Chemical Periodicity

I. Electronic Structure of the Atom
   A. Definition
      1. Number and distribution of electrons about the nucleus
      2. Determines the number and type of bonds an atom can form; this will then determine
         the structure and reactivity of the molecules/ ions/ covalent lattice solids
   B. Atomic emission spectra
      1. The initial understanding of the electronic structures of atoms came from studies of
         electromagnetic radiation that was emitted or absorbed by atoms. It was observed
         that
            a. Each atom absorbs or emits only at a certain frequencies and that these were
               different for each element.
            b. For H atoms, and empirical formula, the Rydberg equation, was developed to
               predict the wavelengths of the emission/absorption

\[
\frac{1}{\lambda} = 9\frac{1}{m^2} \left( \frac{1}{n^2} - \frac{1}{n^3} \right)
\]

where

\( \lambda \) = wavelength of emission or absorption
\( m = 1, 2, 3... \)
\( n = \) an integer greater than \( m \)
\( Y = \) Rydberg constant

2. Niels Bohr gave first theoretical explanation for the Rydberg equation. His
   assumption is based on the understanding that electrons can only have discreet
   energies because only certain wavelengths of light are absorbed.
   a. the angular momentum of an electron was related to Plank’s constant by

\[
mvr = n \left[ \frac{h}{2\pi} \right]
\]
where
\[ m = \text{mass of electron} \]
\[ r = \text{radius of orbit} \]
\[ n = 1, 2, 3... \]
\[ v = \text{velocity of electron} \]
\[ h = \text{Plank’s constant} \]

From this the energies of the electrons can be determined
\[
E = -\frac{2\pi^2 me^4}{h^2 n^2} \quad \text{where } e = \text{charge on an electron}
\]

b. absorption or emission of energy occurs when an electron jumps from one quantized energy level to another.
\[
\Delta E = E_i - E_f = -\frac{2\pi^2 me^4}{h^2} \left[ \frac{1}{n_i^2} - \frac{1}{n_f^2} \right]
\]
c. This can converted to the form of the Rydberg equation by substituting \( hc/\lambda \) for \( E \) and then dividing both sides of the equation by \( h \) and \( c \).
\[
\frac{1}{\lambda} = \frac{2\pi^2 me^4}{h^3 c} \left[ \frac{1}{n_i^2} - \frac{1}{n_f^2} \right]
\]

C. Wave mechanics
1. DeBroglie suggested all matter has wave like properties \( \lambda = h/mv \)
2. Applying this concept to classical mechanics gives an equation relating the wave properties of an electron to its energy
3. Hydrogen Atom
   a. For an atom or ion with a single electron in polar coordinates

![Diagram](image)
1. Schrodinger’s Equation relates the total energy of the electron to the wavefunction for the electron

\[ \hat{H} \Psi = E \Psi \]

where

\[ \hat{H} = -\frac{\hbar^2}{8\pi^2 m} \left[ \frac{\delta^2}{\delta r^2} - \frac{2}{r} \frac{\delta}{\delta r} + \frac{1}{r^2} \frac{\delta^2}{\delta \theta^2} + \frac{\cos \theta}{r^2 \sin \theta} \frac{\delta}{\delta \theta} + \frac{1}{r^2 \sin \theta} \frac{\delta^2}{\delta \phi^2} \right] - \frac{Ze^2}{r} \]

and

- \( h = \) Planck’s constant
- \( m = \) mass of the electron
- \( e = \) the charge of the electron
- \( Z = \) the unit charge on the nucleus

2. Applying the boundary conditions
   a. \( \Psi \) is single valued
   b. \( \Psi \) and its first derivative are continuous
   c. \( \Psi \) approaches 0 as \( r \) approaches \( \infty \)
   d. the probability of finding the electron summed over all space is 1

the equation can be solved by separating the variables in the wavefunction

\[ \Psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \]

and solving for each portion

\[ R(r) = \left( \frac{Z}{a_0} \right)^{3/2} e^{-\frac{\rho}{2} f(r)} \]

where

\[ a_0 = \frac{\hbar^2}{4\pi^2 me^2} \]

\[ \rho = \frac{2Zr}{na_0} \]
\[ Y(\theta, \phi) = \left( \frac{1}{4\pi} \right)^{\frac{1}{2}} y(\theta, \phi) \]

where

\[
\begin{align*}
n & P & m_P & y(\theta, \phi) \\
1 & 0 & 2 & \frac{1}{2\sqrt{2}} (2 - \rho) \\
2 & 0 & 1 & \frac{1}{2\sqrt{6}} \rho \\
3 & 0 & 1 & \frac{1}{9\sqrt{3}} \left( 6 - 6\rho + \rho^2 \right) \\
3 & 1 & 1 & \frac{1}{9\sqrt{6}} (4 - \rho) \rho \\
3 & 2 & 1 & \frac{1}{9\sqrt{30}} \rho^2
\end{align*}
\]

3. the only solutions for the above equations for \( R(r) \) and \( Y(\theta, \phi) \) occur when

- \( n = 1, 2, 3, 4 \ldots \)
- \( 0 \leq P < n - 1 \)
- \( |m_P| \neq 1 \)
plugging specific values for n, P and m_r, we can get expressions for the solutions to the Schrodinger equation

n = 1, P = 0, m_r = 0  
1s orbital

\[ R(r) = 2 \left[ \frac{Z}{a_0} \right]^{\frac{3}{2}} e^{-\frac{Zr}{a_0}} \]  
\[ Y(\theta, \phi) = \left[ \frac{1}{4\pi} \right]^{\frac{1}{2}} \]

n = 2, P = 0, m_r = 0  
2s orbital

\[ R(r) = \frac{1}{2\sqrt{2}} \left[ \frac{Z}{a_0} \right]^{\frac{3}{2}} e^{-\frac{Zr}{2a_0}} \left[ 2 - \frac{Zr}{a_0} \right] \]  
\[ Y(\theta, \phi) = \left[ \frac{1}{4\pi} \right]^{\frac{1}{2}} \]

n = 2, P = 1, m_r = 0  
2p_0 orbital

\[ R(r) = \frac{1}{2\sqrt{6}} \left[ \frac{Z}{a_0} \right]^{\frac{3}{2}} e^{-\frac{Zr}{2a_0}} \left[ Zr/a_0 \right] \]  
\[ Y(\theta, \phi) = \left[ \frac{3}{4\pi} \right]^{\frac{1}{2}} \cos \theta \]

n = 2, P = 1, m_r = \pm 1  
2p_{\pm 1}

\[ R(r) = \frac{1}{2\sqrt{6}} \left[ \frac{Z}{a_0} \right]^{\frac{3}{2}} e^{-\frac{Zr}{2a_0}} \left[ Zr/a_0 \right] \]  
\[ Y(\theta, \phi) = \left[ \frac{3}{8\pi} \right]^{\frac{1}{2}} \sin \theta e^{\pm i\phi} \]

4. complex numbers can be removed from degenerate orbitals using linear combinations of the orbitals

\[ 2p_x = \frac{1}{2} (2p_{+1} + 2p_{-1}) \]
\[ 2p_y = \frac{1}{2} (2p_{+1} - 2p_{-1}) \]

5. energies of the orbitals are calculated from Schrodinger’s Equation

\[ E = \frac{2\pi^2 me^4 \partial Z^2}{n^2 h^2} \]
b. Meaning of the wavefunction

1. the value of $\Psi$ has no direct physical significance. It is a measure of the amplitude of the wavefunction at that particular point in space and may have a positive or negative sign.

2. the value of $\Psi^2$ is related to the probability of finding the electron at a particular point in space.

c. Graphical representation of hydrogen atomic orbitals

1. Radial distribution plot:
   The plot of electron density in a spherical shell at distance $r$ from the nucleus

2. Electron density contour plots
   2 or 3-D surfaces
   $\Psi$ or $\Psi^2$ are constant on each point on the surface.
   the surface is drawn to enclose a certain fraction of the electron density.

3. The $n$ and $\allowbreak \mathcal{P}$ quantum numbers determine both the number of lobes of an orbital in the electron density contour plot and the number of nodes in the radial distribution plot
   number of lobes = $2^\mathcal{P}$
   note that some d and higher orbitals, such as d$_{2\sigma}$ may have fewer nodes because they are combinations of two orbitals
   number of nodes = $n - \mathcal{P} - 1$
D. Poly electron species

1. Approximation only
   a. No exact solutions to Schrodinger equation due to inability to develop an appropriate model for the potential energy term due to interactions between the electrons
   b. Most versatile approximation is to use H orbitals in which the actual nuclear charge, \( Z \), is replaced by an effective nuclear charge \( Z^* \)

\[
Z^* = Z - S \quad \text{where } Z = \text{atomic number and } S = \text{shielding}
\]

c. \( S \) can be calculated using Slater’s rules:
   1. Write electron config. (Only for Slater’s Rule)
      \( (1s)(2s\ 2p)(3s\ 3p)(3d)(4s\ 4p)(4d\ 4f)\ldots \)
   2. Electrons to the right of electron in question contributes 0.
   3. Electron in same group contribute 0.35/e⁻
   4. For s and p e⁻ all n-1 contribute 0.85/e⁻
   5. For s and p all n-2 and lower contribute 1.0/e⁻
   6. For d and f all e⁻ to the left contribute 1.0/e⁻

d. Examples
   calculate \( Z^* \) for a 3p electron in phosphorus
calculate $Z^*$ for a 3d electron in Cr

2. electron configurations
   a. electrons are added to H-like orbitals according to the Pauli Exclusion Principle, Aufbau principle, and Hund’s rule
      1. Pauli Exclusion Principle - each electron must have a unique set of quantum numbers
      2. Hund’s rule - electrons occupy separate orbitals w/ parallel spins before being paired in an orbital
      3. Aufbau principle - electrons are added to the lowest energy orbital possible

<table>
<thead>
<tr>
<th>n</th>
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<th>1</th>
<th>2</th>
<th>3</th>
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<td></td>
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<tr>
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<td>3p</td>
<td>3d</td>
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<td>4d</td>
<td>4f</td>
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<td>5f</td>
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<td>6p</td>
<td>6d</td>
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<td>7</td>
<td>7s</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
b. adjustments are made to take into account the special stabilities of half and completely filled d orbitals

c. examples

P
V
Cr
Mn

II. Periodic Table and Periodic Properties

A. The setup of the Periodic Table reflects the electron configurations of the atoms

\[
\begin{array}{cccc}
\text{n} & \text{ns} & \text{n-1 d} & \text{np} \\
1 & \text{He} & & \\
2 & & & \\
3 & & & \\
4 & & & \\
5 & & & \\
6 & & & \\
7 & & & \\
\end{array}
\]

- d block transition metals
- noble gases
- halogens
- f block transition metals
- n-2 f
- alkaline earths
- alkali metals
- * Lanthanides
- ** Actinides
1. All atoms in the same column (group) have the same valence electron configuration
   a. 1st column - alkali metals  \([\text{core}]\text{ns}^1\)
   b. 2nd column - alkaline earths  \([\text{core}]\text{ns}^2\)
   c. next to last column - halogens  \([\text{core}]\text{ns}^2\text{np}^5\)
   d. last column - noble gases  \([\text{core}]\text{ns}^2\text{np}^6\)
   e. exceptions are the transition metals, lanthanides and actinides due to the closeness of the energies of the ns, (n-1)d and (n-2)f orbitals

2. Because all atoms in a group have the same valence electron configuration, they have a tendency to form the same number and type of bonds
   a. Examples
      1. all alkali metals form \(M^+\) cations while all alkaline earths form \(M^{2+}\) cations
      2. all halogens have a minimum -1 oxidation state while both oxygen and sulfur have -2 oxidation states

3. For main group elements.
   a. maximum oxidation # = column #
      1. example  \(\text{Cl} = +7\)
   b. minimum oxidation = column # - 8
      1. example  \(\text{Cl} = -1\)
   c. intermediate oxidation # = highest - 2n where \(n = 1, 2, 3\ldots\)
      1. this assumes at all atoms have octets and that no atom of the same element are bonded to each other
      2. example  \(\text{Cl} = +5, +3, +1\)

B. Periodicity in Forms (allotropes) of Elements
   1. Noble gases  Group 0
      a. \([\text{core}]\text{ns}^2\text{np}^6\)
      b. all are atomic compounds because they have filled octets
2. Halogens  Group VII A  
   a. $[\text{core}]ns^2np^5$
   b. need one electron to reach octet, these form a single bond w/ another halogen  -diatomic molecular compounds

3. Group VI A  
   a. $[\text{core}]ns^2np^4$
   b. need two electrons to reach octet, these form one double bond or two single bonds
   c. O prefers to form a double bond with another oxygen (general rule: 2nd row prefers double bonds while 3rd row and lower prefer single bonds ) -diatomic molecular compound
   
   d. S most stable when it forms single bonds
4. Group VA N, P
   a. \([\text{core}]\text{ns}^2 \text{np}^3\)
   b. Need three electrons to reach octet - triple bond, double and single bond or three single bonds
   c. N forms a triple bond to another N

   d. P forms three single bonds to other P
      1. white (yellow) phosphorus is a molecular solid and unstable

      2. red phosphorus is an amorphous, polymeric material containing P₈, P₉ or P₁₀ polyhedra linked into long chains by P₂ units.
      3. black phosphorus is a covalent lattice material
5. Group IV A C, Si
   a. \([\text{core}]ns^2np^2\)
   b. need four electrons to reach octet - one triple and one single bond, two double bonds, one double and two single bonds, or four single bonds
   c. three allotropic forms for C
      1. diamond

      2. graphite

      3. buckminsterfullerene
4. graphite is the more stable than diamond because C is a second row element and prefers double bonds.

d. the allotropic form of Si is similar to that of diamond in that each Si forms four single bonds to other Si. This is because Si is a third row element and does not like to form multiple bonds

6. Group III A   B
   a. \([\text{core}]2s^22p^1\]
   
   b. needs five electrons to reach octet. B does not have sufficient electrons to reach its octet by forming normal bonds to other B. Instead it forms clusters to maximize sharing of the electrons

C. Binary Compounds

1. The positions of the elements in the Periodic Table determine the types of binary compounds that are formed
   a. 2 metals \(\text{\textbullet\textbullet\textbullet\textbullet}\) > metal alloy
   
   b. metal + nonmetal \(\text{\textbullet\textbullet\textbullet\textbullet}\) > ionic compound
   
   c. nonmetal + nonmetal \(\text{\textbullet\textbullet\textbullet\textbullet}\) > molecular or covalent-lattice compounds

2. The position of the element in the Periodic Table also determines stoichiometry
   a. metal + nonmetal

   1. metal goes to max. oxidation state while nonmetal goes to minimum oxidation state (does not apply to transition metals).

   \[
   \begin{align*}
   \text{Li} + \text{Cl}_2 & \text{\textbullet\textbullet\textbullet\textbullet}\> \\
   \text{K} + \text{O}_2 & \text{\textbullet\textbullet\textbullet\textbullet}\> \\
   \text{Na} + \text{N}_2 & \text{\textbullet\textbullet\textbullet\textbullet}\> \\
   \text{Al} + \text{S}_8 & \text{\textbullet\textbullet\textbullet\textbullet}\> \\
   \text{Sr} + \text{P}_4 & \text{\textbullet\textbullet\textbullet\textbullet}\>
   \end{align*}
   \]
2. inert s pair effect
   a. Group IIIA, IVA, VA metals in the bottom two rows can exhibit an oxidation state 2 less than their max.
   b. This occurs when only the np valence electrons and not the ns electrons are ionized.
   c. The oxidation state of the metal is determined by the reaction conditions, the oxidizing power of the nonmetal and the position of the metal in the Periodic Table.
   d. examples
      \[
      2 \text{Tl} + \text{I}_2 \rightarrow 2\text{TlI} \quad \text{while} \quad 2\text{Al} + 3 \text{I}_2 \rightarrow 2\text{AlI}_3
      \]
      \[
      16 \text{Bi} + 3 \text{S}_8 \rightarrow 8\text{Bi}_2\text{S}_3 \quad \text{while} \quad 4 \text{Bi} + 5 \text{O}_2 \rightarrow 2\text{Bi}_2\text{O}_5
      \]

3. multiple bonded nonmetals can exhibit intermediate oxidation states in which the bond is not broken:
   a. examples
      \[
      \text{O}_2^- \quad \text{superoxide}
      \]
      \[
      \text{O}_2^{2-} \quad \text{peroxide}
      \]
   b. nonmetal + nonmetal to form a diamagnetic compound which only has bonds between the two different nonmetals
      1. more electronegative element goes to its minimum oxidation state
      2. less electronegative element goes to a positive oxidation state.
      a. this can be either the maximum oxidation state or an intermediate oxidation state depending on the oxidizing ability of the more electronegative nonmetal and the ease with which the less electronegative nonmetal can be oxidized.
      b. the less electronegative element in the compound that is formed must obey the octet rule if it is a second row element.
3. examples

\[ C + Cl_2 \rightarrow C\text{Cl}_2 \]

\[ C + O_2 \rightarrow CO_2 \]

\[ N_2 + F_2 \rightarrow N_2F_2 \]

\[ P_4 + F_2 \rightarrow P_4F_6 \]

\[ I_2 + O_2 \rightarrow IO_2 \]

D. Periodic Properties

1. Ionization Energies (I.E.)

   a. definition: amount of energy to remove an electron from an isolated atom or ion in the gas phase

   1. 1st I.E. \[ M \rightarrow M^+ + 1e^- \]

   2. 2nd I.E. \[ M^+ \rightarrow M^{2+} + 1e^- \]

   b. charge separation means all ionization energies are endothermic

   c. for main group elements

   1. across a row

<table>
<thead>
<tr>
<th>element</th>
<th>1st IE (MJ/mol)</th>
<th>Z*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.5203</td>
<td>1.30</td>
</tr>
<tr>
<td>Be</td>
<td>0.8995</td>
<td>1.95</td>
</tr>
<tr>
<td>B</td>
<td>0.8006</td>
<td>2.60</td>
</tr>
<tr>
<td>C</td>
<td>1.0864</td>
<td>3.25</td>
</tr>
<tr>
<td>N</td>
<td>1.4023</td>
<td>3.90</td>
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<tr>
<td>O</td>
<td>1.3140</td>
<td>4.55</td>
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<tr>
<td>F</td>
<td>1.6810</td>
<td>5.20</td>
</tr>
<tr>
<td>Ne</td>
<td>2.0807</td>
<td>5.85</td>
</tr>
</tbody>
</table>
2. down a column

<table>
<thead>
<tr>
<th>element</th>
<th>$1^{st}$ IE (MJ/mol)</th>
<th>$Z^*$</th>
<th>atomic radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.3120</td>
<td>1.00</td>
<td>120</td>
</tr>
<tr>
<td>Li</td>
<td>0.5203</td>
<td>1.30</td>
<td>180</td>
</tr>
<tr>
<td>Na</td>
<td>0.4958</td>
<td>2.20</td>
<td>230</td>
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<tr>
<td>K</td>
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<td>280</td>
</tr>
<tr>
<td>Rb</td>
<td>0.4030</td>
<td>2.20</td>
<td>?</td>
</tr>
<tr>
<td>Cs</td>
<td>0.3757</td>
<td>2.20</td>
<td>?</td>
</tr>
</tbody>
</table>

explanation:

2. Electron Affinities

a. Two definitions

1. energy released when an $e^-$ is added to an isolated atom or ion in the gas phase
   
   $1^{st}$ EA: $M(g) + e^- \rightarrow M^-(g)$

2. energy needed to remove an $e^-$ from an isolated anion in the gas phase
   
   $2^{nd}$ EA: $M^-(g) + e^- \rightarrow M^+ (g)$

a. This is the definition that we will use because is consistent with the definition for ionization energy
b. The 1st electron affinity can be either endothermic or exothermic because no charge separation occurs. All other electron affinities are exothermic because the negative charge on the anion is being reduced.

b. For p-block elements

1. across a row

<table>
<thead>
<tr>
<th>element</th>
<th>EA (kJ/mol)</th>
<th>Z* (2p)</th>
<th>e⁻ configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>&lt;0</td>
<td>1.60</td>
<td>1s²2s²2p¹</td>
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<tr>
<td>B</td>
<td>26.8</td>
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<td>1s²2s²2p²</td>
</tr>
<tr>
<td>C</td>
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<td>2.90</td>
<td>1s²2s²2p³</td>
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<tr>
<td>N</td>
<td>#0</td>
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<td>1s²2s²2p⁴</td>
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<tr>
<td>O</td>
<td>141.1</td>
<td>4.20</td>
<td>1s²2s²2p⁵</td>
</tr>
<tr>
<td>F</td>
<td>328.0</td>
<td>4.85</td>
<td>1s²2s²2p⁶</td>
</tr>
</tbody>
</table>

explanation:

2. there is no clear trend down a column. This is due to the competing effects of increasing effective nuclear charge and increasing ionic radii which are of approximately the same magnitude but are in opposite directions.

3. Atomic and ionic radii

a. Atomic radii are measured in covalent or metallic compounds. Ionic radii are measured in ionic compounds.

b. trends

1. decreases across a row due to increasing effective nuclear charge Z*
2. increases down a column with the largest increases between the two lightest atoms
3. no effects due to special stabilities of half or completely filled shells are observed.
III. Structure and bonding in molecular materials

A. Covalent bonding (intramolecular bonding)

1. Localized: Valence bond and VSEPR Theory

   a. Atoms in molecules are held together by localized bonds formed by overlap of
      atomic orbitals on adjacent atoms

      1. covalent bond - one half of the electrons come from each atom
      2. coordinate covalent bond - all of the electrons come from one atom

   b. The structures of molecules are such that electron-electron repulsion is minimized
      (VSEPR Theory)

      1. Rules for predicting molecular structures

         a. Areas of electron density are arranged to minimize electron-electron
            repulsion

            1. An area of electron density is defined as a single, double or triple bond
               or an unshared pairs of electrons

<table>
<thead>
<tr>
<th>AREAS OF e- DENSITY</th>
<th>ELECTRONIC GEOMETRY</th>
<th>HYBRIDIZATION</th>
<th>ANGLES</th>
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<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>sp</td>
<td>180</td>
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<tr>
<td>3</td>
<td>trigonal planar</td>
<td>sp²</td>
<td>120</td>
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<td>tetrahedral</td>
<td>sp³</td>
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<td>trigonal bipyramid</td>
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<td>6</td>
<td>octahedral</td>
<td>sp³d²</td>
<td>90</td>
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<tr>
<td>7</td>
<td>pentagonal bipyramid</td>
<td>-</td>
<td>90, 72</td>
</tr>
<tr>
<td></td>
<td>capped octahedron</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
b. Repulsion decreases in the order unshared pair-unshared pair > unshared pair-single bond > single bond-single bond
   1. When unshared pairs are present, bond angles are generally, but not always, smaller than expected
   2. In trigonal bipyramid electronic geometries, the lone pairs always occupy an equatorial site
   3. Lone pairs are always opposite each other in octahedral electronic geometries

c. Multiple bonds take up more space than single bonds

d. Bonds to highly electronegative atoms occupy less space than do bonds to less electronegative atoms.
   1. This is due to the fact that the electron density in bonds to highly electronegative atoms is further from the central atom on the average.
   2. Example: F takes up less space than H as a substituent.

e. If the central atom
   1. is in the third row or below,
   2. would be expected to have a tetrahedral geometry,
   3. has at least one unshared pair of electrons,
   4. and has substituents that are less electronegative than it is, the bonding can be through the p orbitals and not through sp$^3$ hybrid orbitals. This results in bond angles close to 90E rather than the expected 109.5E.

f. Examples
c. Valence Bond Theory - H like orbitals on the central atom are hybridized to form bonds oriented in the direction predicted by VSEPR Theory

1. linear electronic geometry - sp hybridization

   \[
   s + \downarrow p_x \rightarrow \downarrow 2s - 2p_x + \downarrow 2s + 2p_x
   \]

   a. example: HCN

   \[
   C: 1s^22s^22p^2 \rightarrow 1s^22s^12p_x^12p_y^12p_z^1 \rightarrow \rightarrow 1s^2(2sp)^1 \rightarrow 1s^22s^22p_x^12p_y^12p_z^1
   \]

   \[
   N: 1s^22s^22p^3 \rightarrow 1s^22s^22p_x^12p_y^12p_z^1 \rightarrow 1s^2(2sp)^1 \rightarrow 1s^22s^22p_x^12p_y^12p_z^1
   \]

2. trigonal planar electronic geometry - sp\(^2\) hybridization

   \[
   s + p_x + p_y \rightarrow \frac{1}{3}s + \frac{2}{3}p_x + \frac{1}{3}s - \frac{1}{3}p_x - \frac{1}{2}p_y + \frac{1}{3}s - \frac{1}{3}p_x + \frac{1}{2}p_y
   \]
a. example: \( \text{BH}_3 \)

\[
\begin{align*}
\text{B} & \quad 1s^2 2s^2 2p^1 \quad > \quad 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0 \\
\text{H} & \quad > 1s^2 (2s^2)^1 (2p_x^1)^1 (2p_y^1)^1 (2p_z^0)^1
\end{align*}
\]

b. example: \( \text{H}_2\text{CO} \)

\[
\begin{align*}
\text{C} & \quad 1s^2 2s^2 2p^2 \quad > \quad 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1 \\
\text{O} & \quad > 1s^2 (2s^2)^2 (2s^2)^2 (2p_x^2)^2 (2p_y^2)^2 (2p_z^1)^1
\end{align*}
\]

3. tetrahedral electronic geometry - \( \text{sp}^3 \) hybridization

\[
\begin{align*}
\frac{1}{4}s + \frac{1}{4}p_x + \frac{1}{4}p_y + \frac{1}{4}p_z & > 4 \text{ sp}^3 \text{ hybrid orbitals} \\
\frac{1}{4}s + \frac{1}{4}p_x - \frac{1}{4}p_y - \frac{1}{4}p_z & \quad \text{hybrid orbitals} \\
\frac{1}{4}s - \frac{1}{4}p_x - \frac{1}{4}p_y + \frac{1}{4}p_z & \quad \text{hybrid orbitals} \\
\frac{1}{4}s - \frac{1}{4}p_x + \frac{1}{4}p_y - \frac{1}{4}p_z & \quad \text{hybrid orbitals}
\end{align*}
\]
4. octet rule- atoms having only s and p valence orbitals may have a maximum of 8 electrons in the valence shell - this is only for 2nd row elements

5. Trigonal bipyramidal - sp³d hybridization
   a. \( s + p_x + p_y + p_z + d_{x^2-y^2} \) > 5 sp³d orbitals

   b. example: PF₅
      \[
P 1s^22s^22p^63s^23p^33d^0 > 1s^22s^22p^63s^13p_x^13p_y^13p_z^13d_{x^2-y^2}^1 > 1s^22s^22p^6(3sp^3d)^1(3sp^3d)^1(3sp^3d)^1(3sp^3d)^1(3sp^3d)^1
      \]

6. Octahedral
   a. \( s + p_x + p_y + p_z + d_{x^2-y^2} + d_{xy} \) > 6 sp³d² orbitals
b. example: SF6
\[
\text{S} \quad 1s^22s^22p^63s^23p^43d^0 \quad > \quad 1s^22s^22p^63s^13p_x^13p_y^13p_z^13d_{x^2-y^2}^13d_{xy}^1 \quad > \\
1s^22s^22p^6(3sp^3d^2)^1(3sp^3d^2)^1(3sp^3d^2)^1(3sp^3d^2)^1(3sp^3d^2)^1
\]

7. Additional considerations

a. Dative = coordinate covalent bonds - single bonds in which both electrons come from the same atom

1. Example: \( \text{H}_3\text{O}^+ \)

\[
\begin{array}{c}
\text{O} \\
\text{H} \quad \text{H} \\
\text{H}
\end{array} + \quad \text{H}^+ \quad \rightarrow \quad \begin{array}{c}
\text{O} \\
\text{H} \quad \text{H}
\end{array}
\]

2. Example: \( \text{SO}_2 \) and \( \text{SO}_3 \)

b. Resonance - sometimes these are 2 or more acceptable structures for a molecule. In order to explain the observed bond lengths, these structures must be averaged.

1. Rules for drawing resonance structures

a. All forms must have same number of unpaired e\(^-\)

b. All forms must have the same arrangement of atoms.

c. Number of bonds in the structure should be maximized

d. Charge distribution in the resonance form should be reasonable, \( i.e. \) no adjacent like charges, partial negative charges on more electronegative elements and positive charges on less electronegative elements.
2. Example: the S-O bonds in SO\textsubscript{3} bonds are longer than those in SO\textsubscript{2}.

3. Example: the internal N-O bond in N\textsubscript{2}O\textsubscript{5} is longer than the terminal N-O bonds.
2. Delocalized: Molecular Orbital Theory

a. Molecular materials are held together by electrons in bonding orbitals. These orbitals can extend throughout the molecule.

b. Diatomic molecules

1. Homonuclear diatomic molecules

   a. Combine atomic orbitals of similar energy and with a net positive overlap to form molecular orbitals. This can be done by inspection, the use of Group Theory is not necessary.

   b. Write the MO diagram realizing that the bonding molecular orbital is lower in energy than the antibonding molecular orbital, that the difference between bonding and antibonding orbitals is greater for $\sigma$ orbitals than for $\pi$ orbitals and that orbitals with like symmetry repel each other.

1. MO diagrams for $\text{H}_2$ through $\text{N}_2$ and for $\text{O}_2$ through $\text{Ne}_2$, shown on the next two pages, are different because as one moves across the Periodic Table, the energy difference between the 2s and 2p orbitals increases, decreasing the repulsion between the $2\sigma_g$ and $3\sigma_g$ orbitals.

   c. The electron configuration is obtained by filling all electrons from both atoms into the MO diagram.

1. The bond order, which corresponds to the number of bonds that would be drawn in a Lewis dot structure, is determined using the below formula

   \[
   \text{bond order} = \frac{(\text{bonding electrons}) - (\text{antibonding electrons})}{2}
   \]

2. The strength of the bond between the two atoms in the diatomic molecule is directly proportional to the bond order as long as the atoms are from the same row in the Periodic Table.

3. The length of the bond between the two atoms is inversely proportional to the bond order as long as the atoms are from the same row in the Periodic Table.
O_2 - Ne_2

\[ \begin{align*}
2s & \quad 2s \\
\sigma^* & \quad \sigma_u^* \\
\pi_g & \quad \pi_u \\
3\sigma_g & \\
& \\
2p & \quad 2p \\
\end{align*} \]
H₂ - N₂
<table>
<thead>
<tr>
<th>mo configuration</th>
<th>bond order</th>
<th>bond length (pm)</th>
<th>bond dissociation energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1σᵣ²</td>
<td>74.14</td>
<td>432.1</td>
</tr>
<tr>
<td>He₂</td>
<td>1σᵣ² 1σᵤ²</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Li₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ²</td>
<td>1</td>
<td>267.3</td>
</tr>
<tr>
<td>Be₂</td>
<td>1σᵣ² 1σᵤ²² 2σᵣ²²</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>B₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²²</td>
<td>1</td>
<td>159</td>
</tr>
<tr>
<td>C₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 2πᵤ² 2πᵤ²¹</td>
<td>2</td>
<td>124.3</td>
</tr>
<tr>
<td>N₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 2πᵤ² 2πᵤ²² 3σᵣ²²</td>
<td>3</td>
<td>109.8</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 3σᵣ²² πᵤ²¹ πᵤ²¹</td>
<td>2.5</td>
<td>116.6</td>
</tr>
<tr>
<td>O₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 3σᵣ²² πᵤ²¹ πᵣ²¹ πᵣ²¹</td>
<td>2</td>
<td>120.8</td>
</tr>
<tr>
<td>O₂⁻</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 3σᵣ²² πᵤ²¹ πᵤ²¹ πᵣ²¹ πᵣ²¹</td>
<td>1.5</td>
<td>135</td>
</tr>
<tr>
<td>O₂⁻²</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 3σᵣ²² πᵤ²¹ πᵤ²¹ πᵣ²¹ πᵣ²¹ πᵣ²¹</td>
<td>1</td>
<td>149</td>
</tr>
<tr>
<td>F₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 3σᵣ²² πᵤ²¹ πᵤ²¹ πᵣ²¹ πᵣ²¹ πᵣ²¹</td>
<td>1</td>
<td>141</td>
</tr>
<tr>
<td>Ne₂</td>
<td>1σᵣ² 1σᵤ² 2σᵣ² 2σᵤ²² 3σᵣ²² πᵤ²¹ πᵤ²¹ πᵣ²¹ πᵣ²¹ πᵣ²¹ 3σᵤ²²</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

2. Heteronuclear diatomic molecules
   a. The procedure used to set up the molecular orbitals is the same except the energies of the atomic orbitals for the two atoms are different.
   b. HF
   c. The MO diagram for CO is given on a separate page. The 2s orbital of oxygen and the 2pₓ orbital of C are of the appropriate symmetry but of the wrong energies to interact and are therefore nonbonding.
c. Polyatomic Molecules

1. Major differences are seen between valence bond/VSEPR and molecular orbital theories for polyatomic species. A detailed discussion of this is beyond the scope of this course because it involves the use of group theory to determine the orbital overlap.

2. Example: π bonding in NO₂
   a. The σ and π bonding molecular orbitals of NO₂ can be treated differently because they have different symmetries (this is equivalent to saying that there is no net overlap or that they are orthogonal).
   b. π bonding involves a single 2p₂ orbital on each atom that is perpendicular to the plane containing the three atoms.

\[
\Psi^* = \frac{1}{2} 2p_z(O_1) - \frac{\sqrt{2}}{2} 2p_z(N) + \frac{1}{2} 2p_z(O_2)
\]

33
2. nonbonding orbital

\[ \Psi_{ab} = \frac{1}{\sqrt{2}} 2p_z(O_1) - \frac{1}{\sqrt{2}} 2p_z(O_2) \]

\[ \text{mo diagram} \]

3. bonding orbital

\[ \Psi = \frac{1}{2} 2p_z(O_1) + \frac{\sqrt{2}}{2} 2p_z(N) + \frac{1}{2} 2p_z(O_2) \]

\[ \text{mo diagram} \]

d. mo diagram
IV. The Solid State

A. Review and Background

1. Types of solids and bonding
   a. atomic - composed of isolated atoms
      1. Group 0 (VIII A) elements only
      2. held together by London forces, therefore soft with low melting points
   b. metallic - nucleus and core electron in a sea of valence electrons
   c. ionic - ions held together by Coulombic interactions
   d. molecular - molecules held together by weak forces (dipole-dipole, London forces, H-bonding)
   e. covalent lattice - 2-dimensional or 3-dimensional array of atoms held together by covalent bonds. No discreet molecules are present.

2. Solids fall into two types:
   a. amorphous - no long range ordering
      1. like frozen or extremely viscous liquids (glass)
   b. crystalline - long range ordering
      1. every crystalline solid can be described by a 3-dimensional repeat unit called the unit cell

3. unit cells belong to one of seven crystalline systems
   a. each crystal system can be described by three edge lengths and three angles between the edges.
b. crystal systems

<table>
<thead>
<tr>
<th>System</th>
<th>a ≠ b ≠ c</th>
<th>a ≠ β ≠ γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoclinic</td>
<td></td>
<td>α = γ = 90°, β ≠ 90°</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td></td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Tetragonal</td>
<td></td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Cubic</td>
<td></td>
<td>α = β = γ = 90°</td>
</tr>
<tr>
<td>Trigonal</td>
<td></td>
<td>α = β = γ ≠ 90°</td>
</tr>
<tr>
<td>Hexagonal</td>
<td></td>
<td>α = β = 90°, γ = 120°</td>
</tr>
</tbody>
</table>

1. the corners of the crystal must be the same kind of atom, ion or molecule

4. the number of equivalent points in a cell may vary
   a. P = primitive
      number of lattice points = 8 corners (1/8) = 1

   b. C = C-centered
      number of lattice points = 8 corners (1/8) + 2 face (1/2) = 2
c. I = body centered
   number of lattice points = 8 corners (1/8) + 1 body (1) = 2

   ![Body centered lattice diagram]

   ![Face centered lattice diagram]

5. combining the 7 crystal systems with the different arrangements of equivalent points
gives the 14 Bravais lattices. Every crystal belongs to one of these lattices.

a. Bravais lattices
   Triclinic: P
   Monoclinic: P, C
   Orthorhombic P, C, I, F
   Tetragonal P, I
   Cubic P, I, F
   Trigonal P
   Hexagonal P
b. the reason that 28 (4 times 7) Bravais lattices are not observed is because some of the combinations give equivalent structures

6. Closest Packing of Spheres
   a. the most efficient packing of spheres is a layer in which each sphere has six nearest neighbors. This arrangement has the least empty space
   b. when a second layer is added, the spheres in the second layer are placed over holes in the first layer. Note that only one half of the holes in the first layer are covered by spheres in the second layer
   c. there are two ways to place the third layer

1. spheres in the third layer are over spheres in the first layer. This gives an arrangement in which every other layer repeats and is referred to as an AB stacking pattern
   a. the unit cell that correspond to an AB stacking pattern is a primative hexagonal unit cell
   b. this arrangement is thus called a hexagonal closest packed array
2. spheres in the third layer are over holes in the first layer. This gives an arrangement in which every third layer repeats and is referred to as an ABC stacking pattern
   a. the unit cell that corresponds to an ABC stacking pattern is a face centered cubic unit cell
   b. this arrangement is thus called a cubic closest packed array

d. in a closest packed structure, each sphere has twelve nearest neighbors: three below, six around and three above. This is referred to as having a coordination number of 12.

e. there are two types of holes in closest packed structures, tetrahedral and octahedral. It is possible to fill either the tetrahedral holes or the octahedral holes but not both because they overlap. The relative arrangement of the holes relative to the closest packed spheres in two adjacent layers is shown below.
1. octahedral - formed by three spheres in one row and three in the next

   ![octahedral diagram]

   a. there is one octahedral hole per sphere in the closest packed array
   b. octahedral holes are midway between the layers

2. tetrahedral - formed by three spheres in one row and one in the next

   ![tetrahedral diagram]

   a. there are two tetrahedral holes per sphere in the closest packed array
   b. half of the tetrahedral holes are closer to the lower layer (T') and half are
closer to the upper layer (T)

3. cubic and hexagonal closest packed lattices have the same number and type of
holes because they have the same arrangement of lattice points for two
adjacent layers.

   ![lattice diagram]

   f. inert gases and most metals crystallize in closest packed arrays (exception: alkali
metals, Ba and some transition metals crystallize with a body centered cubic unit
cell).

   g. many salts with monoatomic ions also crystallize in closest packed arrays. In
contrast salts with polyatomic ions and molecular materials generally crystallize
in nonclosest packed arrays because of the lower symmetry of the ions and
molecules.
B. Ionic Solids

1. Properties
   a. Form when atoms with very different ionization energies and electron affinities are combined
      1. Cations = groups IA, IIA, IIIA and lower oxidation states of some transition metals
      2. Anions = groups VIIA, VIA, N, and oxyanions
   b. Conductivity - electrical
      1. low in solid state due to immobility of ions
      2. high in molten state due to mobility of ions
   c. Melting point
      1. high because melting requires charge separation
   d. Hard but brittle
      1. Strong interactions between ions make ionic solids hard
      2. The fact that the attractive interactions can be converted to repulsive interactions by displacing one plane of ions relative to another makes ionic solids brittle

2. Ionic Crystals
   a. ionic crystals are three-dimensional lattices in which one ion occupies the lattice points and the other ion occupies holes in the lattice
      1. ionic crystals will generally be closest packed lattices if
         a. the ionic solid contains spherical ions
         b. the ions are in the correct ratio (1:1 or 2:1)
         c. the ratio of the ionic radius of the cation to the anion is in a certain range
b. 1:1 salts with ½ of the tetrahedral filled
1. ZnS  Wurtzite
   $S^{2-}$ in
   $Zn^{2+}$ in
   $\# S^{2-} =$
   $\# Zn^{2+} =$
   coordination $\# S =$
   coordination $\# Zn =$
2. ZnS  Zinc blende
   $S^{2-}$ in
   $Zn^{2+}$ in
   $\# S^{2-} =$
   $\# Zn^{2+} =$
   coordination $\# S =$
   coordination $\# Zn =$
c. 1:1 salts with all octahedral holes filled
1. NiAs  - nickel arsenide
   $As^{\text{III}}$ in
   $Ni^{\text{II}}$ in
   $\# As^{\text{III}} =$
   $\# Ni^{\text{II}} =$
   coordination $\# As^{\text{III}} =$
   coordination $\# Ni^{\text{II}} =$
2. NaCl

\[
\text{Cl}^- \text{ in} \\
\text{Na}^+ \text{ in} \\
\# \text{Cl}^- = \\
\# \text{Na}^+ = \\
\text{coordination \# \text{Cl}^- =} \\
\text{coordination \# \text{Na} =}
\]

d. Other salts

1. CaF$_2$ - Fluorite

\[
\text{Ca}^{2+} \text{ in} \\
\text{F}^- \text{ in} \\
\# \text{Ca}^{2+} = \\
\# \text{F}^- = \\
\text{coordination \# \text{Ca}^{2+} =} \\
\text{coordination \# \text{F}^- =}
\]

2. CsCl

\[
\text{Cl}^- \text{ in} \\
\text{Cs}^+ \text{ in} \\
\# \text{Cl}^- = \\
\# \text{Cs}^+ = \\
\text{coordination \# \text{Cl}^- =} \\
\text{coordination \# \text{Cs}^+ =}
\]
3. TiO$_2$ - white pigment in paint

\[a = b \neq c; \quad \alpha = \beta = \gamma = 90^\circ\]

Ti$^{4+}$ in

O$^{2-}$ in

$\#_{\text{Ti}^{4+}} = \ldots$

$\#_{\text{O}^{2-}} = \ldots$

coordination $\#_{\text{Ti}^{4+}} = \ldots$

coordination $\#_{\text{O}^{2-}} = \ldots$

4. CaTiO$_3$ - perovskite

Ca$^{2+}$ in

Ti$^{4+}$ in

O$^{2-}$ in

$\#_{\text{Ca}^{2+}} = \ldots$

$\#_{\text{Ti}^{4+}} = \ldots$

$\#_{\text{O}^{2-}} = \ldots$

coordination $\#_{\text{Ca}^{2+}} = \ldots$

coordination $\#_{\text{Ti}^{4+}} = \ldots$

coordination $\#_{\text{O}^{2-}} = \ldots$
Zn\textsuperscript{2+} = S\textsuperscript{2-} = Na\textsuperscript{+} = Cl\textsuperscript{-}

Zinc Blende (cubic ZnS)

Wurtzite (hexagonal ZnS)

Nickel Arsenide

NaCl

\(\bigcirc = S^{2-}\)
\(\bigotimes = \text{Zn}^{2+}\)
\(\bigcirc = \text{As}^{3+}\)
\(\bigotimes = \text{Ni}^{3+}\)
\(\bigcirc = \text{Cl}^{-}\)
\(\bigotimes = \text{Na}^{+}\)
e. Radius ratio

1. For 1:1 salts, the type of unit cell that forms depends in part on the relative radii of the two ions
   a. We assume that the smallest cation that will be stable in a particular type of hole will be one that touches all of the anions. Any smaller cation will go into a smaller hole
   b. We can use this to determine the cation to anion ratios that will give certain types of 1:1 solids

2. Example: cation in an octahedral hole

\[
\begin{align*}
\text{if } r_- & \text{ is the radius of the anion and } r_+ \text{ is the radius of the cation, we can calculate the minimum radius ratio } (r_+/r_-) \text{ at which a cation will be stable in this hole.}
\end{align*}
\]
3. If we carry out the same type of calculations for other types of holes, we can generate the following table. The data in this table can be used to predict the type of unit cell that might be expected for a 1:1 salt with monoatomic cations and anions

<table>
<thead>
<tr>
<th>Hole Type</th>
<th>Inequality</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrahedral hole</td>
<td>$0.225 \leq \frac{r_+}{r_-} &lt; 0.414$</td>
</tr>
<tr>
<td>octahedral hole</td>
<td>$0.414 \leq \frac{r_+}{r_-} &lt; 0.732$</td>
</tr>
<tr>
<td>cubic hole</td>
<td>$0.732 \leq \frac{r_+}{r_-}$</td>
</tr>
</tbody>
</table>

4. As the size of the cation increases relative to that of the anion, we go from

zinc wurtzite/zinc blende > NaCl, NiAs > CsCl

f. Lattice energy

1. Stability of an ionic lattice is a function of Coulombic attractions and repulsions between ions and also the repulsion between any two ions at close distances due to interpenetration of electron clouds

2. Born Equation - average potential energy for an isolated pair of ions

$$\text{P.E.} = \frac{Z_1 Z_2 e^2}{d} + \frac{b e^2}{d^n}$$

where

- $d =$ distance between the ions, $Z_1$ and $Z_2 =$ unit charges on ions,
- $b =$ Born repulsion coefficient, $n =$ Born exponent

3. For an ion (1) in a lattice, the equation for P.E. becomes a series

$$\text{P.E.} = \sum_{i=2}^{n} \frac{Z_i Z_1 e^2}{d_{ii}} + \frac{Be^2}{d^n}$$

where

- $Z_i =$ charge on the ith ion, $d_{ii} =$ distance between ion 1 and ion i,
- $B =$ $b($# nearest neighbors$)$,
- $d =$ distance between ion 1 and its nearest neighbors
a. For NaCl (Cl\(^-\) in a face centered cubic unit cell with Na\(^+\) in all the octahedral holes), this becomes
b. The Madelung constant as written for NaCl will be the same for any face-centered cubic unit cell with all of the octahedral holes filled because these will all have the same arrangement of ions and the same relative charges on the ions.

c. Because of this, we can simplify the expression of the potential energy to

\[ P.E. = -\frac{AZ^2 e^2}{d} + \frac{Be^2}{d^n} \]

where

\[ A = \text{the Madelung constant for the crystal}, \]
\[ Z = \text{highest common charge on the ions} \]

4. Because we are interested in the lowest energy for the lattice, we can simplify the above equation

a. first we differentiate and set the differentiated equation equal to zero

\[ \frac{\delta(P.E.)}{\delta d} = -\frac{AZ^2 e^2}{d^2} + \frac{nBe^2}{d^{n+1}} = 0 \]

b. solving for B, we get

\[ B = \frac{d_0^{n-1} AZ^2}{n} \]

c. substituting this into the expression for the P.E. from 3.c. and simplifying, we get

\[ (P.E.)_0 = \frac{AZ^2 e^2}{d_0} \left( \frac{1}{n} - 1 \right) \]

5. the lattice energy of an ionic crystal is defined as the energy released by the formation of one mole of a salt from isolated, gaseous ions. To convert the expression in 4.c. to lattice energy, we must change the sign and multiply by Avagadro's number (N).

\[ U_0 = -N(P.E.)_0 = \frac{NAZ^2 e^2}{d_0} \left( 1 - \frac{1}{n} \right) \]
a. The Born exponent is a measure of the interpenetration of the electron clouds and increases with increasing molecular weight

1. Example:

<table>
<thead>
<tr>
<th>cation</th>
<th>Cu⁺</th>
<th>Ag⁺</th>
<th>Au⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>9</td>
<td>10</td>
<td>12</td>
</tr>
</tbody>
</table>

6. If the structure of an ionic solid is not known, the lattice energy can be approximated using the Kapustinskii equation

\[
U_0 = \frac{121,000vZ^+Z^-}{r_0}\left(1 - \frac{34.5}{r_0}\right) \quad (kJ/mol)
\]

where

- \(v\) = number of ions in the empirical formula
- \(Z^+\) = unit charge on the cation
- \(Z^-\) = unit charge on the anion
- \(r_0\) = sum of the ionic radii of the cation and anion in pm

a. Example: Estimate the lattice energy of CaCO₃ using the Kapustinskii equation given that the ionic radius of Ca²⁺ is 114 pm and the ionic radius of CO₃²⁻ is 185 pm.
G. Born-Haber Cycle

1. Hess’s law - the enthalpy of a reaction is the same whether the reaction takes place in one step or several steps.

2. The Born-Haber cycle relates the heat of formation of an ionic solid to fundamental properties of the elements that make up the solid and the lattice energy of the solid.

3. Example: Calculate $\Delta H_f$ for NaCl
4. Example: Explain why NaCl₂ is not formed by the reaction of Na and Cl₂ given that the \( U_0 \) for NaCl₂ is estimated to be -2155 kJ/mol.
C. Metals

1. Physical properties
   a. high reflectivity - metallic luster
   b. high electrical conductivity that generally decreases as temperature increases
   c. high thermal conductivity
   d. malleable and ductile

2. many metal properties correlate with the strength with which the atoms are held together (atomization energy). These include chemical reactivity, hardness, tensile strength, m.p., b.p.
   a. Example
      
      | Metal | M.P. | Atomization Energy(kJ/mol) |
      |-------|------|-----------------------------|
      | Cr    | 1900 | 95                          |
      | Mo    | 2610 | 157.6                       |
      | W     | 3380 | 205.5                       |

   b. Example
      
      | Metal | Reactivity | Atomization Energy | Valence electrons |
      |-------|------------|-------------------|------------------|
      | Na    | highest    | 25.6              | 1                |
      | Ca    | intermediate | 35.0             | 2                |
      | Al    | lowest     | 78.7              | 3                |

3. Band Theory
   a. Band theory is an attempt to explain some of the properties of metals using molecular orbital theory. The molecular orbitals of solids are called bands because a large number of orbitals often are very close to each other in energy.
   b. Example Li
      
      for Li₂  \( 1\sigma_g^2 1\sigma_u^{2*} 2\sigma_g^2 \)

\[
\begin{array}{c}
2s \\
\text{2s} \\
2\sigma_g \\
\end{array}
\]
for Li₃

for Li₄

for Liₙ

the Liₙ the energy levels are so close together that the electrons can move freely between the levels

c. electrical conductivity

1. because the HOMO band of the Li is half filled, the electrons can move through the material. This allows the conduction of electricity.

2. Example: Mg
   a. in Mg, the band arising from the 3s orbitals is filled. This would suggest that Mg should be an insulator.
b. this is not the case because the empty band from the 3p orbital overlaps with the filled band from the 3s orbital to create a partially filled band. The 3p and 3s bands form one large band that is partially filled, allowing Mg to be a good conductor.

D. Covalent-lattice materials

1. Covalent lattice materials are formed when nonmetals or semimetals are covalently bonded to each other in such a way that the bonds extend throughout the solid (i.e. no molecules are present).

2. Covalent lattice materials are generally either insulators or semiconductors. This behavior can be explained using band theory
   a. insulator - a material with a large energy gap between its highest energy filled band (HOMO-valence band) and its lowest energy empty band (LUMO-conduction band).
   b. metal - a material with either no energy gap or a very small energy gap between the valence and conduction bands
   c. semiconductor - a material with an energy gap between the valence and conduction bands that is intermediate between that of metals and insulators
d. example

<table>
<thead>
<tr>
<th>element</th>
<th>band gap (kJ/mol)</th>
<th>resistivity (Ω-cm)</th>
<th>classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (diamond)</td>
<td>580</td>
<td>$10^6$</td>
<td>insulator</td>
</tr>
<tr>
<td>Si</td>
<td>105</td>
<td>$6 \times 10^4$</td>
<td>semiconductor</td>
</tr>
<tr>
<td>Ge</td>
<td>58</td>
<td>50</td>
<td>semiconductor</td>
</tr>
<tr>
<td>Sn (gray)</td>
<td>7</td>
<td>1</td>
<td>near metal</td>
</tr>
</tbody>
</table>

3. Intrinsic semiconductors are pure elements or compounds
   a. some conduction can occur in semiconductors because some electrons have enough thermal energy to jump between the energy bands - intrinsic semiconduction

1. the conductivity of a semiconductor is proportional to the temperature because as the temperature increases more electrons have sufficient energy to jump from the valence to the conduction bands.
2. Explanation - Boltzmann energy distribution

![Graph showing Boltzmann energy distribution with two temperatures T1 and T2, and number on the y-axis and energy on the x-axis.]

4. Imperfect or defect semiconductors
   a. If a pure semiconductor is doped with an element containing fewer electrons, a p-type semiconductor may be formed.

![Diagram of conduction band and valence band with electrons and holes indicated.]

1. In this type of semiconductor, the electron deficient element has empty energy levels that lie just above the valence band. Promotion of electrons from the valence band into the empty acceptor levels creates positive holes in the valence band which can conduct electricity.
2. examples:
   Ga in Ge
   B in Si

b. if a pure semiconductor is doped with an element containing more electrons, an n-type semiconductor may be formed

1. the amount of conduction depends on the energy gap between the impurity levels and the bottom of the conduction band and the amount of the impurity that is added.

2. examples
   As in Ge
   P in Si

5. purification of semiconductor materials
   a. Si
      1. chemical purification

\[
3 \text{HCl (g)} + \text{Si(s)} \xrightarrow{350 \degree C} \text{SiHCl}_3 + \text{H}_2 \xrightarrow{\text{distill}} \text{SiHCl}_3 \xrightarrow{>350 \degree C} \text{Si}
\]
2. zone refining - once the pure Si obtained, the final purification is carried out using zone refining. In this process, and ingot of Si is melted and then cooled as a heater moves along the ingot. The impurities remain in the liquid phase while the pure Si crystallizes as the heater moves away.

b. Ge
1. chemical purification

\[ \text{Ge (s)} + \text{GeI}_4 (g) \xrightarrow{500 \degree C} \xrightarrow{350 \degree C} 2 \text{GeI}_2 (g) \]

![Chemical reaction diagram]

2. the Ge is then zone refined using the same procedure as for the Si

6. applications of semiconductors
a. photoelectric cell

![Photoelectric cell diagram]
1. light promotes electrons from the valence band into the conduction band. Due to the band bending at the surface, the hole in the valence band stays on the surface while the electrons in the conduction band move into the body of the semiconductor.
2. oxidation occurs at the surface of the semiconductor by the electrons being removed to fill the holes in the valence band.
3. reduction occurs at the metal by electrons from the conduction band.
4. net effect is to turn light energy into chemical bond energy

b. photovoltaic cell

1. irradiation of a p/n-junction causes electrons to jump from the valence band into the conduction band leaving holes in the valence band.
2. the holes then move up into the valence band of the p-type semiconductor and the electrons move down into the conduction band of the n-type semiconductor.
3. this creates a current flow
4. net effect is to turn light energy into electric energy (current)
c. rectifier - diode

1. current can flow from n-type semiconductor to p-type semiconductor (p+ n-)
   because electrons and holes can combine at the p/n-junction

2. current cannot flow from p-type semiconductor to n-type semiconductor
   because the p/n-junction becomes depleted in charge carriers.

3. the net effect is to convert an AC current (two way current flow) into a DC current (one way current flow).
d. insulated-gate field-effect transistor (FET)

1. when there is no charge on gate, there is no current flow because the current cannot cross the p to n junction

2. when there is a + charge on gate, the + charge on the gate drives the holes from the surface temporarily converting the p-type semiconductor into an n-type semiconductor. This allows the current to flow because it no longer has to cross a p to n junction.

3. the transistor controls the current flow by allowing it to be either on or off. This allows it to serve in binary devices.
E. Molecular and Atomic Solids

1. Physical properties
   a. Low melting points
   b. Soft
   c. Poor electrical and thermal conductors

2. Molecular solids have molecules at the lattice points and holes in a unit cell
   a. example: H$_2$O
      1. oxygens are located at the lattice points of a face-centered cubic unit cell and in one half of the tetrahedral holes.
      2. each water forms four hydrogen bonds to other water molecules. Two are through the hydrogens of the water molecule and the other two are through the lone pairs on the oxygens.
   b. Molecules are held together by weak non-covalent intermolecular interactions
      1. H-bonding
      2. dipole-dipole
      3. London forces
   c. When the solid is melted, the weak non-covalent interactions are disrupted. The covalent bonds holding the molecules together are not broken. Because weak non-covalent interactions are disrupted, the melting points are low.
   d. the solids are soft because when they are deformed, only weak non-covalent interactions are disrupted.

V. Liquids and Solutions

A. Liquids have properties intermediate between solids and gases
   1. Short range order $\rightarrow$ density like solid
   2. No long range order $\rightarrow$ fluids like gases

B. Most liquids are composed of molecules
   1. solutions are generally composed of ionic substances, molecular substances or atomic substances dissolved in molecular substances. To understand solutions, it is necessary to understand the various types of interactions that can occur between ions and molecules. These are referred to as non-covalent interactions.
2. ion-dipole - strongest interaction  
   a. a dipole is defined as two equal and opposite partial charges, \( q^+ \) and \( q^- \), separated by a distance, \( r' \). All polar molecules have a dipole.  
      1. example: dichloromethane  
      \[
      \text{H} \quad \text{Cl} \quad \text{C} = \quad \text{Cl} \quad +Z \quad -Z \quad q^+ \quad q^- \quad q^+ \quad q^- \quad q^+ \quad q^- \quad q^- \quad q^+ \]
   b. cations interact with the negative end of the dipole and anion interact with the positive end  
   c. these are fairly strong interactions that are important in solutions of ionic materials in polar solvents.  
   d. the energy of the interaction is proportional to \( 1/r^2 \) where \( r \) is the distance between the center of the ion and the center of the dipole.  
3. dipole-dipole  
   a. two types are possible with the end to end being the most important  
   b. not as strong as ion-dipole because both molecules only have partial charges  
   c. important in solid and liquid phases of polar molecules and in solutions of a polar molecule in a polar solvent.  
   d. the energy of the interaction is proportional to \( 1/r^3 \) where \( r \) is the distance between the centers of the dipoles.
4. ion-induced dipole
   a. An ion will distort the electron cloud of a nonpolar molecule forming a temporary dipole. The strength of the interaction increases as the ease with which the electron cloud (polarizibility) of the nonpolar material increases. Remember, polarizibility generally increases with increasing molecular weight.
   b. Not as strong as ion-dipole because the induced dipole is generally smaller than the permanent dipole.
   c. Important when ions are dissolved in nonpolar liquids (not very common).
   d. The energy of the interaction is proportional to $1/r^4$ where $r$ is the distance between the centers of the ion and the molecule.

5. dipole-induced dipole
   a. A dipole can also distort the electron cloud of a nonpolar molecule forming a temporary dipole.
   b. Weaker than ion-induced dipole because the dipole only has a partial charge.
   c. Important in solutions containing both polar and nonpolar molecules.
   d. The energy of the interaction is proportional to $1/r^6$ where $r$ is the distance between the centers of the dipole and the molecule.
6. instantaneous dipole-induced dipole = London forces
   a. although nonpolar molecules on the average have a symmetrical charge distribution, this does not have to be true at any particular time. The unsymmetrical charge distribution in a molecule can induce a dipole in a neighboring molecule.

   \[\text{q}^+ \quad \text{q}^- \quad \text{q}^+ \quad \text{q}^-\]

   b. weaker than dipole-induced dipole because the instantaneous dipole is not permanent.
   c. occurs in all solutions, but most important in solutions of nonpolar materials.
   d. the energy of the interaction is proportional to \(1/r^6\) where \(r\) is the distance between the centers of the two molecules.

7. H - bonding (strong)
   a. occurs in any system in which
      1. a hydrogen is covalently bonded to an electronegative atoms (generally N, O or F) and
      2. an electronegative atom has an unshared pair of electrons

   \[\text{H} - \text{N} - \text{H} - \text{N} - \text{H} - \text{N} - \text{H} - \text{N} - \text{H}\]

   b. unsymmetric H-bond (most common) - the hydrogen is within a normal single bond distance to one electronegative atom (0.9 to 1.0 \(\Delta\)) and significantly farther from the second electronegative atom (1.6 to 2.1 \(\Delta\)). The E-H-E angle is generally close to 180 \(\varepsilon\).
1. cannot be a covalent bond because the hydrogen has only one 1s orbital that can be involved in bonding.
2. stronger than a normal dipole-dipole interaction

c. symmetric H-bonds (less common) - the hydrogen is equidistant from both electronegative atoms.
   1. these tend to be stronger than the unsymmetric H-bonds
   2. occur in HF solutions and in solutions of some carboxylic acids
   3. example:
      
      F-H-F⁻ is an anion with symmetrical H-bonds whose salts can be isolated

d. H-bonding is the reason that 2nd row binary hydrides have anomalously high melting points and boiling points when compared to other hydrides in the same group.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>b.p. (EC)</th>
<th>intermolecular forces</th>
<th>trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>-60.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂Se</td>
<td>-42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂Te</td>
<td>-2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C. Effects of Bonding on Properties of Materials

1. ionic materials
   a. ion-ion interactions are very strong and must be disrupted to melt or deform ionic solids
   b. therefore, these materials
      1. tend to be found only as solids
      2. have high melting points
      3. are hard and brittle

2. covalent lattice materials
   a. covalent bonds are very strong and must be disrupted to melt or deform covalent-lattice solids
b. therefore, these materials
   1. tend to be found only as solids
   2. have high melting points
   3. are hard and brittle

3. metallic materials
   a. metal-metal interactions are highly variable and nondirectional
   b. therefore, these materials
      1. can exhibit a wide range of melting points but generally have high boiling points.
      2. may be hard or soft
      3. ductile and malleable

4. molecular materials
   a. intermolecular forces are relatively weak
   b. therefore these materials
      1. are generally low melting solids, liquids or gases
      2. generally soft

5. atomic materials
   a. interatomic forces are very weak
   b. therefore these materials are always gases

6. we can predict the relative melting or boiling points of materials if we understand the forces that must be disrupted when these materials are melted or vaporized.
   a. example: predict the relative melting points of the below materials
      
      HCl  Si  Ar  HF
b. example: predict the relative melting points of the below materials

SiO₂  Mg  CH₃OH  CH₂Cl₂

D. Dissolution in liquids - thermodynamic process

1. thermodynamics of dissolution processes
    a. if $\Delta G$ is negative, the dissolution will occur
    b. if $\Delta G$ is positive, dissolution will not occur
    c. $\Delta G = \Delta H - T\Delta S$

1. $\Delta H$ depends on intermolecular forces
based on the preceeding diagram, solubility is favored by
a. Strong solute - solvent interactions
b. Weak solute - solute interactions
c. Weak solvent - solvent interactions

2. $\Delta S$ depends on the relative ordering of molecules in the solution versus that of molecules in the solute + solvent.
   a. $T\Delta S$ needs to be positive to be favorable for dissolution
   b. entropy generally favors a dissolution process because these are generally accompanied by an increase in the disorder of the system which means $T\Delta S$ will be positive.
   c. exception: hydrophobic effect
      1. example: $\text{C}_3\text{H}_8 (\text{P}) \rightarrow \text{C}_3\text{H}_8 (\text{aq})$
         $\Delta H = -8 \text{ kJ/mol}$
         $\Delta S = -80 \text{ J/mol K}$
         $\Delta G = 16 \text{ kJ/mol}$
      2. explanation
         a. The polar water does not effectively solvate the nonpolar $\text{C}_3\text{H}_9$. Thus, the water actually has less space after the addition of the $\text{C}_3\text{H}_9$. This forces the water to become more ordered and thus causes $\Delta S$ to be negative.
         b. Because the water does not effectively solvate the $\text{C}_3\text{H}_9$, few $H$-bonds are broken so there is little change in $\Delta H$.
         c. The net result is that at 298 K, $\Delta G$ is predominately due to the $T\Delta S$ term and is positive. This means little dissolution will occur.
2. Dissolution of ionic solids in H₂O and organic solvents
   a. Hess’s Law cycle for dissolution process

\[
MX (s) \xrightarrow{-U_o} M^{n+} (g) + X^{n-} (g)
\]

\[
\Delta H_{\text{soln}} = \Delta H_{\text{hyd (cation)}} + \Delta H_{\text{hyd (anion)}} - U_o
\]

1. \(\Delta H_{\text{soln}} = \Delta H_{\text{hyd (cation)}} + \Delta H_{\text{hyd (anion)}} - U_o\)

b. hydration

![Hydration diagrams]

c. cases

1. dissolution of ionic solid in polar liquid
   a. \(\Delta H_{\text{hyd}}\) is due to ion-dipole interactions and thus will be relatively strong. Its magnitude will depend on the charges on the ions and the dipole moment.
   b. if the charges on the ions are low
      1. the sum of the heats of hydration is of approximately the same magnitude as is the lattice energy, and \(\Delta H\) for dissolution is only slightly negative (endothermic) or positive (exothermic).
      2. this means that the dissolution is driven by the entropy (\(\Delta S\) is positive).
3. these ionic solids will be soluble.
   c. if the charges on the ions are high
      1. the heat of hydration does not increase as much as does the lattice
         energy because the lattice energy scales as the square of the charge
         while the heat of hydration scales linearly with charge.
      2. this means dissolution is always highly endothermic, and the entropy
         cannot make up for it.
      3. these ionic solids will be insoluble.

2. dissolution of an ionic solid in a nonpolar solution.
   a. \( \Delta H_{\text{hyd}} \) is due to ion-induced dipole interactions and thus will be weak.
   b. this means dissolution is always highly endothermic, and the entropy
      cannot make up for it.
   c. ionic solids are generally insoluble in nonpolar solvents.

3. dissolution of organic solids and liquids in organic liquids
   a. like dissolves like
      1. if either solute-solute or solvent-solvent interactions are strong, then solute-
         solvent interactions must also be strong to balance.
      2. if both solute-solute and solvent-solvent interactions are weak, then solute-
         solvent interactions can also be weak.
   b. cases

<table>
<thead>
<tr>
<th>solute-solute</th>
<th>solvent-solvent</th>
<th>solute-solvent</th>
<th>solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-bonding</td>
<td>H-bonding</td>
<td>H-bonding</td>
<td>H-bonding</td>
</tr>
<tr>
<td>H-bonding</td>
<td>dipole-dipole</td>
<td>H-bonding</td>
<td>H-bonding</td>
</tr>
<tr>
<td>H-bonding</td>
<td>dipole-dipole</td>
<td>dipole-dipole</td>
<td>dipole-dipole</td>
</tr>
<tr>
<td>H-bonding</td>
<td>London forces</td>
<td>dipole-induced dipole</td>
<td>dipole-induced dipole</td>
</tr>
<tr>
<td>dipole-dipole</td>
<td>dipole-dipole</td>
<td>dipole-dipole</td>
<td>dipole-dipole</td>
</tr>
<tr>
<td>dipole-dipole</td>
<td>London forces</td>
<td>dipole-induced dipole</td>
<td>dipole-induced dipole</td>
</tr>
<tr>
<td>London forces</td>
<td>London forces</td>
<td>London forces</td>
<td>London forces</td>
</tr>
</tbody>
</table>
VI. Lewis Acid-Base Theory

A. Definitions

1. Lewis acid - electron pair acceptor (must have an empty orbital)
   a. examples: H⁺, BF₃

2. Lewis base - electron pair donor (must have unshared pair of electrons)
   a. examples: NH₃, OH⁻

3. Lewis acid-base reaction - the reaction of a Lewis acid with a Lewis base to form an acid-base adduct.
   a. example: BF₃ + NH₃ \rightarrow F₃B←NH₃

B. Factors Affecting the Strengths of Lewis Acids and Bases

1. electronic
   a. position of the donor or acceptor atom in the Periodic Table
      1. base strength decreases from left to right across a row but acid strength
         increases from left to right across a row because the increasing
         electronegativity of the element makes it a poorer electron pair donor and a
         better electron pair acceptor.
         a. base strength: Me₃N > Me₂O > MeF
         b. acid strength: Me₃B > Me₂Be > MeLi
      2. both acid and base strength decrease from top to bottom down a column
         because the orbital overlap decreases as the size of the orbitals increase.
         a. base strength
            | base        | ΔH_{rxn} with Me₃B | stability of HCl adduct |
            | Me₃N       | -74 kJ/mol         | sublimes at 250 EC      |
            | Me₃P       | -67 kJ/mol         | sublimes at 125 EC      |
            | Me₃As      | exists only at -80 EC | unstable at 21 EC      |
            | Me₃Sb      | does not exist     | unstable at -80 EC      |
         b. acid strength: Be²⁺ > Mg²⁺ > Ca²⁺
b. hard-soft nature of acids and bases
1. two class of acids and bases have been observed
   a. hard acids form strongest adducts with second row bases
      1. $F^- >> Cl^- > Br^- > I^-$
         $R_2O >> R_2S$
         $R_3N >> R_3P$
      2. hard acids include
         $H^+$, $SO_3$, $BF_3$
         alkali metal and alkaline earth cations
         first row transition metals in higher oxidation states
   b. soft - form strongest adducts with third, fourth and fifth row bases
      1. $F^- < Cl^- < Br^- < I^-$
         $R_2O << R_2S > R_2Se > R_2Te$
         $R_3N << R_3P > R_3As > R_3Sb$
      2. soft acids include
         $BH_3$
         first row transition metals in lower oxidation states
         second and third row transition metals
2. hard acids and bases interact primarily through electrostatic interactions; soft acids and base interact primarily through covalent interactions
3. in competitive situations where two acids and two bases are present, hard acids will preferentially bond to hard bases and soft acids to soft bases
   a. example:

   $MeHgF + HSO_3^- \rightleftharpoons MeHgSO_3^- + HF \quad K_{eq} = 10^3$

   soft acid- hard acid- soft acid- hard acid-
   hard base  soft base  soft base  hard base
b. example:

\[
\text{MeHgOH} + \text{HSO}_3^- \rightleftharpoons \text{MeHgSO}_3^- + \text{H}_2\text{O} \quad \text{Keq} > 10^7
\]

<table>
<thead>
<tr>
<th>soft acid-</th>
<th>hard acid-</th>
<th>soft acid-</th>
<th>hard acid-</th>
</tr>
</thead>
<tbody>
<tr>
<td>hard base</td>
<td>soft base</td>
<td>soft base</td>
<td>hard base</td>
</tr>
</tbody>
</table>

4. if only one base or acid is present, both the strength and the hard/soft nature must be taken into account

a. example: a stronger soft base can displace a weaker hard base from a hard acid.

\[
\text{SO}_3^{2-} + \text{HF} \rightleftharpoons \text{HSO}_3^- + \text{F}^- \quad \text{Keq} = 10^4
\]

b. example: a stronger hard base can displace a weaker soft base from a soft acid.

\[
\text{OH}^- + \text{MeHgSO}_3^- \rightleftharpoons \text{MeHgOH} + \text{SO}_3^{2-} \quad \text{Keq} = 10
\]

c. substituent effects

1. inductive effects

a. electron withdrawing substituents weaken bases and strengthen acids

b. electron donating substituents strengthen bases and weaken acids

c. example: base strength: \text{Me}_3\text{N} > \text{H}_3\text{N} > \text{F}_3\text{N}

d. example: acid strength: \text{Me}_3\text{B} < \text{H}_3\text{B} < \text{F}_3\text{B}

e. explanation
2. resonance effects
   a. if the atom with the empty orbital in a Lewis acid is directly bonded to an atom with nonbonding electron pairs, the Lewis acidity may be lower than expected due to $\pi$-bonding.
   b. example: boron trihalides

2. steric effects (not important when the Lewis acid is $\text{H}^+$)
   a. bulky substituents near the atom that is either accepting or donating a pair of electrons can reduce the strength of acids and bases by keeping them from approaching optimal bond distances. This is referred to as F-strain.
   1. example

   $\text{N} \text{CH}_3$ versus $\text{N}$
   forms stronger adduct with $\text{H}^+$

   a. explanation
F-strain can be eliminated when the substituents are bonded to each other in such a way as to prevent them from interfering with the formation of the acid-base adduct. This is often referred to as B-strain.

2. example

\[
\begin{array}{c}
\text{H}_3\text{C} & \text{N} & \text{CH}_3 \\
\end{array}
\]

does not form adduct with Me\textsubscript{3}B but does form a stable adduct with Et\textsubscript{3}Al

2. a. explanation

b. F-strain can be eliminated when the substituents are bonded to each other in such a way as to prevent them from interfering with the formation of the acid-base adduct. This is often referred to as B-strain.

1. example

\[
\begin{array}{c}
\text{N} \quad \text{Me_3B} & \text{Et_3Al} \\
\end{array}
\]

\[\Delta H_{\text{rxn}} \text{ with Me_3B} \quad -42 \text{ kJ/mol} \quad -84 \text{ kJ/mol}\]

1. a. explanation
VII. Coordination Chemistry

A. History - 1880's and 1890's

1. Main group elements exhibited either 1 fixed valence, like C (IV), or several fixed valences like P (III or V). Once these valences were filled, no further bonds could be formed.

2. Transition metals, in contrast, appeared to be able to form bonds after the fixed valence was reached
   a. Examples
      \[
      \begin{align*}
      \text{CrCl}_3 + 6 \text{NH}_3 & \rightarrow \text{CrCl}_3(\text{NH}_3)_6 \\
      \text{PtCl}_2 + 4 \text{NH}_3 & \rightarrow \text{PtCl}_2(\text{NH}_3)_4
      \end{align*}
      \]

3. Jorgenson attempted to explain this bonding using concepts of the day but was unsuccessful.

   \[
   \begin{array}{c}
   \text{Cl—NH}_3 \\
   \backslash \text{NH}_3—\text{Pt—NH}_3 \\
   \backslash \text{NH}_3—\text{Cl}
   \end{array}
   \]

3. Alfred Werner was able to explain this behavior
   a. Empirical formula  # ionic Cl’  # ions  true formula
      \[
      \begin{array}{cccc}
      \text{PtCl}_4•6 \text{NH}_3 & 4 & 5 & \text{PtCl}_4(\text{NH}_3)_6 \\
      \text{PtCl}_4•5 \text{NH}_3 & 3 & 4 & \text{PtCl}_4(\text{NH}_3)_5 \\
      \text{PtCl}_4•4 \text{NH}_3 & 2 & 3 & \text{PtCl}_4(\text{NH}_3)_4 \\
      \text{PtCl}_4•3 \text{NH}_3 & 1 & 2 & \text{PtCl}_4(\text{NH}_3)_3 \\
      \text{PtCl}_4•2 \text{NH}_3 & 0 & 0 & \text{PtCl}_4(\text{NH}_3)_2 \\
      \end{array}
      \]

   b. Empirical formula  # ionic Cl’  color  true formula
      \[
      \begin{array}{cccc}
      \text{CoCl}_3•6 \text{NH}_3 & 3 & \text{yellow} & \text{CoCl}_3(\text{NH}_3)_6 \\
      \text{CoCl}_3•5 \text{NH}_3 & 2 & \text{purple} & \text{CoCl}_3(\text{NH}_3)_5 \\
      \text{CoCl}_3•4 \text{NH}_3 & 1 & \text{green} & \text{CoCl}_3(\text{NH}_3)_4 \\
      \text{CoCl}_3•4 \text{NH}_3 & 1 & \text{violet} & \text{CoCl}_3(\text{NH}_3)_4 \\
      \end{array}
      \]
c. the number of isomers that were observed determined the coordination geometry about the metal ion

<table>
<thead>
<tr>
<th></th>
<th>Planar</th>
<th>Trigonal Prismatic</th>
<th>Octahedral</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>MA₄B₂</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>MA₄B₂</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

B. Coordination compounds (transition metal complexes) are compounds formed by the coordination of one or more Lewis bases (ligands) to a transition metal Lewis acid.

1. primary coordination sphere - metal atom or ion and the ligands directly bonded to it. Enclosed in brackets [ ] in a line formula unless every ligand in the line formula is in the primary coordination sphere.

2. coordination number - the number of coordinate-covalent bonds formed between the ligands and the metal.

3. ligand - a neutral or anionic Lewis base coordinated to the metal.

a. definitions

1. dentate (teeth) - defines the number of coordinate-covalent bonds formed between a ligand and any number of metals.

   a. monodentate = 1
   b. bidentate = 2
   c. tridentate = 3
   d. tetradentate = 4
   e. polydentate = many (general term for ligands that form two of more coordinate-covalent bonds to metals)

b. the number of atoms donating electrons to the metal center is designated by an $\eta^#$ in which the # is the number of donor sites. This is placed in from the ligand name or formula and separated by a hyphen (-).

   1. example: $\eta^5$-C₅H₅ or $\eta^5$-cyclopentadienyl
   2. chelating (claw or pincer) ligands are polydentate ligands that form all coordinate-covalent bonds to the same metal.
3. Bridging ligands are polydentate ligands that form coordinate-covalent bonds to two or more different metal. These are designated by a mu in front of the ligand.

4. Examples

b. Metal ligand bonding

1. Most ligands bond to metals via coordinate covalent bonds which are formed by donation of electrons from an unshared pair on the ligand into an empty hybrid orbital on the metal.
   a. Example: \([\text{Pt(NH}_3\text{)}_6]^{4+}\)

2. In addition, some ligands are capable of accepting electron density from partially filled d orbitals on the metal. These ligands either have empty p, d or \(\pi^*\) orbitals. Such ligands are referred to as \(\pi\)-acceptor ligands.
   a. Example: d-\(\pi^*\)
b. Example: d-d

![Diagram of d-d interaction](image)

c. Example: d-p

![Diagram of d-p interaction](image)

3. Alkenes and alkynes can serve as ligands even though they do not have unshared pairs of electrons - Chatt-Dewar-Duncanson Model

![Diagram showing hybrid orbitals](image)

c. Common ligands

1. H⁻ - hydride
   a. two-electron σ-donor
   b. bonds to soft metals

2. C-donor ligands
   a. :C=O: - carbonyl
      1. two-electron σ-donor through C; π-acceptor into π* orbitals
      2. bonds to soft metals
b. :C≡N;`

1. anionic, two-electron σ-donor through C; π-acceptor into π* orbitals
2. bonds to both hard and soft metals

C. alkenes and alkynes

1. alkenes are two-electron σ-donors through π-orbital and π-acceptor into π* orbitals
2. alkynes can be either two-electron σ-donors (if monodentate) or four-electron σ-donors (if bridging and bidentate) through π-orbital and are π-acceptors into π* orbitals.
3. both bond to soft metals

D. cyclic aromatic compounds

1. benzene
   a. neutral, six-electron σ-donor through π-orbitals and also π-acceptors into π* orbitals
   b. bonds to soft metals

2. cyclopentadienyl (C₅H₅⁻)

![Image of cyclopentadienyl structure]

a. anionic, six-electron σ-donor through π-orbitals and also π-acceptors into π* orbitals
b. bonds to hard and soft metals
e. carbenes

1. two-electron \( \sigma \)-donor through sp\(^2\) hybrid orbital on carbon and \( \pi \)-acceptors into 2p orbital on C.
2. bonds to soft metals

f. carbanions = alkyl and aryl ligands

1. two-electron \( \sigma \)-donors through sp\(^3\) hybrid orbital on C and aryl may be \( \pi \)-acceptors into \( \pi^* \) orbitals (?).
2. bonds to both soft and hard metals

g. acyl ligands

1. two-electrons \( \sigma \)-donor through sp\(^2\) hybrid orbital on carbon and \( \pi \)-acceptor into \( \pi^* \) orbitals (?).
2. bonds to soft metals
h. allyl ligands

\[ \text{H} - \text{C} \equiv \text{C} - \text{C} \equiv \text{H} \]

1. four-electron $\sigma$-donor through $\pi$ orbitals and $\pi$-acceptor into $\pi^*$ orbitals.
2. bonds to soft metals

3. N-donor ligands
   a. aliphatic amines
      1. two-electron $\sigma$-donor through $sp^3$ orbital on nitrogen
      2. bonds to hard metals
   b. heterocyclic nitrogen bases
      1. two-electrons $\sigma$-donor through $sp^2$ hybrid orbital on nitrogen and $\pi$-acceptor into $\pi^*$ orbitals (?).
      2. bonds to both soft and hard metals
      3. examples

   \[
   \begin{align*}
   \text{pyridine} & \quad \text{imidazole} & \quad 2,2'\text{-bipyridine} \\
   \end{align*}
   \]

c. imines

\[ \text{R} = \text{N} - \text{H} \]

\[ \text{R'} \]
1. two-electron $\sigma$-donor through sp$^2$ hybrid orbitals on N and $\pi$-acceptor into $\pi^*$ orbital.
2. bonds to both soft and hard metals
d. nitriles (R-C≡N:)
   1. two-electron $\sigma$-donor through sp hybrid orbital on N and $\pi$-acceptor into $\pi^*$ orbitals ($?$)
   2. bonds to both hard and soft metals.
e. dinitrogen (:N≡N:)
   1. two-electron $\sigma$-donor through sp hybrid orbital on N and $\pi$-acceptor into $\pi^*$ orbitals.
   2. bonds to soft metals
f. nitric oxide = nitrosyl
   1. found in two forms linear (most common) and bent

   linear
   
   bent

2. linear is cationic, two-electron $\sigma$-donor through sp hybrid orbital on N and $\pi$-acceptor into $\pi^*$ orbitals.
3. bent is anionic, two-electron $\sigma$-donor through sp$^2$ hybrid orbital on N and a $\pi$-acceptor into $\pi^*$ orbital.
4. both bond to soft metals
5. P-donor ligands
   a. all are soft donor ligands and $\sigma$-donate two electrons per phosphorus, and
      phosphites may also serve as $\pi$-acceptors into d-orbitals.
   b. examples

   ![Phosphine and Phosphite Structures]

6. O-donor ligands
   a. ethers, alcohols and water are all two-electron $\sigma$-donor ligands and weakly
      coordinate to hard metals.
   b. alkoxides and aryloxides are also two-electron $\sigma$-donor ligands and
      strongly coordinate to hard metals.
   c. $\beta$-diketones are good ligands for soft metals because they can easily be
      deprotonated to generate an anionic, four-electron donor chelating ligand
      ($\sigma$-donor through electron pairs on O and $\pi$-acceptor into $\pi^*$ orbital).

   ![Beta-Diketone Structure]

   d. carboxylates are good ligands for hard metals
      1. example: EDTA - chelating, six-electron $\sigma$-donor ligand that is ideal
         for coordinating to all six sites in an octahedron

   ![EDTA Structure]
7. S-donor ligands
   a. thiolates (R-S⁻) are good two-electron σ-donors for soft metals
   b. dithiocarbamate is a chelating, four-electron σ-donor

![Dithiocarbamate structure](image)

8. Halide-donor ligands
   a. halides can either serve as two-electron σ-donor ligands or as bridging,
      four-electron σ-donor ligands

9. Macroyclic ligands
   a. ligands which have multiple donor atoms in a cyclic structure form
      complexes that are more stable than are those with similar monodentate
      ligands
   b. porphyrins - dianionic, eight-electron σ-donor (2 per N) and π-acceptor
      ligands found in many biological systems such as oxygen transport
      proteins (hemoglobin) and electron transport proteins (cytochromes c and
      f) and oxidation catalysts (cytochrome P450).

![Porphyrin structure](image)
c. crown ethers - excellent ligands for alkali metal cations and other hard metal cations. These donate two-electrons per oxygen. The size of the ring determines the selectivity for the various hard metal cations.

\[ \text{Diagram of crown ether} \]

d. cryptands - three dimensional crown ethers. These are even better for binding alkali metal cations and other hard metal cations. These donate two-electrons per each oxygen and nitrogen.

\[ \text{Diagram of cryptand} \]

C. 18-electron rule

1. in general, a complex may have no more than 18 valence electrons (electrons in the \( n-1d \), ns and np orbitals)

   a. valence electrons are defined as the d electrons on the metal plus electrons donated to the metal by the ligands via coordinate-covalent bonds. Note that electrons involved in metal to ligand \( \pi \) bonding are not included in this.
2. example: show that \([\text{Pt(NH}_3\text{)}_6]^{4+}\) obeys the 18 electron rule

3. example: show that \([\text{RhCl(CO)(PPh}_3\text{)}_2]\) obeys the 18 electron rule

4. example: determine the oxidation state of the Co and the number of valence electrons in \([\text{Co(NO)(CO)}_3]\)
5. example: determine the oxidation state of the Mn and the number of valence electrons in \([\text{Mn}(\eta^5-C_5\text{H}_5)\{\text{C(O)CH}_3\}\{(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\}]\)

D. Structures of Coordination Compounds

1. isomers are complexes with the same empirical formulas but with different arrangements of ligands and metals
   a. structural isomers contain the same ligands and metals but have different ligand metal bonds
   b. stereoisomers contain the same ligands and metals and have the same metal-ligand bonds but have different arrangements of the ligands about the metal.

2. structural isomers
   a. coordination isomers differ in the ligands that are coordinated to two or more metal centers.
      1. Example: \([\text{Co(NH}_3)_6][\text{Cr(CN)}_6]\) and \([\text{Cr(NH}_3)_6][\text{Co(CN)}_6]\)
   b. ionization isomers differ in the anionic ligands that are incorporated into the primary coordination sphere.
      1. Example: \([\text{Pt(NH}_3)_4\text{Cl}_2]\text{Br}_2\) and \([\text{Pt(NH}_3)_4\text{Br}_2]\text{Cl}_2\)
   c. solvate isomers differ in whether solvent molecules are incorporated into the primary coordination sphere, thereby displacing an anionic ligand, or are simply incorporated into the crystal lattice.
      1. Example: \([\text{Cr(H}_2\text{O})_6]\text{Cl}_3, \text{[Cr(H}_2\text{O})_5\text{Cl}]\text{Cl}_2\text{•H}_2\text{O and [Cr(H}_2\text{O})_4\text{Cl]}\text{Cl•2H}_2\text{O}}\)
   d. linkage isomers differ in the atom by which a ligand is coordinated to a metal.
      1. Example: \([\text{Pt(NH}_3)_2(\text{SCN})_2]\) and \([\text{Pt(NH}_3)_2(\text{NCS})_2]\)
      2. Example: \([\text{Co(NH}_3)_5(\text{NO}_2)]\text{Cl}_2\) and \([\text{Co(NH}_3)_5(\text{ONO})]\text{Cl}_2\)
3. stereoisomers
   a. two types of stereoisomers are observed
      1. geometrical isomers have the ligands in different positions relative to each other - these isomers have different physical and chemical properties
      2. optical isomers are nonsuperimposable mirror images of each other - these have identical chemical and physical properties and differ only in the way in which they rotate polarized light.
   b. the types of stereoisomers that are observed depend on the coordination geometry of the ligands.
      1. coordination number 4
         a. tetrahedral complexes
            1. this coordination geometry is favored on steric grounds
            2. optical isomers are observed when all four ligands are different
            3. Example: [TiClBrI(OMe)]

   b. square planar complexes
      1. this coordination geometry is favored on electronic grounds when the metals have d⁸ electron configurations.
      2. geometrical isomers may observed but optical isomers are not
      3. Example: Pt(NH₃)₂Cl₂
2. coordination number 5
   a. trigonal bipyramidal
      1. this coordination geometry is favored on steric grounds and is often observed when all of the ligands attached to the metal are similar.
      2. both geometrical and optical isomers may be observed.
      3. Example: TaCl$_4$Br

4. Example: TaCl$_3$Br$_2$

5. Example: TaCl$_2$BrI(OMe)
b. square pyramidal
   1. most often observed when one of the ligands is very different from the others.
   2. both geometrical and optical isomers may be observed
   3. Example: \( [V(\eta^5-C_5H_5)(CO)_2(PPh_3)_2] \)

   4. Example: \( [W(\eta^5-C_5H_5)(CO)Cl(PPh_3)_2] \)
3. coordination number 6
   a. octahedral
      1. by far the most common, favored on both steric and electronic grounds
      2. both geometrical and optical isomers are observed
      3. Example: \([\text{Mo(CO)}_4(\text{PPh}_3)_2]\)

4. Example: \([\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]\)
5. distorted octahedral complexes are often encountered.
   a. trigonal distortion - ligands on opposite triangular faces are pulled away from each other.
   b. tetragonal distortion - opposite ligands are pulled away from each other.

E. IUPAC Rules for Nomenclature
1. in ionic complexes, the cation is named first and then the anion, regardless of which is the coordination complex
2. the ligands are named before the metal for the coordination complex
3. the names of anionic ligands end in -o, neutral ligands have the same name as the molecule and cationic ligands end in -ium
a. common exceptions

\[ \text{H}_2\text{O} = \text{aquo}, \text{CO} = \text{carbonyl}, \text{NO} = \text{nitrosyl}, \text{NH}_3 = \text{ammine}, \text{C}_5\text{H}_5 = \text{cyclopentadienyl} \]

4. the names of the ligands are listed in alphabetical order without any separation by spaces or hyphens. Complex ligand names may be enclosed in parentheses for clarity. Alphabetization does not include prefixes indicating the numbers of the ligands.

5. if more than one of a ligand or metal is present, its number is indicated by a prefix.
   a. for simple names, the prefixes are bi (two), tri (three), tetra (four), etc. and are written attached to the name of the ligand
   b. for complex names, the prefixes are bis (two), tris (three), tetrakis (four), etc. These are written before the name which is enclosed in parentheses.

6. the oxidation number of the metal is written in Roman numerals and enclosed in parentheses. It is written after the name of the metal.

7. the name of the metal is the same as in the Periodic Table if the coordination complex is either cationic or neutral. If the complex has a negative charge, the root+ate is used for the metal name
   a. Fe ferrate  Ti titanate  V vanadate
   Cu cuprate  Cr chromate  Mn manganate

8. a bridging ligand (one that joins two or more metal centers) is indicated by \( \mu^- \) in front of the ligand name. If more than two metals are bridged, the number of metal centers bridged may be indicated by a subscript after the \( \mu \).

9. the number of atoms in a polydentate ligand that are bound to the metal center may be indicated by an \( \eta^\# \) - before the ligand name.

10. if the metal complex has geometric isomers, the geometry is indicated by an abbreviation in italics - in front of the name of the coordination complex.

11. examples

\[ \text{Mo(CO)}_6 \]
Mo(CO)$_5$(PPh$_3$)

Mo(CO)$_4$(PPh$_3$)$_2$

[Cr(H$_2$O)$_6$](NO$_3$)$_2$

[Cr(H$_2$O)$_4$Cl$_2$](NO$_3$)

K$_2$[Pt(SCN)$_6$]

(NH$_4$)$_2$[CrOF$_4$]

Na$_3$[Fe(CN)$_5$CO]

![Chemical structure](image)

cis-diaminedichloroplatinum(II)
cis,cis,trans-dicarbonyldichlorobis(triphenylphosphine)ruthenium(II)

triamminetriiodopalladium(IV) perchlorate

sodium decacarbonyldimolybdate(-I)

F. Bonding Theories
   1. Valence Bond Theory - Linus Pauling
      a. The formation of a complex is assumed to occur via Lewis acid-base reactions in
         which the metal is the Lewis acid and the ligands are the Lewis bases. Ligands
         are attached to the metal via coordinate-covalent bonds.
      b. The metal is hybridized in such a way as to be consistent with the observed
         numbers of unpaired electrons and the geometry of the complex.
c. example: explain why square planar Pt(II) complexes are diamagnetic

d. example: explain why tetrahedral Ni(II) complexes are paramagnetic

e. example: how many unpaired electrons would a paramagnetic, octahedral Co(III) complex have.
f. Valence bond theory has a number of serious limitations and is no longer used. The major limitations are that it has no predictive power and that it cannot explain the colors and electronic spectra of transition metal complexes.

2. Crystal (Ligand) Field Theory

a. In crystal field theory, the interaction between the ligands and the metal is assumed to be primarily electrostatic. The primary effect of the ligand electron pairs is to break the degeneracy of the d-orbitals.

b. Splitting of metal d-orbitals in an octahedral complex

1. The ligand electron pairs lie along the x, y, and z axes of a Cartesian coordinate system.

2. Repulsion between the ligand electron pairs and electrons in the d orbitals raises the energies of all of the d orbitals, but not to the same extent.

   a. $d_{z^2}$ and $d_{x^2-y^2}$ - lobes point directly at the ligand electron pairs and thus are higher in energy.
b. \( d_{xy}, d_{xz} \) and \( d_{yz} \) are not raised as much because the ligand electron pairs point between the lobes of the orbitals.
c. electron configurations of octahedral complexes

1. because the d orbitals have different energies, there are two arrangements of the electrons in these orbitals with certain numbers of d electrons.
   a. high spin - fill both t<sub>2g</sub> and e<sub>g</sub> orbitals with one electron before pairing any electrons
   b. low spin - fill the t<sub>2g</sub> set of orbitals completely before putting any electrons in the e<sub>g</sub> set of orbitals

2. these configurations may have different energies because of the difference in energies of the t<sub>2g</sub> and e<sub>g</sub> orbitals and the different numbers of paired electrons. The difference in energy of between that of the octahedral field and of the hypothetical spherical field is called the Crystal Field Stabilization Energy (CFSE).
   a. CFSE = \(-0.4(# \text{t}_2\text{g~e}^-)\Delta_o + 0.6(# \text{e}_g^-)\Delta_o + (# \text{additional e}^- \text{pairs})P\)

   P = pairing energy
3. summary of d electron configurations for octahedral complexes

<table>
<thead>
<tr>
<th>High Spin</th>
<th>Low Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td># config. unpaired e⁻CFSE</td>
<td>config. unpaired e⁻CFSE</td>
</tr>
</tbody>
</table>

4. whether a low or high spin configuration is observed depends on the relative magnitudes of $\Delta_o$ and $P$
   a. example: $d^4$ configuration

![Diagram showing the relationship between $P$, CFSE, and $\Delta_o$ for high and low spin configurations.](image-url)
b. a complex will be high spin when $P > \Delta_0$. Such complexes are also referred to as weak field complexes

c. a complex will be low spin when $P < \Delta_0$. Such complexes are also referred to as strong field complexes

d. factors affecting pairing energy and $\Delta_0$

1. pairing energy

   a. inherent - repulsion which must be overcome to force two electrons into the same orbital. This remains essentially constant for all transition metals in a particular row.

   b. loss of exchange energy - there are more possible arrangements for configurations in which the electrons are unpaired than for those in which the electrons are paired. This means that configurations with paired electrons are of higher energy. The difference in energy between the configurations with paired and unpaired electrons is proportional to the number of pairs of electrons that can be arranged to form $n$ parallel spins and thus is greatest for a $d^5$ configuration. This is the explanation of the special stability of the half filled $d$ shell.

2. $\Delta_0$

   a. position of the metal in the Periodic Table.

      1. $\Delta_0$ increases as you move down a column in the Periodic Table because the size of the $d$ orbitals increase and the electrons in these orbitals are closer to the ligand electron pairs.

      2. the result of this is that nearly all second and third row transition metal complexes are low spin.

   b. oxidation state of the metal

      1. $\Delta_0$ increases as the oxidation state of the metal increases because the ligands move closer to the metal, and thus their electron pairs are closer to the metal $d$ electrons
c. nature of the ligands
   1. spectrochemical series

   $I^{−} < Br^{−} < S^{2−} < SCN^{−} < Cl^{−} < NO_{3}^{−} < F^{−} < OH^{−} < H_{2}O < NCS^{−} < MeCN < NH_{3} < NO_{2}^{−} < PR_{3} < CN^{−} < CO$

   2. the above ordering cannot be explained by the basicity of the ligands and shows that the d-orbital splitting is not due entirely to electrostatic factors.

   3. Because so many factors affect the values of both $P$ and $\Delta_o$, it is not possible to \textit{a priori} predict whether a complex with be high or low spin simply by inspection of the metal and ligands present.

e. evidence for crystal field stabilization energy - if crystal field stabilization energy is real, its effects should be exhibited in the physical and chemical properties of the complexes.

   1. ionic radii of transition metals in coordination complexes
2. hydration energies of transition metal cations
\[ M^{2+}(g) + n \text{H}_2\text{O} (\text{P}) \rightleftharpoons M(\text{H}_2\text{O})_n^{2+} \text{(aq)} \] (all are high spin)

3. octahedral complexes with either one or nine d electrons exhibit a single UV-vis transition due to an electron moving from the \( t_{2g} \) to \( e_g \) orbitals. The energy of this transition is related to the ligands on the metal (spectrochemical series).
   a. complementary colors, wavelengths and energies

   - energy increases from red to violet
   - wavelength decreases from red to violet
b. Example: Ti$^{3+}$ forms octahedral complexes with both F$^{-}$ and CN$^-$. One complexes is blue and the other is orange. On the basis of the spectrochemical series, determine which ligand gives the orange complex.

f. splitting of d orbitals in nonoctahedral coordination geometries

1. tetrahedral coordination geometry
   a. In a tetrahedron, ligands can be considered to be at alternate corners of a cube in which the faces are perpendicular to the axes of the Cartesian coordinate system.

   ![Tetrahedral Coordination Geometry Diagram]

   b. $\Delta_T$ is smaller than $\Delta_o$ because there are fewer ligands. This means that all tetrahedral complexes are high spin/weak field.
   c. This arrangement is essentially the reverse of that observed for octahedral complexes and reverses the order of the d orbital splitting.
2. square planar coordination geometry

a. square planar coordination geometry is derived from octahedral geometry by removing the two ligands along the z axis. This lowers the energy of the d orbitals along the z axis relative to those that in the xy plane.

b. comparison of octahedral and square planar coordination geometries

G. Reactions at Transition Metal Centers

1. Ligand Substitution Reactions

a. generic reaction:

\[ Y + MX_n \rightleftharpoons YMX_{n-1} + X \]

where

Y is the entering ligand
X is the leaving ligand
MX_n is the metal complex
b. formation constants

1. stepwise

\[ Y + MX_n \leftrightarrow MYX_{n-1} + X \]

\[ K_1 = \frac{[MYX_{n-1}][X]}{[Y][MX_n]} \]

\[ Y + MYX_{n-1} \leftrightarrow MY_2X_{n-2} + X \]

\[ K_2 = \frac{[MY_2X_{n-2}][X]}{[Y][MYX_{n-1}]} \]

\[ Y + MY_2X_{n-2} \leftrightarrow MY_3X_{n-3} + X \]

\[ K_3 = \frac{[MY_3X_{n-3}][X]}{[Y][MY_2X_{n-2}]} \]

\[ \Lambda \]

\[ Y + MY_{n-1}X \leftrightarrow MY_n + X \]

\[ K_n = \frac{[MY_n][X]}{[Y][MY_{n-1}X]} \]

a. the general trend that is observed in the stepwise formation constants is \( K_1 > K_2 > K_3 > ... > K_n \). This trend is due to the decrease in the number of leaving ligands with each successive substitution.

2. overall

\[ nY + MX_n \leftrightarrow MY_n + nX \]

\[ \beta_n = \frac{[MY_n][X]^n}{[Y]^n[MX_n]} \]

a. \( \beta_n = K_1K_2K_3...K_n \)

3. chelate effect

a. when \( K_1 \) for a chelating, bidentate ligand complex is compared to \( \beta_2 \) for the corresponding bis(monodentate ligand) complex, \( \beta_2 \) is generally much smaller. This is due to the more favorable entropy for the reaction involving the chelating ligand. This favorable entropy arises because there are more product molecules than reactant molecules, and thus the disorder of the system increases

1. example

\[ [\text{Cu(H}_2\text{O)}_6]^{2+} + \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \equiv [\text{Cu(H}_2\text{O)}_4(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)]^{2+} + 2 \text{H}_2\text{O} \]

\[ \log K_1 = 10.6 \quad \Delta H = -54 \text{ kJ mol}^{-1} \quad \Delta S = 23 \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ [\text{Cu(H}_2\text{O)}_4]^{2+} + 2 \text{NH}_3 \equiv [\text{Cu(H}_2\text{O)}_4(\text{NH}_3)]^{2+} + 2 \text{H}_2\text{O} \]

\[ \log \beta_2 = 7.7 \quad \Delta H = -46 \text{ kJ mol}^{-1} \quad \Delta S = -8.4 \text{ J K}^{-1} \text{ mol}^{-1} \]
c. ligand substitution reactions in transition metal complexes

1. rates of ligand substitution at metal centers range from very slow \( (k = 10^{-9} \text{ mol}^{-1} \text{ s}^{-1}, \text{ half life} = 30 \text{ yr.}) \) to extremely fast \( (k = 10^{9} \text{ mol}^{-1} \text{ s}^{-1}, \text{ half life} = 10^{-9} \text{ s}) \) at 25 \( \text{EC} \). Complexes in which ligand substitution occurs rapidly are called labile while those in which it occurs slowly are called inert.

2. all ligand substitution reactions are nucleophilic displacement reactions. The mechanisms can be classified as either dissociative (d) or associative (a) and either stoichiometric (an intermediate can be observed) or intimate (no intermediate can be observed).
   a. associative - bond making is more important than bond breaking
      1. stoichiometric - A \( (S_N2 \lim) \)

         \[
         \begin{align*}
         \text{ML}_nX + Y & \overset{k_1}{\underset{k_-1}{\rightleftharpoons}} \text{ML}_nXY \\
         \text{ML}_nXY & \overset{k_2}{\rightarrow} \text{ML}_nY + X
         \end{align*}
         \]

      2. intimate - I\(_a\) \( (S_N2) \)
         a. one step mechanism in which the bond formation is nearly complete before the bond breaking has occurred to a significant extent
         b. intermediate has nearly complete bonds to both the entering and leaving ligands.
   b. dissociative - bond breaking is more important than bond making
      1. stoichiometric - D \( (S_N1 \lim) \)

         \[
         \begin{align*}
         \text{ML}_nX & \overset{k_1}{\underset{k_-1}{\rightleftharpoons}} \text{ML}_n + X \\
         \text{ML}_n + Y & \overset{k_2}{\rightarrow} \text{ML}_nY
         \end{align*}
         \]
2. intimate – I_d (S_N1)
   a. one step mechanism in which the bond breaking is nearly complete
      before bond forming has occurred to a significant extent.
   b. intermediate has very weak bonds to both the entering and leaving
      ligands.

d. factors affecting rates of ligand exchange in octahedral complexes
   1. charge on the metal atom - the higher the charge, the more tightly the ligands
      are held and the more slowly ligand exchange occurs.

      \[
      \begin{array}{c|c|c}
      \text{complex} & \text{k for H}_2\text{O exchange at 25 EC} & \text{ionic radius} \\
      \hline
      \text{Na(H}_2\text{O)}_6^{+} & 8 \times 10^9 \text{s}^{-1} & 0.95 \Delta \\
      \text{Ca(H}_2\text{O)}_6^{2+} & 2 \times 10^8 \text{s}^{-1} & 0.99 \Delta \\
      \text{Mg(H}_2\text{O)}_6^{2+} & \sim 10^5 \text{s}^{-1} & 0.65 \Delta \\
      \text{Ga(H}_2\text{O)}_6^{3+} & \sim 10^3 \text{s}^{-1} & 0.62 \Delta \\
      \end{array}
\]

   2. size of metal atom - the smaller the atom, the more tightly the ligands are held
      and the more slowly ligand exchange occurs.

      \[
      \begin{array}{c|c|c}
      \text{complex} & \text{k for H}_2\text{O exchange at 25 EC} \\
      \hline
      \text{Mg(H}_2\text{O)}_6^{2+} & \sim 10^5 \text{s}^{-1} \\
      \text{Ca(H}_2\text{O)}_6^{2+} & 2 \times 10^8 \text{s}^{-1} \\
      \text{Sr(H}_2\text{O)}_6^{2+} & 4 \times 10^8 \text{s}^{-1} \\
      \end{array}
\]

   3. electron configuration - if a transition metal in an octahedral complex contains
      electrons in the e_g* antibonding orbitals or has an empty t_2g orbital the
      complex will be labile.

      \[
      \begin{array}{c|c|c}
      \text{electron configuration} & \text{labile or inert} & \text{complex} \\
      \hline
      d^0 (t_2g^0) & & \text{TiCl}_6^{2-} \\
      d^1 (t_2g^1) & & \text{Ti(H}_2\text{O)}_6^{3+} \\
      d^2 (t_2g^2) & & \text{V(phen)}_3^{3+} \\
      d^3 (t_2g^3) & & \text{Cr(en)}_2\text{Cl}_2^+ \\
      d^4 (t_2g^4) & \text{ls} & \text{Cr(CN)}_6^{4-} \\
      \end{array}
\]
\[
d^4 (t_{2g}^3 e_g^1) \text{ hs} \quad \text{Cr(H}_2\text{O)}_{6}^{2+}
\]
\[
d^5 (t_{2g}^5) \text{ ls} \quad \text{Mn(CN)}_{6}^{4-}
\]
\[
d^5 (t_{2g}^3 e_g^2) \text{ hs} \quad \text{Mn(H}_2\text{O)}_{6}^{2+}
\]
\[
d^6 (t_{2g}^6) \text{ ls} \quad \text{Fe(CN)}_{6}^{4-}
\]
\[
d^6 (t_{2g}^4 e_g^2) \text{ hs} \quad \text{Fe(H}_2\text{O)}_{6}^{2+}
\]
\[
d^7 (t_{2g}^6 e_g^1) \text{ ls} \quad \text{Co(NH}_3)_{6}^{2+}
\]
\[
d^7 (t_{2g}^5 e_g^2) \text{ hs} \quad \text{Co(H}_2\text{O)}_{6}^{2+}
\]
\[
d^8 (t_{2g}^6 e_g^2) \quad \text{Ni(en)}_{3}^{2+}
\]
\[
d^9 (t_{2g}^6 e_g^3) \quad \text{Cu(NH}_3)_{4}(\text{H}_2\text{O)}_{2}^{2+}
\]
\[
d^{10} (t_{2g}^6 e_g^4) \quad \text{Ga(ox)}_{3}^{3+}
\]

\[\text{phen} = 1,10\text{-phenanthroline, en = ethylene diamine, ox = oxylate}\]

**e. ligand substitution reactions in square planar complexes**

1. for the reaction

\[
\text{ML}_2\text{AX} + \text{Y} \quad \rightarrow \quad \text{ML}_2\text{AY} + \text{X}
\]

the observed rate law is

\[
\text{rate} = (k_1 + k_2[Y])\text{[ML}_2\text{AX]}
\]

where

\[k_1 \text{ is a function of the solvent}\]

2. ligand exchange mechanism

\[
\text{ML}_2\text{AX} + \text{S} \rightarrow \text{ML}_2\text{AS} \quad \text{ML}_2\text{AY} + \text{S}
\]
3. kinetic trans effect – the rate of ligand substitution in a square planar
transition metal complex depends on the ligand trans (T) to the leaving ligand
(X)

\[
\begin{align*}
H_2O < OH^- < F^- < RNH_2 < py < NH_3 < Cl^- < Br^- < I^- < SCN^- < NO_2^- < Ph^- < \\
S=\text{C(NH}_2\text{)}_2 < \text{Me}^- < NO < H^- < \text{PR}_3 < C_2H_4 < CN^- < CO
\end{align*}
\]

a. we can use our knowledge of the kinetic trans effect to design syntheses to
prepare a cis or trans geometric isomer

1. example

\[
\begin{align*}
\text{Cl}_2\text{PtCl}_2 \xrightarrow{\text{NH}_3} & \text{Cl}_2\text{PtNH}_3^- \\
\text{NH}_3 \xrightarrow{\text{Cl}^-} & \text{NH}_3\text{PtCl}_2
\end{align*}
\]

2. example

\[
\begin{align*}
\text{Cl}_2\text{PtCl}_2 \xrightarrow{\text{NH}_3} & \text{Cl}_2\text{PtNH}_3^- \\
\text{Cl}_2\text{PtCl}_2 \xrightarrow{\text{NO}_2^-} & \text{Cl}_2\text{PtNO}_2^- \\
\text{Cl}_2\text{PtCl}_2 \xrightarrow{\text{NH}_3} & \text{NH}_3\text{PtNO}_2^- \\
\end{align*}
\]
b. Explanation of the kinetic trans effect

1. substitution will occur opposite the group that is more stable in the equatorial position of the trigonal bipyramidal intermediate.

2. ligands are more stable in the equatorial position if they are
   a. good π-acceptors
   b. good σ-donors

3. ligands are more stable in the axial position if they are
   a. poor π-acceptors
   b. poor σ-donors
4. The rate of ligand substitution also depends on the nature of the entering and leaving ligands
   a. for the reaction
      \[ \text{Pt(dien)X}^- + \text{Y} \rightarrow \text{Pt(dien)Y}^+ + \text{X} \]
      dien = H₂NCH₂CH₂NHCH₂CH₂NH₂
      1. \( \text{Y} = \text{SC(NH}_2\text{)}_2 \)
      \( \text{X} = \text{NO}_3^- \sim \text{H}_2\text{O} \sim \text{Cl}^- \sim \text{Br}^- \sim \text{I}^- \gg \text{N}_3^- \sim \text{NO}_2^- > \text{SCN}^- > \text{CN}^- \)
      2. \( \text{Y} = \text{pyridine} \)
      \( \text{NO}_3^- > \text{H}_2\text{O} > \text{Cl}^- > \text{I}^- > \text{SCN}^- > \text{CN}^- \)
   b. in general, for reactions of the type
      \[ \text{trans-PtL}_2\text{X}_2 \rightarrow \text{trans-PtL}_2\text{YX} \]
      1. variation in Y has little effect on rate when Y forms a stronger bond to Pt than does X
      2. variation in Y has large effect on rate when Y forms a weaker bond to Pt than does X
      3. variation in X has little effect on rate when Y forms a stronger bond to Pt than does X
      4. variation in X has large effect on rate when Y forms a weaker bond to Pt than does X
   c. to explain this, we must consider the effects of the bond strengths on the energies of the starting materials and transition states because these determine the activation energies, and thus the rates for the process.
2. Electron transfer reactions
   a. outer-sphere electron transfer
      1. if electron transfer occurs more rapidly than does ligand exchange, then
         electron transfer must occur through intact coordination spheres. This is
         referred to as outer-sphere electron transfer and is generally a slow process.
      2. steps in outer sphere reaction - Taube Theory
         a. reactants diffuse together to form an outer sphere complex in which both
            metal coordination spheres remain intact.
         b. bond distances around each metal change to become more product like.
         c. the solvent shell around the outer sphere complex reorganizes.
         d. the electron is transferred
         e. the products diffuse away (generally fast).
   3. outer-sphere electron transfer will occur when both complexes are inert
      a. example
         \[ \text{Fe(CN)}_{6}^{4-} + \text{IrCl}_{6}^{2-} \rightarrow \text{Fe(CN)}_{6}^{3-} + \text{IrCl}_{6}^{3-} \]
   4. outer-sphere electron transfer will also occur if only one of the complexes is
      inert as long as this complex does not have a ligand capable of bridging the
      two metal centers.
      a. example
         \[ \text{Co(NH}_{3})_{6}^{3+} + \text{Cr(H}_{2}O)_{6}^{2+} \rightarrow \text{Co}^{2+} + \text{Cr(H}_{2}O)_{6}^{3+} \]
         one product complex is labile and so the ligands are scrambled on this
         complex
   b. inner-sphere electron transfer
      1. if electron transfer and ligand exchange occur at the same rate then electron
         transfer occurs via ligand exchange. This is referred to as inner-sphere
         electron transfer and in generally a rapid process.
      2. in inner-sphere electron transfer, an intermediate forms in which the two
         metals are connected via a bridging ligand

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3. electron transfer can also occur through extended bridges

a. example

\[
\text{(H}_3\text{N)}_5\text{Co}^3+ + \text{Cr(H}_2\text{O)}_6^{2+} \rightarrow \text{Co}^{2+} + \text{Cr(H}_2\text{O)}_6^{3+}
\]

\[k = 4.0 \times 10^{-3} \ M^{-1} \text{s}^{-1}\]

b. example

\[
\text{(H}_3\text{N)}_5\text{Co}^- + \text{Cr(H}_2\text{O)}_6^{2+} \rightarrow \text{Co}^{2+} + \text{Cr(H}_2\text{O)}_5^{3+}
\]

\[k = 17.4 \ M^{-1} \text{s}^{-1}\]
H. Homogeneous Catalysis

1. most catalytic processes can be broken down into a series of simple reactions
   a. ligand exchange - we have already discussed this in detail
   b. oxidative addition and reductive-elimination
      1. oxidative addition
         a. two types
            1. $M^{m+} + A-B \rightarrow A-M^{(m+2)}-B$
               a. an electron is transferred from the metal to A and to B breaking the
                  A-B bond and generating two, anionic ligands
               1. the number of d electrons on the metal decreases by two and
                  the number of valence electrons in the complex increases by
                  two.
               2. the ligands always add cis to the metal if it is a true, concerted
                  oxidative addition reaction. Free radical mechanisms can give
                  similar results can give trans ligands.
         b. examples
            $\begin{align*}
            \text{Cl}\text{Rh-PPh}_3 + \text{H}_2 & \rightarrow \text{H-Rh-PPh}_3 \\
            \text{PPh}_3 & \text{Cl} \\
            \text{Ph}_3\text{P}\text{Pt-PPh}_3 + \text{CH}_3\text{I} & \rightarrow \text{Ph}_3\text{P}\text{Pt-I} \\
            \text{Ph}_3\text{P} & \text{CH}_3 \\
            \end{align*}$
            2. $M^{m+}-M^{m+} + 2A-B \rightarrow A-M^{(m+1)} + B-M^{(m+1)}$
               a. each metal transfers one electron to A-B to break the A-B bond
                  and form two anionic ligands.
               1. the number of d electrons on each metal decreases by one and
                  the number of valence electrons in each complex increases by
                  one.
               2. these reactions are less common than those of the first type.
b. example

\[ 2 \text{Co(CN)}_5^{3-} + \text{H}_2 \xrightarrow{\text{fast}} 2 \text{CoH(CN)}_5^{3-} \]

2. reductive elimination
   a. reductive elimination is the reverse of oxidative addition. These reactions are generally hard to study because they occur readily and it is difficult to find starting materials.
   b. in a reductive elimination, the number of metal d electrons increases by two and the number of valence electrons decreases by two.
   c. example

\[
\begin{array}{c}
\text{PPh}_3 \quad \text{H} \\
\text{PPh}_3 \\
\text{Pt} \quad \text{CH}_2\text{CN} \\
\text{PPh}_3 \\
\end{array} \xrightarrow{\text{hv}} \quad \begin{array}{c}
\text{Ph}_3\text{P} \\
\text{PPh}_3 \\
\text{Pt} \quad \text{CH}_2\text{CN} \\
\text{PPh}_3 \\
\end{array} \xrightarrow{\text{fast}} \begin{array}{c}
\text{Pt} \\
\text{PPh}_3 \\
+ \text{CH}_3\text{CN} \\
\end{array}
\]

c. migratory insertion reactions
   1. these are called migratory insertion because the product can form either by insertion of one ligand into another metal-ligand bond or by migration of one ligand to another ligand.

\[
\begin{array}{c}
\text{R} \\
\text{C}=\text{O} \\
\text{M} \quad \text{L} \\
\end{array} \xrightarrow{+\text{L}} \begin{array}{c}
\text{R} \\
\text{M} \quad \text{C}=\text{O} \\
\text{L} \\
\end{array} \xrightarrow{+\text{L}} \begin{array}{c}
\text{L} \\
\text{M} \quad \text{C}=\text{O} \\
\text{R} \\
\end{array}
\]

insertion \quad migration

2. these reactions always occur with cis ligands and can be either 1,1 or 1,2

\[
\begin{array}{c}
\text{M} \quad \text{L} \\
\end{array} + \begin{array}{c}
\text{A} \equiv \text{B} \\
\end{array} \xrightarrow{1,1} \begin{array}{c}
\text{M} \equiv \begin{array}{c}
\text{L} \\
\text{A} \\
\text{B} \\
\end{array} \\
\end{array} \xrightarrow{1,2} \begin{array}{c}
\text{M} \equiv \begin{array}{c}
\text{B} \\
\text{A} \\
\text{L} \\
\end{array} \\
\end{array}
\]

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3. examples

\[ (\text{CO})_2\text{MnCH}_3 + \text{CO} \rightarrow (\text{CO})_2\text{MnC(O)CH}_3 \quad 1,1 \]
\[ (\text{Ph}_3\text{P})_2\text{ClPtH} + \text{H}_2\text{C}=\text{CH}_2 \rightarrow (\text{Ph}_3\text{P})_2\text{ClPtCH}_2\text{CH}_3 \quad 1,2 \]

2. characteristics of a catalyst

a. the microscopic catalyst site operates in a cyclic fashion through a series of reactions that are repeated each time a molecule of product is formed.
b. the actual catalyst is not necessarily the same compound that you put into the reaction mixture. Precatalytic reactions that transform the precatalyst into the catalyst often give rise to an induction period before any reaction is observed.
c. kinetic effect - a catalyst can accelerate a thermodynamically allowed reaction but cannot make a thermodynamically forbidden one occur.

3. alkene hydrogenation

a. reaction

\[ \text{CH}_2=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{-CH}_3 \]

b. catalyst

\[ \text{RhCl(PPh}_3)_3 \quad \text{- Wilkinson's catalyst} \]
c. reaction sequence

\[
\begin{align*}
L^-\text{Rh}^{\alpha}_L^\text{Cl} + S & \iff L^-\text{Rh}^{\alpha}_S^L + L \\
L^-\text{Rh}^{\alpha}_L^\text{Cl} + \text{H}_2 & \iff L^-\text{Rh}^{\alpha}_S^L \\
L^-\text{Rh}^{\alpha}_S^L + \text{H}_2\text{C}=\text{CH}_2 & \iff L^-\text{Rh}^{\alpha}_L^\text{Cl} + \text{S} \\
L^-\text{Rh}^{\alpha}_L^\text{Cl} + \text{S} & \iff L^-\text{Rh}^{\alpha}_L^\text{Cl} + \text{CH}_2=\text{CH}_2 \\
L^-\text{Rh}^{\alpha}_L^\text{Cl} + \text{CH}_2=\text{CH}_3 & \iff L^-\text{Rh}^{\alpha}_S^L + \text{H}_3\text{C}=\text{CH}_3
\end{align*}
\]
d. Tolman catalytic loop

1. a catalytic reaction can be represented by a cyclic pathway in which the only net inputs are the reactants and the only net outputs are the products. During each cycle, one molecule of product is formed.

2. Tolman catalytic loop for alkene hydrogenation
4. alkene hydroformylation
   a. reaction

   \[
   \begin{align*}
   &\text{R}H & \text{H} & \text{H} & + & \text{C=}\text{O} & + & \text{H}_2 \\
   \rightarrow & \text{H} & \text{H} & \text{H} & \text{R}H & \text{H} & \text{H} & \text{CHO} & + & \text{H} & \text{H} & \text{R} & \text{H} & \text{H} & \text{CHO}
   \end{align*}
   \]

   b. catalyst

   \[\text{RhCl(CO)(PPh}_3 \rangle_2\]

c. Tolman catalytic loop

![Tolman catalytic loop diagram]