

## Review Outline Cumulative Chemistry 1B-02, Fall 2016

### ----- Chapter 12 -----

#### I. Experiments and findings related to origin of quantum mechanics

- A. Planck:  $E=h\nu$ ,  $\lambda\nu=c$
- B. Davisson-Germer (electrons diffract; behave as waves)
- C. DeBroglie  $p\lambda=h$
- D. Photoelectric effect
- E. Uncertainty Principle ( $m\Delta u$ ) ( $\Delta x$ )  $\geq h/4\pi$
- F. Meaning of the "electron wave"
- G. Bohr and Rydberg and hydrogen atom  
 $[E=-2.18 \times 10^{-18} \text{ J } (1/n^2)]$   
 $[\Delta E=h\nu=hc/\lambda= -2.18 \times 10^{-18} \text{ J } (1/n_1^2 - 1/n_2^2) ] (n_2 > n_1)$

#### II. Quantum mechanics of the hydrogen atom

- A. Wavefunction for an electron ( $\Psi$ ), probability ( $\Psi^2$ ), and radial probability ( $4\pi r^2\Psi^2$ )
- B. Quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$  of allowed orbitals
  1.  $n = 1, 2, 3, \dots$
  2.  $\ell = 0, 1, 2, \dots (n-1)$  [s, p, d, f, ...]
  3.  $m_\ell = -\ell \dots +\ell$  [( $2\ell + 1$ ) components (values of  $m_\ell$ ) for each  $\ell$ ]
- C. Pictures of the orbitals and nodes
  1. ( $n-\ell-1$ ) radial nodes
  2.  $\ell$  angular nodes
  3. s,  $p_x$ ,  $p_y$ ,  $p_z$ ,  $d_{z^2}$ ,  $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$
- D. Meaning of the  $n$ ,  $\ell$ ,  $m_\ell$  quantum numbers
  1.  $n$ - energy, radial nodes, average distance of electron from nucleus
  2.  $\ell$ - shape of orbital
  3.  $m_\ell$  - orientation of orbital

#### III. Many-electron atoms and ions

- A. Stern-Gerlach and electron spin ( $m_s = +1/2 \uparrow$ ,  $m_s = -1/2 \downarrow$ )
- B. Pauli exclusion principle
- C.  $Z_{\text{eff}}$  and shielding by inner electrons and electrons in same shell
- D.  $E \approx -2.18 \times 10^{-18} \text{ J } (Z_{\text{eff}}^2/n^2)$
- E.  $r \approx (0.529 \times 10^{-10} \text{ m}) (n^2/Z_{\text{eff}})$
- F.  $Z_{\text{eff}}$  of 2s  $>$   $Z_{\text{eff}}$  of 2p due to penetration
- G.  $E_{2s} < E_{2p}$
- H.  $E_{3s} < E_{3p} < E_{3d}$
- I. Mnemonic diagram for energy ordering in neutral atoms (e.g.  $E_{4s} < E_{3d}$ )
- J. In transition metal cations  $E_{3d} < E_{4s}$  ( $Z_{\text{eff}}$  vs  $n$ )
- K. Aufbau principle, Hund's Rule, and atomic configurations
- L. Ground, excited, and not allowed configurations

**To Here Midterm #1**

#### IV. Periodic properties of atoms

- A.  $Z_{\text{eff}}$  increases as one goes across period
- B.  $n$  increases as one goes down a group
- C.  $E \approx -2.18 \times 10^{-18} \text{ J } (Z_{\text{eff}}^2/n^2)$       $r \approx (0.529 \times 10^{-10} \text{ m}) (n^2/Z_{\text{eff}})$
- D. Concepts of ionization energy (IE) and electron affinity (EA)
- E. IE increases across a period, decreases down a group
- F. Atomic radius decreases across a period, increases down a group
- G. EA (magnitude) increases across a period (until inert gasses) and decreases down a group
- H.  $Z_{\text{eff}}$  for positive and negative ions, relative size and IE of positive and negative ions
- I. Higher ionization energies
  - 1.  $\text{IE}_1 < \text{IE}_2 < \text{IE}_3 \dots$
  - 2. big jumps in  $\text{IE}_x$  when removing electrons from next inner shell (how to use configurations of ions to rationalize successive IE's)
- J. Metals and nonmetals in periodic table

----- Chapter 13 -----

#### V. General considerations regarding bonding in molecules

- A. G.N. Lewis and the origin of the octet argument
- B. Electronegativity and periodic trends in electronegativity (metallic and nonmetallic elements)
- C. What types of atoms form ionic, covalent, or metallic compounds
- D. Ionic compounds
  - 1. Which elements form ionic compounds
  - 2. Molecular formulas for ionic compounds based on periodic table [know polyatomic anions]
  - 3. Lattice energy and charge and size (distance) effects on trends in lattice energy
  - 4. Properties of ionic compounds [high boiling and melting; 'crack' or fracture; conduct electricity in molten (liquid) or in solution]
- E. Covalent compounds [strong intramolecular bond, weaker intermolecular ; low boiling and melting points; poor conductors]
- F. Polar bonds and electronegativity
- G. Metallic bonding [moderate melting points; malleable; conduct electricity]

#### VI. Classical theories of chemical bonding and geometry

- A. Lewis electron dot structures
  - 1. Octets
  - 2. Lone pairs
  - 3. Multiple bonds
  - 4. Resonance structures
  - 5. Exceptions (reason why some atoms can form 10, 12, 14 electron shells)
  - 6. Formal charge from Lewis structures
  - 7. Bond energy and bond length
- B. Valence State Electron Pair Repulsion theory (VSEPR)
  - 1. Basic concepts (how electron group arrangement is related to electronic geometry and molecular shape)
  - 2. How to determine number of electron groups (steric number, SN)

3. Arrangement of electron groups (electronic geometry) based on SN
4. Molecular shape (i.e. molecular geometry) based on electronic geometry and placement of lone pairs
5. Various molecular shapes and bond angles and effect of lone pairs on bond angles
6. Dipole moments in polyatomic molecules

----- Chapter14 -----

**VII. Quantum mechanics of covalent bonding**

- A. Constructive interference of a.o.s to gives bonding molecular orbital
  1. Bonding m.o. has lower energy than energy of constituent a.o.s
  2. Bonding mo gives larger electron density in region between nuclei than would the sum of noninteracting atomic orbitals
- B. Destructive interference of a.o.s gives antibonding molecular orbital
  1. Antibonding m.o. has higher energy than energy of constituent a.o.s
  2. Antibonding mo gives smaller electron density in region between nuclei than would the sum of noninteracting atomic orbitals (has a node in bonding region)
- C.  $\sigma$  and  $\pi$  m.o.s

**VIII. Molecular orbitals for diatomic molecular orbitals**

- A. General rules for when a.o.s combine to for m.o.s
  1. A.O.s must have similar energies
  2. A.O.s must have nonzero overlap; must be able to have net constructive or destructive interference
  3. Identification of "pictures" of m.o.s
- B. M.O.s and energy ordering for 2<sup>nd</sup> row homonuclear diatomics
  1. Simple scheme:  
 $\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}, \sigma_{2p}, \pi_{2p}, \pi^*_{2p}, \sigma^*_{2p}$  ; applies to O<sub>2</sub> , F<sub>2</sub>
  2. Complex scheme with 2s $\leftrightarrow$ 2p mixing:  
 $\sigma_{1s}, \sigma^*_{1s}, \sigma_{2s}, \sigma^*_{2s}, \pi_{2p}, \sigma_{2p}, \pi^*_{2p}, \sigma^*_{2p}$  ; applies to B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>
- C. Aufbau principle and molecular properties for homonuclear diatomics and ions
  1. Write and/or identify ground, excited, impossible molecular orbital configurations
  2. Bond order, bond energy, and stability of molecule
  3. Unpaired electrons and paramagnetism or diamagnetism
  4. Know how bond order is related to vibrational frequency
- D. Additional considerations for heteronuclear diatomics  
Same general principles as for homonuclear diatomics (see IX .A. above) but:
  1. Differing a.o.'s on two atoms may have similar energies (e.g. H1s and F2p in HF)
  2. A.O.s do not contribute equally
    - a. Lower energy a.o. contributes more to bonding m.o.
    - b. Higher energy a.o. contributes more to antibonding m.o.
    - c. Polar bonds arise from this unequal mixing

**To Here Midterm #2**

### IX. Bonding in polyatomic molecules

- a. Energy costs and gains for hybridization
- b. Pictures of hybridized orbitals
- c. Types of hybrids [type, number of hybrids, geometry, number of unhybridized p-orbitals]
- d. [ $sp^3$ , four, tetrahedral, none]
- e. [ $sp^2$ , three, trigonal planar, one]
- f. [ $sp$ , two, linear, two]
- g. For a molecule be able to:
- h. Identify hybrids (or nonhybridization) for each atom
- i. Identify hybrids or a.o.s involved in formation of bonds (including double and triple bonds)
- j. Identify hybrids or a.o.s used for lone pairs
- k. Identify geometry and/or bond angles around an atom
- l. Cases where atoms in a molecule remain unhybridized (e.g.  $H_2S$ ,  $PH_3$ )
- m. (non) Rotation around single and double bonds and geometric isomers
- n. Delocalized molecular orbitals
- o. Quantum mechanical (best!) way to describe molecules with several resonance structures
- p. Conjugated pi-electrons

### X. Transition metal coordination complexes

- A. Coordinate covalent bond
  1. Central metal ion
  2. Ligands
- B. Structural features of ligands
  1. Lone pairs
  2. Ability to form 5- 6-member rings in multi-dentate ligands
- C. Common mono-, bi-, and polydentate ligands
- D. Aspects of coordination chemistry accounting (given coordination number)
  1. Determining charge on complex
  2. Determining number of ligands
  3. Determining charge on metal ion
  4. Determining number of d electrons
- E. Basic aspects of color appearance and magnetic properties of transition metal complexes
- F. Crystal field theory of octahedral transition metal complexes
  1. Why ligands in octahedral geometry cause the metal's d-orbitals to have two differing energy levels ( $t_{2g}$  and  $e_g$ );  $\Delta_o$
  2. How to distribute metal's d-electrons among the  $t_{2g}$  and  $e_g$  levels for strong- and weak-field ligands (be able to write configurations for d-electrons in an octahedral complex)
  3. Spectrochemical series (know  $CN^-$  and  $CO$  are strong-field; know  $Cl^-$ ,  $F^-$ ,  $Br^-$ ,  $I^-$  are weak-field; be able to utilize information when told a ligand is strong-field or weak-field in specific cases.
  4. Predicting diamagnetism or paramagnetism of transition metal complexes
  5. Problems involving the color of transition metal complexes
- G. Hemoglobin is important example of coordination complexes as biologically important molecules

**XI. Spectroscopy (see handout)**

- A. Energy order and names of radiation of various wavelengths/frequencies
- B. For each spectral region
  - 1. Type (name) of spectroscopy
  - 2. Nature of excitation in atoms/molecules caused by photons
  - 3. Information available from spectroscopy at these wavelengths
- C. Ordering of bonding and antibonding energy levels in polyatomic molecules ( $\sigma$ ,  $\pi \approx n$ ,  $\pi^*$ ,  $\sigma^*$ )
- D. What types of molecules absorb visible wavelengths (are colored)
- E. Information available from IR and NMR spectroscopy (identifying molecules by IR and NMR)
- F. Vocabulary
  - 1. Fluorescence
  - 2. Phosphorescence
  - 3. Radiationless decay (nonradiative transition)
  - 4. Chemiluminescence

----- Chapter15 -----

**XII. Chemical Kinetics**

- A. Differential rates
  - 1. The form of the rate equation in terms of the rate constant and the orders of the each reactant concentration.
  - 2. Evaluating the order in each reactant from initial rate data
  - 3. Evaluating the rate constant
- B. Integrated rate expressions
  - 1. The difference between differential and integrated rate expressions
  - 2. Integrated expressions for 0<sup>th</sup>, 1<sup>st</sup>, and 2<sup>nd</sup> order rates (relevant equations will be provided on exam)
  - 3. Using integrated expressions and plots of reactant concentration and time to identify order of reaction
- C. Definition of half-life and  $t_{1/2}$  for first-order reaction
- D. Reaction mechanisms
  - 1. Elementary reactions
    - a. Molecularity
    - b. Rate expressions
  - 2. Overall rate for slow step followed by rapid reaction
- E. Reaction energy profile
  - 1. Reaction coordinate
  - 2. Activated transition state
  - 3. Stable intermediate
  - 4. Energies of reactants and products
  - 5. Forward activation energy
  - 6. Reverse activation energy

- F. Arrhenius expression
  - 1. Pre-exponential factor
  - 2. Temperature dependence of rate constant
- G. Catalysis
  - 1. Enzymatic, surface (heterogeneous), homogeneous
  - 2. Effect of catalysis on  $E_a$

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