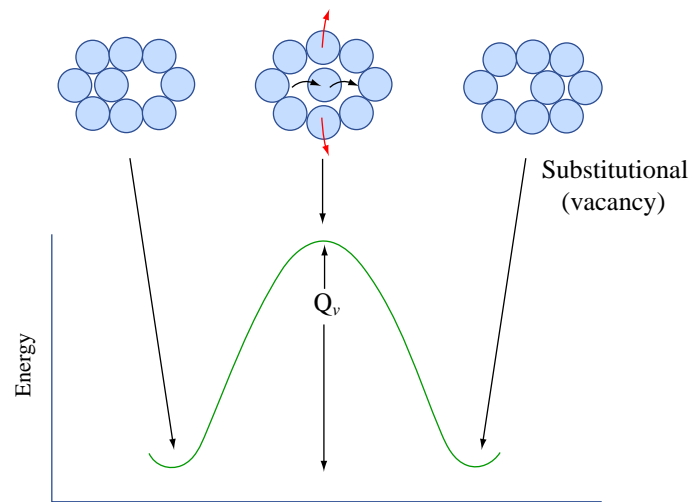


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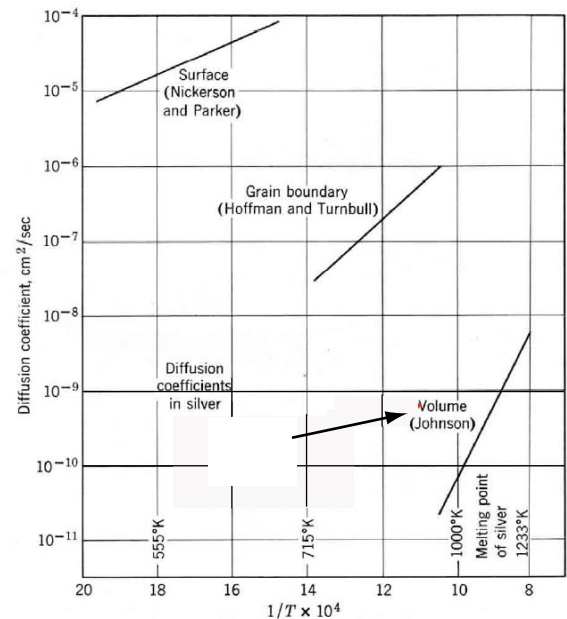
- **Fick’s First Law (FFL)**
 - Flux is proportional to the concentration gradient
 - $J = -D \frac{dC}{dx}$
 - → Use if in steady-state
 - In steady-state, this results in a linear concentration gradient (i.e. straight line) through a material
 - D=diffusivity, units = cm²/s,
 - $D = D_o \exp\left(-\frac{Q}{RT}\right)$, $R = k_B N_A$
 - Maxwell-Boltzmann distribution again

- **Fick’s Second Law (FSL)**

- Introduce time-varying concentration profile.
- $\frac{dC}{dt} = -D \frac{d^2C}{dx^2}$, → one solution is:

$$\frac{C(x,t) - C_s}{C_o - C_s} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

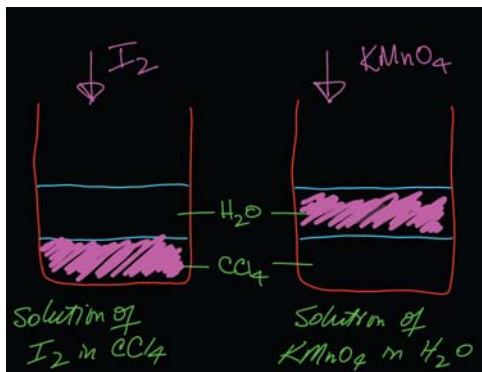
- Note: solution is for semi-infinite system with constant surface concentration
- erf = special function. erf (0) = 0, erf(infinity) = 1, erf (x) ~ x for 0 < x < 0.6
- Approximate diffusion distance (distance an impurity will dissolve into a sample to an appreciable level over a given time): $x \approx \sqrt{Dt}$



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Lecture 25 – Nov 9: SOLUTIONS

- “Like Dissolves Like”



taxonomy of colloids			
dispersed phase	dispersion medium	name	example
solid	liquid	sol	jelly
liquid	liquid	emulsion	milk, mayo
gas	liquid	foam	meringue, whipped cream
solid	gas	aerosol	soot
liquid	gas	aerosol	fog, hair spray
solid	solid	solid sol	cranberry glass
liquid	solid	solid emulsion	butter
gas	solid	solid foam	pumice

- Measure of solubility:
 - Molar (M) = (moles solute) / (liters of solution – both solute and solvent)
- Soluble if $C_{\text{solute}} > 0.1 \text{ M}$, insoluble if $C_{\text{solute}} < 0.001 \text{ M}$
- Equilibrium Constant, K: $aA + bB \rightleftharpoons cC + dD$
 - $K = \frac{[A]^a[B]^b}{[C]^c[D]^d}$
 - Most other “K’s” are based on the form of this ‘K’, but exclude one term.
- Solubility Product $A_aB_b \rightarrow aA^{b+} + bB^{a-}$ (i.e. $\text{MgCl}_2 \rightarrow \text{Mg}^{2+} + 2\text{Cl}^-$)
 - Coefficients become the exponents in K_{sp} eqn.
 - $K_{\text{sp}} = [A^{b+}]^a[B^{a-}]^b = K[A_aB_b]$
- Common Ion Effect:
 - If $[B^{a-}]$ added via another compound, K_{sp} must remain the same, therefore, $[A^{b+}]$ must decrease.

Lecture 26 – Nov 13: ACIDS AND BASES

- $\text{pH} = -\log_{10}[\text{H}^+]$,
- $\text{pOH} = -\log_{10}[\text{OH}^-]$,
- $\text{pH} + \text{pOH} = 14$

Definitions:

	<u>Arrhenius</u>	<u>Bronsted-Lowry</u>	<u>Lewis</u>
Acid:	p^+ donor	p^+ donor	e^- pair acceptor
Base:	OH^- donor	p^+ acceptor	e^- pair donor

- General Rxn: $\text{HA} + \text{B} \rightarrow \text{BH}^+ + \text{A}^-$
 - Conjugate acid-base pairs
 - HA & A^-
 - B & BH^+
 - For an acid, B can equal $[\text{H}_2\text{O}]$
- K_a and K_b describe the degree of dissociation of an acid/base, respectively.
- In aqueous systems, with $\text{B} = [\text{H}_2\text{O}]$:
 - $K_a = K [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}]$
- Amphiprotic: can act as an acid or a base (i.e. H_2O)
- Strong acids \rightarrow complete dissociation ($K_a \gg 1$)

To solve some of these problems,

1. write out reaction equation
2. set up chart: initial, change, and final concentrations, with 'x' as the change the concentration of the base or acid.
3. solve for x and K_a or K_b are related, using formula above.

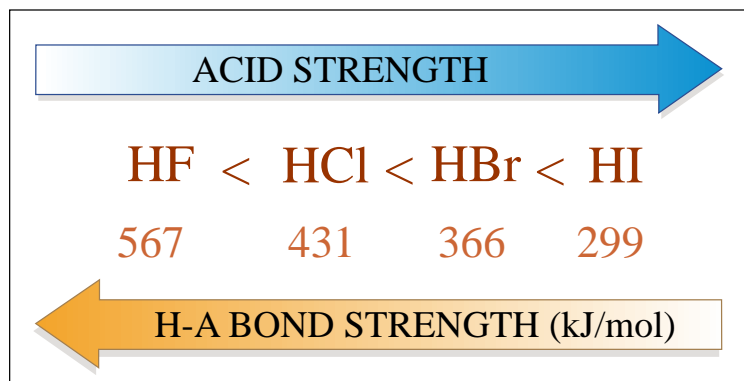


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Lecture 27 – Nov 16: ORGANIC CHEMISTRY

- Naming Nomenclature
- Prefix (# of carbons in chain)
 - 1 = meth
 - 2 = eth
 - 3 = prop
 - 4 = but
 - 5 = pent
 - 6 = hex
 - 7 = hept
 - 8 = oct
- Add '-ane' or '-ene', or '-yne' based on bond type.
- Isomer: same chemical formula, but different configuration
 - **Constitutional Isomers**: Same chemical formula, but atoms bonded together in a different order (different side-groups)
 - (i.e butane vs. 2-methyl propane)
 - **Stereoisomers**: Same chemical formula, same side-groups, but different configuration (i.e. left-hand vs. right-hand). cis- vs. trans-
- Aromatic compounds:
 - Double and single bonds 'share' delocalized π -bond
 - e^- conductivity.

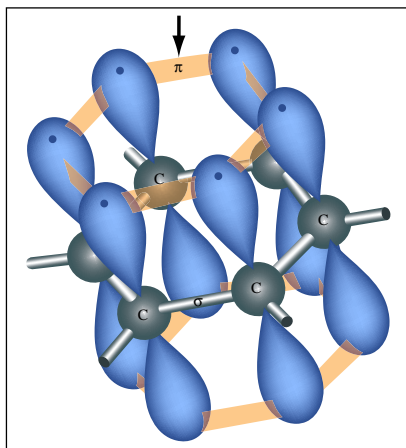


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taxonomy of hydrocarbons		
alkanes	alkenes	alkynes
$sp^3 -$	$sp^2 =$	$sp \equiv$
$\approx sp^3 \sigma$	$\approx sp^2 \sigma, \pi$	$\approx sp \sigma, \pi$
sat ^d	unsat ^d	unsat ^d
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
C_2H_6 ethane	C_2H_4 ethene ethylene	C_2H_2 ethyne acetylene
$-C_2H_5$ ethyl	$-C_2H_3$ vinyl	

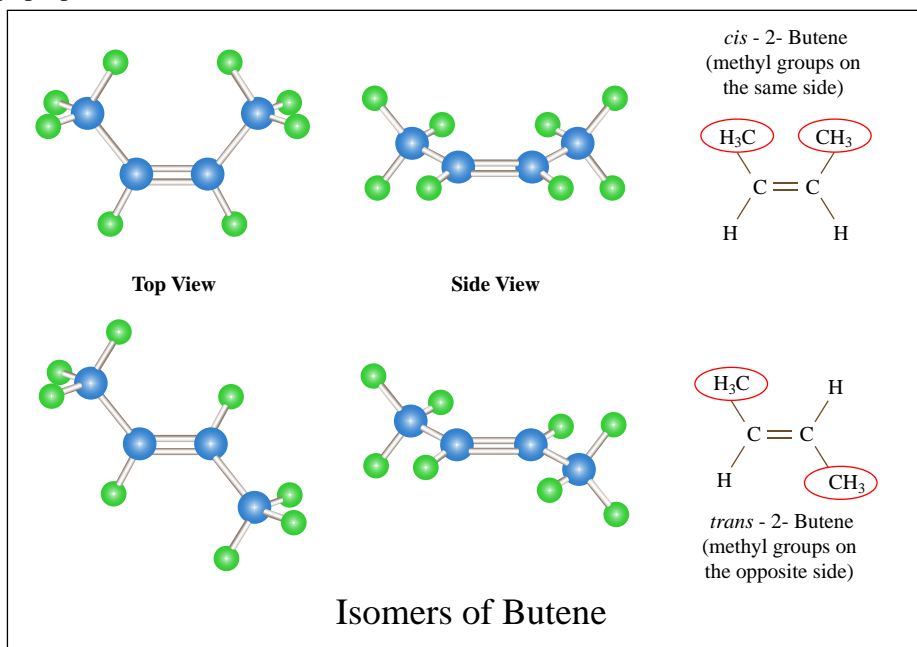


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Lecture 28 – Nov 18: POLYMERS I

- Applied organic chem => polymers
- Polymers are macromolecules – long chains of molecules with repeating chemical structure. Poly = “many” mer = “repeat unit”
 - Can be x-talline, amorphous, or a combination of both → XRD can verify this

Tailoring Molecular Architecture:

I. Composition:

- Random copolymer (AABBBABBAAA...)
- Regular copolymer (ABABA...)
- Block copolymer (AAAAAABBBBBBB...)
- Graft copolymer (BBBBBBBBB... with AAA...and S side chains)

II. Tacticity

- Polymer can also be classified by side-group orientation
 - atactic, syndiotactic, isotactic

III. Backbone:

- Linear chain
- Branched chain: harder to xtalize
- Crosslinked: Enabled by sulfur. Rubbery!

Synthesis:

- Addition polymerization
 - Need free radicals and double bonds to carry synthesis
- Condensation polymerization
 - Formed by rxns between the start and ends of mers
 - Polymer loses mass when synthesized (e.g. the condensation)

Thermoplastic: only Van der Waals acting between neighboring polymers, liquefies upon melting and are easy to recycle.

Thermoset: caused by the cross linking of polymers with disulfide bonds. There are covalent bonds between polymers, so the material strengthens but as a result is extremely hard to recycle.

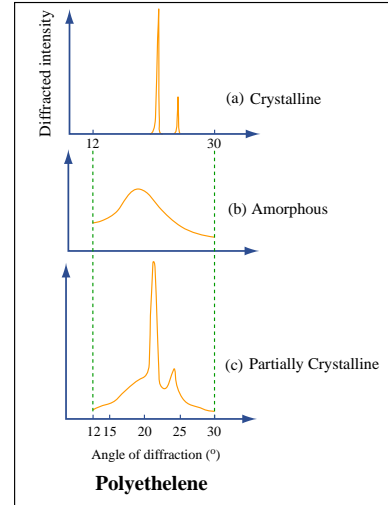
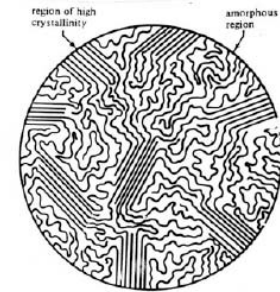


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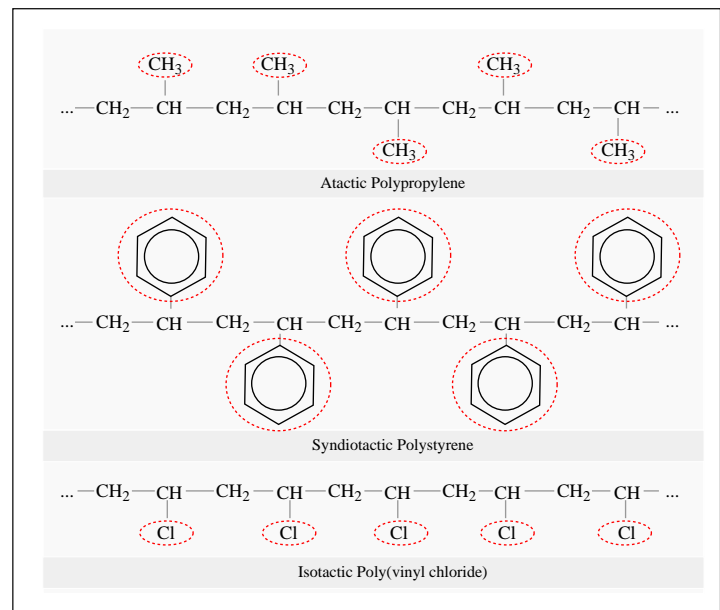


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Lecture 29 – Nov 20: POLYMERS II:

Polymer Synthesis:

1. Addition Polymerization
 - Uses an initiator (R radical) to break a double or triple C-C bond (of a mer unit)
 - i.e. $R^* + CH_n=CH_n \rightarrow R-CH_n-CH_n^*$
 - growth by subsequent mer attachment
2. Condensation Polymerization
 - Uses the reaction between an H and an OH on two separate molecules to form an amide or peptide both, and releasing H_2O
 - i.e. $R_1H + R_2OH \rightarrow R_1-R_2 + H_2O$
 - mass polymer < Sum (mass of reactants)

Plastics can have zones of random configuration and zones of crystallization, which can make the material stronger and denser.

Factors favoring crystallization:

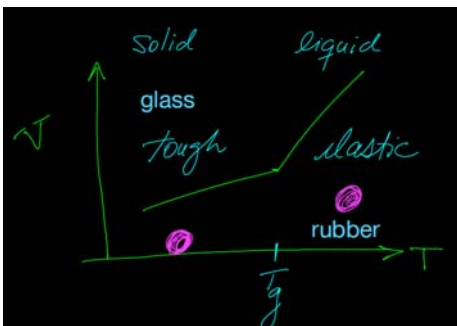
1. composition - homopolymer over copolymer)
2. tacticity – isotactic attractive
3. conformation – linear over branched

Properties of polymers

- e⁻ insulating, transparent to visible light, low density, solid at room temp.

Recall:

- Nylon pull-out video
- glass transition temperature of different polymers



Lecture 30 – Nov 25: BIOCHEMISTRY:

Amino Acids:

- Contain an amine group, carboxylic acid group, and a side chain, R.
- R can be anything. But in our bodies, there are just 20 different R's, giving rise to twenty different amino acids
- R can be 1) nonpolar, 2) polar, 3) hydrophilic + acidic, 4) hydrophilic + basic
- 3) and 4) can be 'titratable' (i.e. can accept or give off a H⁺, depending on the local pH)

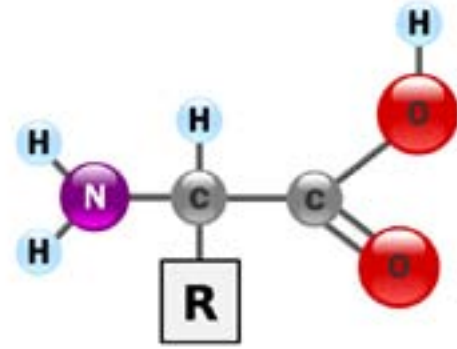


Image by Yassine Mrabet on Wikipedia.

Amino acids are usually Chiral (i.e. Left (L) or Right (D) handedness → L- or D-enantiomers)

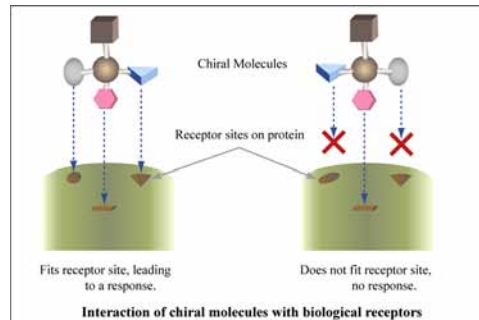
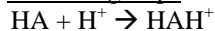


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Amino acids are Zwitterions:

- In water at neutral pH, COOH group gives up an H⁺, and the amine group accepts an H⁺, causing the molecule to be net neutral, but have local +ive and -ive charges
- At high pH (low [H⁺]), H⁺ are stripped off of NH₃⁺
- At low pH (high [H⁺]), H⁺ are added to COO⁻

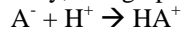
For titratable groups on the amino acid (i.e. a group that can gain or lose a H⁺):



$$K_1 = \frac{[H^+][HA]}{[A^-]} \quad (K \text{ is basically the equilibrium constant})$$

$$pK_1 = pH + \log_{10}([HAH^+]/[HA])$$

Similarly, at high pH



$$K_2 = \frac{[H^+][A^-]}{[HA]} \quad (K \text{ is basically the equilibrium constant})$$

$$pK_1 = pH + \log_{10}([HA]/[A^-])$$

pI = isoelectric point.

When net charge of all molecule is zero (i.e. [HA] >> [HAH⁺],[A⁻])

It happens ½ way between pK₁ and pK₂.

$$pI = (pK_1 + pK_2)/2$$

Lecture 31 – Nov 30: PROTEIN STRUCTURE:

Plot of pH as a function of 'extent of reaction':

"Equivalents of OH⁻" is the same as the negative of [H⁺]. i.e. the number of [H⁺] in the system (both free, and bound to the Zwitterion) increases from right to left.

Gel Electrophoresis:

Apply a voltage across a gel tube with varying pH. Amino acids (zwitterions) introduced at one end. Zwitterions are propelled to migrate in the electric field as long as they have charge. When they reach the pH equivalent to their pI, they no longer have net charge, so they stop. This allows researchers to measure the pI of an amino acid / zwitterion.

Proteins formed by condensation reaction between amides, forming polyamides.

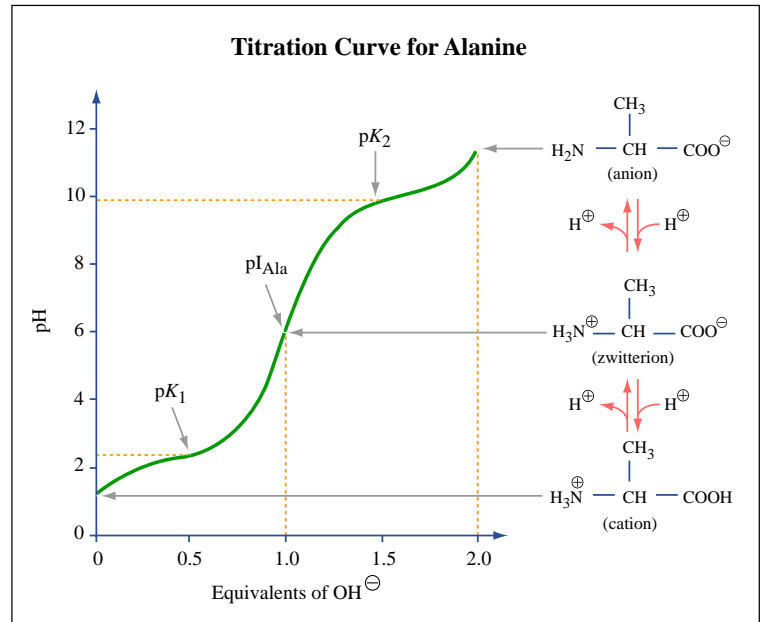


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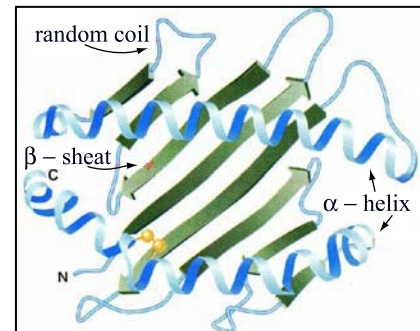
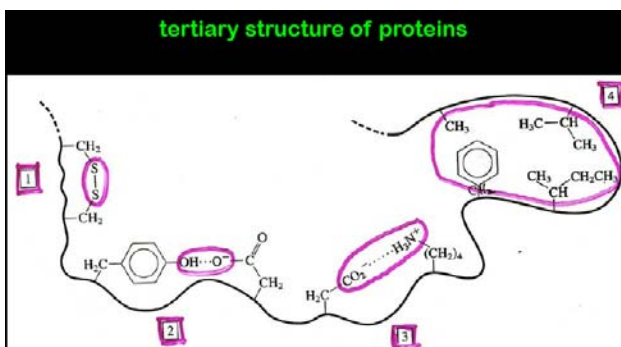
TABLE P.2 Common Condensation Polymers

Structure	Trade Name Common Name
$\text{(-NH-(CH}_2\text{)}_6\text{-NH-C(=O)-(CH}_2\text{)}_4\text{-C(=O)-)}_n$ <p><i>Handwritten notes:</i> amino end, amide bond, carboxylic acid end</p>	Nylon 6, 6

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Tertiary structure of proteins ("random" coils):

- "random" structure determined by secondary bonding, i.e. 1) disulfide bonds, 2) H-bonding, 3) columbic, 4) hydrophobic regions



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Lecture 32 – Dec 2: LIPIDS, NUCLEIC ACIDS, DNA

Proteins can be denatured (i.e. breaking secondary bonding) by changes in:

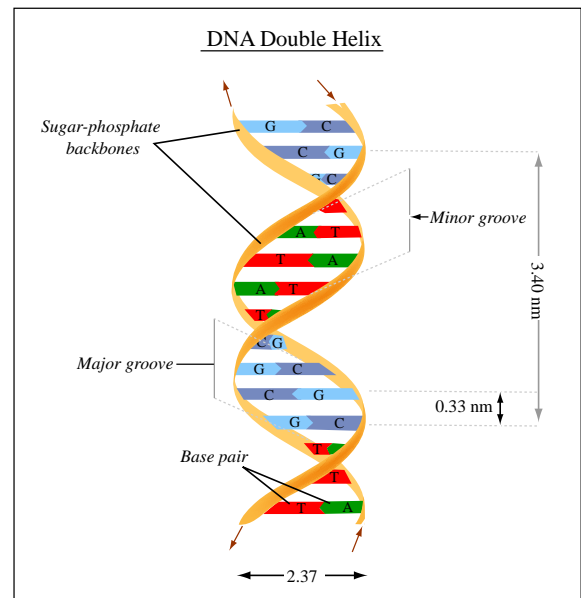
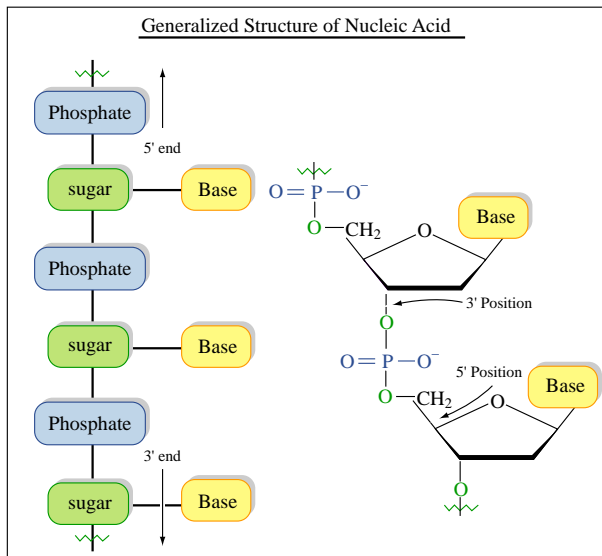
- 1) Temperature, 2) pH, 3) oxidizing/reducing agents to create/destroy -S-S- bonds), 4) detergents

Lipids: defined by their properties – soluble in solvents of low polarity – includes fats, oils, cholesterol, hormones.

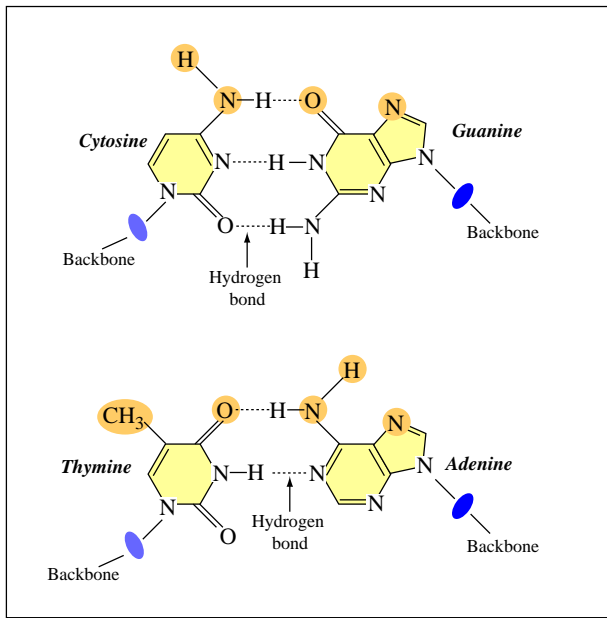
- Some have a hydrophilic head and a hydrophilic tail (amphipathic molecules)
- can arrange in a lipid bilayer in a polar solvent → Cell wall!

Nucleic acids

- Building block of nucleotides → DNA
- DNA contain sugar (amine link) and a phosphate backbone, with one of four of five amine groups that make up the ‘code’ (AGCU for RNA, and AGCT for DNA)
- A pairs with T (2 H bonds), C pairs with G (3 H bonds). Spacing is important.
- These chains makeup a double-helix structure → DNA



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Lecture 33 – Dec 4: PHASE DIAGRAMS, ONE COMPONENT - UNARY

- Triple point is where the three lines meet, a region where three phases coexist in equilibrium
- Slope of solid/liquid interface (2 phase region) characterized the density of the material in either phase
- Super critical fluid is a one phase regime
- “Normal” conditions means 1 atm of pressure

more examples

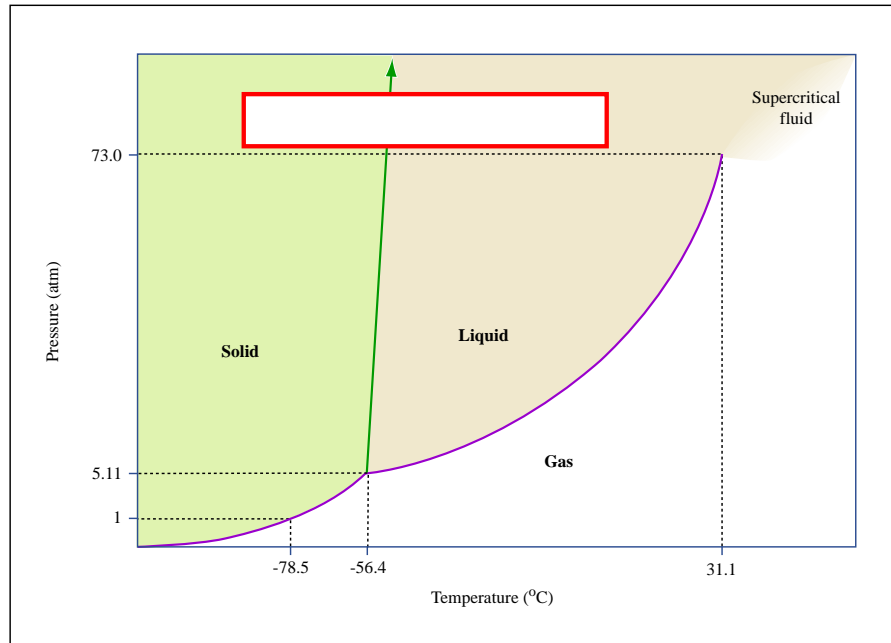
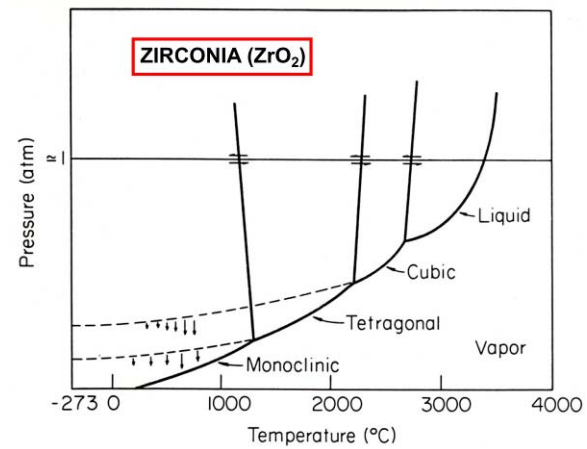
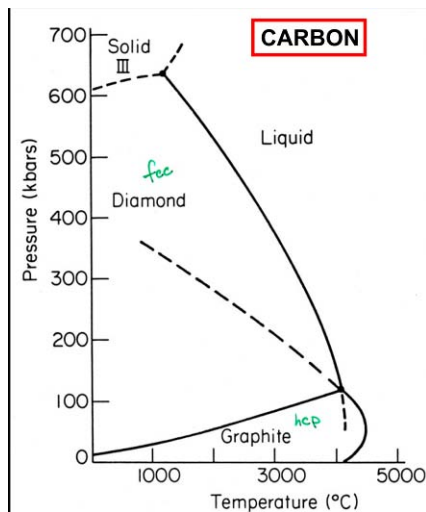


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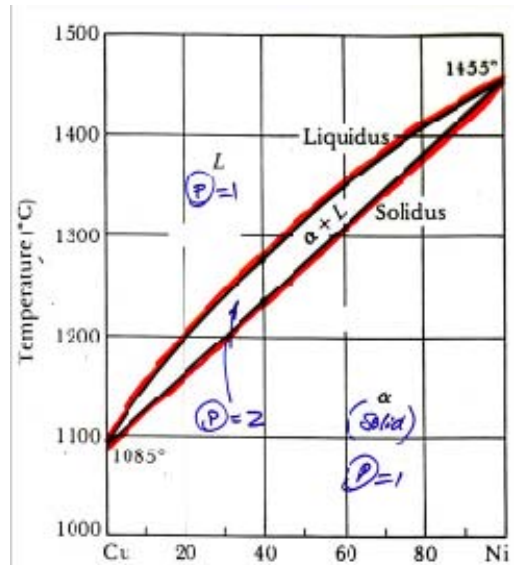
Source: Bergeron, C., and S. Risbud. *Introduction to Phase Equilibria in Ceramics*. American Ceramic Society, 1984. Reprinted with permission of The American Ceramic Society, www.ceramics.org. Some rights reserved.

Lecture 34 – Dec 7: PHASE DIAGRAMS – BINARY – LENTICULAR/IMMISCIBILITY

○ Sadoway's system classification

○ Type 1

- Complete solubility as solids and liquids
- Isomorphism – lens shape
- Properties include:
 - Identical crystal structures
 - Similar atomic volumes
 - Small electronegativity differences
- When $(c) > 1$, impossible to move from one single phase field to another single phase field
- **Liquidus:** lowest temperature at which all liquid is stable
- **Solidus:** highest temperature at which all solids are stable



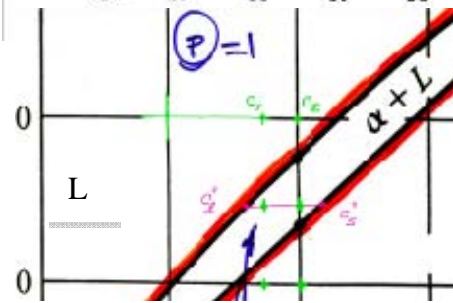
○ LEVER RULE

- $(P) = 2$
- Used to compute percentages of the relevant phases in equilibrium
- For the example on the right:
 - Held at c_2 (you can do the same for c_1)

$$\% \text{liquid} = \frac{c_s^* - c_2}{c_s^* - c_l^*}$$

$$\% \text{solid} = \frac{c_2 - c_l^*}{c_s^* - c_l^*}$$

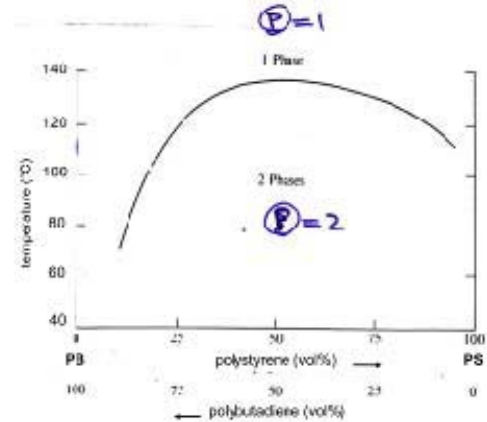
- c_l^* is the equilibrium concentration in the liquid phase
- c_s^* is the equilibrium concentration in the solid phase



○ Type 2

- partial or limited solubility of both components in each other
- no change of state – always solid or always liquid
- generates “Synclinal” coexistence curve

Polystyrene - Polybutadiene phase diagram

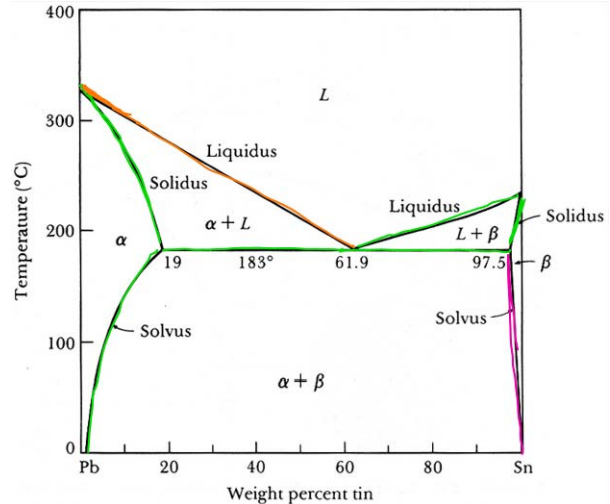


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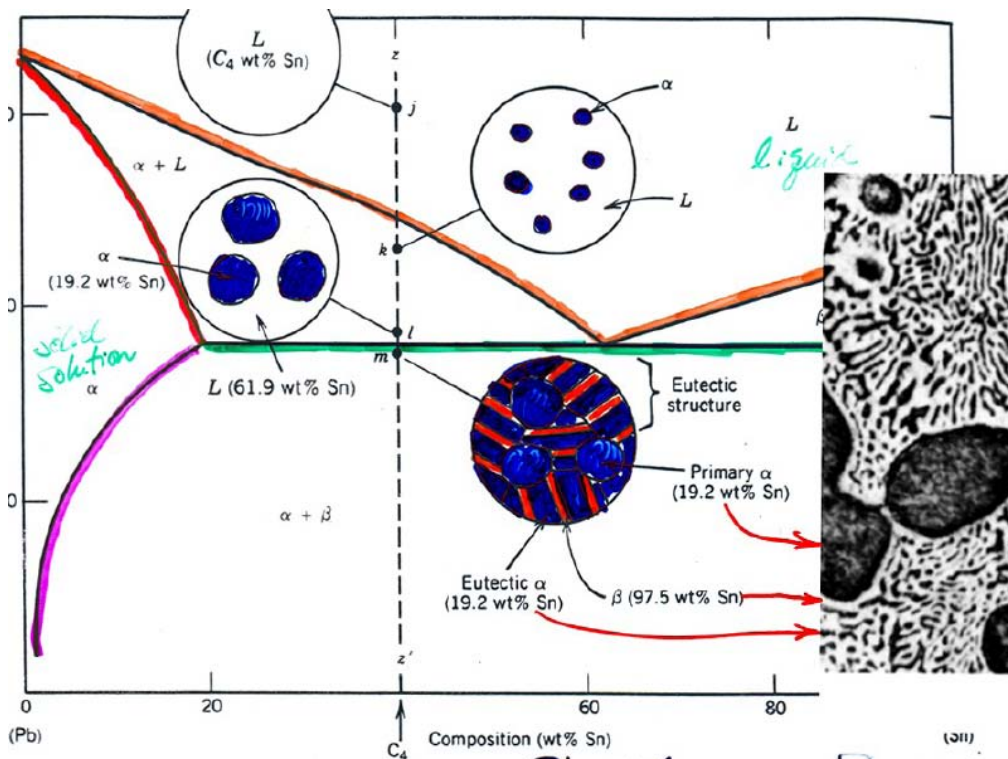
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Lecture 35 – Dec 9: PHASE DIAGRAMS – BINARY – LIMITED SOLUBILITY

- Type 3
 - Partial solubility of A and B
 - Change of state
 - “hybrid between lens and syncline”
 - Freezing point depression of both components
 - **Eutectic:** composition and temperature where three phases coexist in equilibrium.
 - **APPLY LEVER RULE TO TWO PHASE REGIONS!!!**
 - $\alpha + \beta$, $\alpha + L$, $L + \beta$
 - Top example:
 - α is a Pb-rich phase
 - β is a Sn-rich phase
 - You can tell a lot about the history of a material by looking at the microstructure



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 Source: Source: Fig. 10-6 in Askeland, Donald R. *The Science and Engineering of Materials*. 2nd ed. Boston, MA: PWS-Kent, 1989.



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