
To understand chemical bonding, we must first understand atomic structure:

- Atom is comprised of
  1. positively charged nucleus (protons and neutrons)
  - Number of protons defines the atomic number of an element;
    - 5 protons in B; 22 protons in Ti; 78 protons in Pt, etc.
  - Number of (protons+neutrons) defines the isotope (and atomic weight);
    - \(^{6}\text{Li}\) (7.42% natural abundance) has 3p+3n; \(^{7}\text{Li}\) (92.58%) has 3p+4n
    - \(^{16}\text{O}\) (99.759%), 8p+8n; \(^{17}\text{O}\) (0.037%), 8p+9n; \(^{18}\text{O}\) (0.204%), 8p+10n
  - 2. negatively charged electrons
    - atoms have neutral charges (#electrons = #protons)
    - ions are charged (#electrons ≠ #protons)

Bohr Atom:
Before 1913, many studies of emission and absorption of light from atoms indicate that spectral positions (see hydrogen emission spectrum) conformed to patterns, as described by Rydberg equation:

\[
\nu = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)
\]

where \(m=1,2,3,4\ldots\), \(n=(m+1),(m+2),(m+3)\ldots\), and \(R\) is empirical constant (109,678 cm\(^{-1}\))

Niels Bohr (1913) proposed that these lines represented electrons orbiting the nucleus. He could derive the Rydberg equations by assuming that the angular momentum of the electron \((mvr)\) was quantized, that is given by the equation:

\[
mvr = n\frac{h}{2\pi}, \text{where } n = 1,2,3,4\ldots
\]

From this assumption, Bohr could calculate the energy and radius of each orbit, providing a 'first principle' basis for the Rydberg constant. The ultraviolet lines (Lyman series), then result from the excitation of an electron to an orbit to a higher energy \((n>1)\) and its subsequent de-excitation to the \(n=1\) orbit. The other series arise when an electron drops from the upper orbits to those with \(n=2\) (visible series) and \(n=3\) (infrared series), as illustrated in C&W, Fig 2-2:
Bohr atom: electrons orbiting atomic nucleus. Imprecise picture: radiating electrons would lose energy and spin into the nucleus and we cannot determine simultaneously both the position and energy of electrons (Heisenberg uncertainty principle).

Atom size is dominated by electron orbitals: (~10^{-8} cm vs. 10^{-13} cm for a nucleus).

The electron orbitals are grouped into shells:
- named K, L, M, N, ...
- numbered 1, 2, 3, 4, ...

Wave Mechanics:
One problem with the Bohr model is the treatment of electrons as 'orbiting particles' neglecting theoretical and experimental evidence for their wavelike properties. DeBroglie (1924) suggested that small particles traveling at a velocity, \( v \), would possess an associated wave character such that the wavelength, \( \lambda \), is related to their mass, \( m \), and velocity according to

\[
\lambda = \frac{h}{mv}
\]

This idea was subsequently validated by the observation that a beam of electrons could be diffracted in the same manner as a beam of x-rays.

Schrödinger proposed that all such 'moving particles' could be described by his 'wave equation'.
- Position of electron as a discrete particle cannot be precisely defined
- Wave function (\( \psi \)) describes position
  - \( \psi^2 \) defines probability of finding electron 'particle' at any given point, or
  - electron defined as 'smeared out' distribution of negative charge whose density varies from point-to-point according to \( \psi^2 \)

C&W figure 2-4 shows radial distribution function of electron density for atomic hydrogen; maximum at the Bohr radius (\( a_0 \)).
Atomic Orbitals
Consider now the entire set of wave functions for the electron in the hydrogen atom. (called orbitals since they are the wave-mechanical analogs of Bohr’s orbits).

Again, use the principal quantum number \( n \) to describe energy 'shells'.

These shells are further divided into sub-shells:
- designated by letters s, p, d, f which indicate the values of
- the orbital quantum number \( l \) which have the values
- \( s(l=0), p(l=1), d(l=2), f(l=3) \)
- \( l \leq (n-1) \)
- \( l \) describes the eccentricity (shape) of an orbital
- \( m (-l \leq m \leq +l) \) describes orientation of the orbital (C&W Fig 2-5)

Note: whether numbers or letters are used for \( n \) and \( l \) is a matter of convention.

So, for a 2p electron, \( n=2, l=1 \), and it is in the L-shell. There are three possible orientations for these orbitals \( (m=-1, 0, +1: 2px, 2py, 2pz) \)

Electron Spin
Consider the electron as a particle spinning like top. A fourth quantum number \( (s=\pm \frac{1}{2}) \) describes whether the spin is clockwise or counter-clockwise (and so distinguishes electrons with magnetic dipole moments that point up or point down. Useful for explaining the different magnetic properties of materials.

Exclusion Principle
When an electron is assigned to an orbital, it can be fully defined by the four quantum numbers.
1. The principle quantum number of the orbital, \( n \).
2. The \( l \) quantum number of the orbital, defining shape, s, p, d, f, etc.
3. The \( m \) value of the orbital, which describes orientation (px, py, pz, etc.)
4. The spin quantum number \( (s=\pm \frac{1}{2}) \) of the electron itself.

The fundamental rule, which must be obeyed in placing two or more electrons in the orbitals of an atom, is the exclusion principle:

No two electrons in one atom can have an identical set of quantum numbers.

As a result, no orbital (defined by \( n, l, m \) ) can have more than two electrons. (These two electrons will have opposite spins, so the net magnetic moment of a filled orbital is zero.)
**Electron Configuration**: how electrons occupy the orbitals in an atom.

- **Aufbau Principle** ("to build up")

- In any shell (given \( n \)), an electron in a \( s \)-orbital has a lower energy (and so is filled first) than one in a \( p \)-orbital, which is lower than one in a \( d \)-orbital……

- Sequence of energy levels within the atom follows the sequence \((n+l)\). If two \((n+l)\) sequences are equal, then the one with the lower \( n \) will be filled first. So, \( 4s \) orbitals \((4+0)\) are filled before the \( 3d \) \((3+2)\) orbitals, and \( 3d \) orbitals are filled before \( 4p \) orbitals \((4+1)\).

![Electron Orbitals Diagram](image)

| 1H | 1s\(^1\) |
| 2He | 1s\(^2\) |
| 3Li | 1s\(^2\) 2s\(^1\) |
| 4Be | 1s\(^2\) 2s\(^2\) |
| 5B  | 1s\(^2\) 2s\(^2\) 2p\(^1\) |
| 6C  | 1s\(^2\) 2s\(^2\) 2p\(^2\) |
| 7N  | 1s\(^2\) 2s\(^2\) 2p\(^3\) |
| 8O  | 1s\(^2\) 2s\(^2\) 2p\(^4\) |
| 9F  | 1s\(^2\) 2s\(^2\) 2p\(^5\) |
| 10Ne | 1s\(^2\) 2s\(^2\) 2p\(^6\) |
| 11Na | [Ne] 3s\(^1\) |
| 12Mg | [Ne] 3s\(^2\) |
| 13Al | [Ne] 3s\(^2\) 3p\(^1\) |
| 14Si | [Ne] 3s\(^2\) 3p\(^2\) |
| 15P  | [Ne] 3s\(^2\) 3p\(^3\) |
| 16S  | [Ne] 3s\(^2\) 3p\(^4\) |
| 17Cl | [Ne] 3s\(^2\) 3p\(^5\) |
| 18Ar | [Ne] 3s\(^2\) 3p\(^6\) |
| 19K  | [Ar] 4s\(^1\) |
| 20Ca | [Ar] 4s\(^2\) |
| 21Sc | [Ar] 4s\(^2\) 3d\(^1\) |
| 22Ti | [Ar] 4s\(^2\) 3d\(^2\) |
| 30Zn | [Ar] 4s\(^2\) 3d\(^{10}\) |
| 31Ga | [Ar] 4s\(^2\) 3d\(^{10}\) 4p\(^1\) |
| 32Ge | [Ar] 4s\(^2\) 3d\(^{10}\) 4p\(^2\) |
| 36Kr | [Ar] 4s\(^2\) 3d\(^{10}\) 4p\(^6\) |

Repeat the patterns, filling \( 5s \), \( 4d \), \( 5p \) orbitals to Xe; after Xe, available orbitals are \( 6s \), \( 4f \), \( 5d \), \( 6p \), etc.

Note that the electron configurations reveal periodic patterns that coincide with the same periodic arrangements of elements formulated by Mendeleyev from chemical similarities.

- **Periodic Table**
  - Rows: defined by principle quantum number \((n)\)
  - Columns: grouped by orbital quantum number \((l)\) of outermost orbital (outermost electrons determine the chemical properties of an element)
Each column lists elements with similar chemical properties (alkali metals to noble gases).

1. **Main Group Elements**: outer shells consist of s and p orbitals
   - **Noble Gases** (last column): filled orbitals, \( ns^2 \; np^6 \) configurations
   - **Alkali Metals** (first column): follow noble gases: \([NG] \; ns^1 \) configurations
     - Li, Na, K, Rb, Cs, Fr
   - **Alkaline Earth Metals**: follow the alkalis: \([NG] \; ns^2 \) configurations
     - Be, Mg, Ca, Sr, Ba, Ra (Radium)
   - **Halogens** (‘salt-formers’): precede noble gases: \( ns^2 \; np^5 \) configurations
     - F, Cl, Br, I, At (Astatine)
   - **Chalcogens** (‘from copper’): precede halogens: \( ns^2 \; np^4 \) configurations
     - O, S, Se, Te, Po
   - \( ns^2 \; np^3 \) configurations: N, P, As, Sb, Bi
   - \( ns^2 \; np^2 \) configurations: C, Si, Ge, Sn, Pb
   - \( ns^2 \; np^1 \) configurations: B, Al, Ga, In, Tl

2. **Transition Elements**
   - d-block elements with unfilled \( nd^x \) outer orbitals
   - f-block elements, with unfilled \( nf^x \) outer orbitals
     - lanthanides (4f: Ce-Lu)
     - actinides (5f: Th-Lr)

Columns of chemically similar elements are ‘groups’ that are numbered to correspond to the number of valence shell electrons: IA, IIA, etc. (main group elements); IB, IIB, etc. (transition elements).

It’s important to know the elements and something about their properties (and so, something about electron configuration).

- **Periodic Table** represents the pantry for a glass scientist; contains all the ingredients you need to make a glass.

Electron Configuration \( \rightarrow \) Chemical Nature \( \rightarrow \) Glass Properties

Mnemonic aids for remembering element names and order:
- the alkali metals: Little **Nate Kissed Ruby C’s Frog**
- the halogens: **Foul Clara Broke Ida’s Atlas**
Ceramists are interested in electron structures of ions, not atoms. The structure and properties of crystals (and glasses) depend on:

- ion size (radius)
- ion charge
- ion polarizability

Valence state affects ion size:

- elemental S (z=16) \([\text{Ne}]\ 3s^2\ 3p^4\) 1.04Å
- cation: S\(^{6+}\) \([\text{Ne}]\) 0.37Å (Ne radius is 0.57Å)*
- anion: S\(^{2-}\) \([\text{Ne}]\ 3s^2\ 3p^6\) 1.84Å (Ar radius is 0.88Å)

*Why is S\(^{6+}\) smaller than Ne, despite similar electron configurations? More protons in \(^{16}\text{S}\) than \(^{10}\text{Ne}\) mean greater nuclear attraction and so smaller orbital size. Similar explanation for why \(^{16}\text{S}^{2-}\) is larger than \(^{18}\text{Ar}\).

Cations are smaller than anions. Cations with similar sizes and valences (Ca\(^{2+}\), Mn\(^{2+}\), Zn\(^{2+}\)) will have similar crystal structures; replacing a similar cation (or anion, F\(^-\) for OH\(^-\)) will not alter the basic crystal structure.

So, ions are our building blocks: How do we combine them to form materials?
**Field Strength**

- parameter that quantifies the effect of a cation size and valence has on the structure/properties of crystals and glasses

Start with ionic bond strength (Coulombic interactions) in terms of an electrostatic force ($F$):

$$ F = -\frac{Z_cZ_ae^2}{a^2} $$

where $Z_c$ and $Z_a$ are the cation and anion valence, respectively, $e$ is the electronic charge ($1.60\times10^{-19}$ coul), and '$a$' is the anion-cation separation distance ($a=r_a+r_c$).

If we consider only oxides, then $Z_a$ is a constant and can be ignored, as can $e$, leaving the following relationship as our definition for field strength:

$$ F.S. = \frac{Z_c}{a^2} $$

So, cations with:
- larger valences
- smaller radii
have larger field strengths, and so

oxides with large F.S. cations will tend to have stronger bonds to oxygen. This is (sometimes) reflected in the oxide melting points

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cation</th>
<th>r(CN), Å</th>
<th>$r_{ox}(CN)$, Å</th>
<th>F.S.</th>
<th>Melt. Pt., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Si$^{4+}$</td>
<td>0.40 (IV)</td>
<td>1.21 (II)</td>
<td>1.54</td>
<td>1710</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>Na$^+$</td>
<td>1.16 (VI)</td>
<td>1.26 (VI)</td>
<td>0.17</td>
<td>subl.</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Al$^{3+}$</td>
<td>0.67 (VI)</td>
<td>1.22 (III)</td>
<td>0.84</td>
<td>2050</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg$^{2+}$</td>
<td>0.86 (VI)</td>
<td>1.26 (VI)</td>
<td>0.44</td>
<td>2800</td>
</tr>
<tr>
<td>CaO</td>
<td>Ca$^{2+}$</td>
<td>1.14 (VI)</td>
<td>1.26 (VI)</td>
<td>0.35</td>
<td>2572</td>
</tr>
<tr>
<td>SrO</td>
<td>Sr$^{2+}$</td>
<td>1.27 (VI)</td>
<td>1.26 (VI)</td>
<td>0.31</td>
<td>2430</td>
</tr>
<tr>
<td>BaO</td>
<td>Ba$^{2+}$</td>
<td>1.50 (VI)</td>
<td>1.26 (VI)</td>
<td>0.26</td>
<td>1923</td>
</tr>
</tbody>
</table>

Note: alkaline earth oxides each have the rock salt structure and so the F.S. vs. M.P. relationship holds. SiO$_2$ and Al$_2$O$_3$ have different structures and so a more complicated F.S-M.P dependence.
**Acid/Base Concepts**

- The acidity of an oxide is related to the power of the cation to draw electrons from oxygens surrounding it into chemical bonding.

- This power of the cation can be represented by its field strength in an oxide system. The field strengths of the cations are a measure of oxide acidity.

  - High F.S. cations (e.g., Si$^{4+}$, FS=1.54) form acidic oxides (SiO$_2$)
    - P$^{5+}$>Si$^{4+}$>V$^{5+}$>B$^{3+}$>Ge$^{4+}$>Ti$^{4+}$ (most to least acidic)

  - Low F.S. cations (e.g., Na$^+$, FS=0.17) form basic oxides (Na$_2$O)
    - Cs$^+$<Rb$^+$<K$^+$<Na$^+$<Li$^+$<Ba$^{2+}$<Pb$^{2+}$<Ca$^{2+}$<Mg$^{2+}$ (most to least basic)

- Intermediate FS cation oxides can act either as acids or bases, depending on what they are reacting with.
  - **Amphoteric oxides** (Al$_2$O$_3$, ZrO$_2$, BeO, etc.)

- Reactions between oxides to form compounds are analogous to acid-base neutralization processes that form salts.

  - Na$_2$O + 2SiO$_2$ → Na$_2$Si$_2$O$_5$ (or Na$_2$O•2SiO$_2$)  
    (base)      (acid)      (salt)

  - Larger $\Delta$FS (between cations in oxides), more ready (faster, lower temperatures) reactions to form compounds or glasses
    - Glass melting temperatures decrease in the order Li$_2$O•2SiO$_2$< Na$_2$O•2SiO$_2$< K$_2$O•2SiO$_2$< Cs$_2$O•2SiO$_2$

  - Smaller $\Delta$FS, lower reaction tendencies
    - Acids tend not to react with acids, bases with bases.
      - e.g., MgO (FS=0.44) does not react with CaO (FS=0.35); instead forms limited solid solution.

- **Nomenclature**: *base then acid.*
  - Example: using amphoteric Al$_2$O$_3$
    - Al$_2$O$_3$ (FS=0.84, acid) + CaO (FS=0.35, base) → CaAl$_2$O$_4$: Ca-aluminate
    - Al$_2$O$_3$ (FS=0.84, acid) + 2SiO$_2$ (FS=0.35, base) → Al$_2$Si$_2$O$_7$: 'aluminosilicate'

- We refer to ‘alkali silicate’ glasses, ‘borosilicates’ (not silicoborates), ‘aluminophosphates’ (not ‘phospho-aluminates’) etc.
Types of Chemical Bonds

- structure is determined by the strongest bonds in a system, but properties are dependent on the weakest.

1. Ionic Bonds
   - Consider the Coulombic attraction between ions: electron transfer from cation to anion to create oppositely charged ions that are electrostatically attracted.
   - Favored in the reaction between an atom of low ionization potential (alkali metals) with an atom of high electron affinity (halides).
   - Respective ions will have 'noble gas' configurations
     - Na\(^0\): [Ne] 3s\(^1\) → Na\(^+\): [Ne]
     - Cl\(^0\): [Ne] 3s\(^2\) 3p\(^5\) → [Ne] 3s\(^2\) 3p\(^6\) ≈ [Ar]

   ![Diagram of Coulombic interaction between ions](image.png)

   No bonding is completely ionic- but many compounds can be treated to a reasonable approximation as if the bonding forces were just electrostatic attractions between oppositely charged ions: NaCl, MgO, NiBr\(_2\), etc.

2. Covalent Bonds
   - How can you form a bond between like atoms? e.g., H\(_2\)?
     - **Two atoms each donate one electron to a shared pair that no longer belongs to either atom alone, but occupies a single orbital common to both.**
     - Chemical bonds result when outer orbitals on different atoms overlap so as to concentrate electron density between the atomic cores. Increased electron density leads to increased electrostatic attraction → bond formation.
     - Overlapping orbitals → *Molecular Orbitals*
     - New energy levels to be occupied by the electrons from individual atoms; constrained by the same exclusion principles that apply to atomic orbitals (only two electrons, with opposite spins, per MO).
       - Covalent bond will form if the resulting molecular orbital has a lower energy than the two separate atomic orbitals.
Note: the spins of the two electrons in the bonding MO are opposite (and so lower energy) whereas the spins in the antibonding MO are alike, and so increase energy (can’t be brought together because it violates exclusion).

Hybrid Orbitals

Consider BeH$_2$: $^4$Be: 1s$^2$2s$^2$. If Be is to form two bonds by sharing one electron with each of two other atoms, it must be first put into a state where each electron is in a different orbital and each spin is uncoupled from the other so that it is ready to be paired with the spin of an electron on the atom to which the bond is to be formed. (This puts the atom into the valence state).

For $^4$Be, energy must be expended to promote one electron from the 2s to the 2p orbital: 1s$^2$2s$^1$2p$^1$. The 2s and 2p orbitals can mix to form two $sp$ hybrid orbitals. Each of these orbitals then overlap with the 1s orbital from a H atom to create a linear H-Be-H molecule. Hybridization leads to lowest energy molecular configuration.

Hybridization of molecular orbitals imparts specific geometries on covalently bonded materials:
- $sp^2$ hybrids give a linear molecule;
- $sp^3$ hybrids give a plane triangular molecule
  - $^5$B: 1s$^2$2s$^2$2p$^1$ → 1s$^2$2s$^1$2px$^1$2py$^1$
  - trigonal planar (BO$_3$)$_3^-$ anions are important in borate glasses
- $sp^3$ hybrids give a tetrahedral molecule
  - $^{14}$Si: [Ne] 3s$^2$ 3p$^2$ → [Ne] 3s$^1$3px$^1$3py$^1$3pz$^1$
  - tetrahedral (SiO$_4$)$_4^-$ anions are important in silicate glasses

Other hybrids involving d-orbitals lead to a variety of molecular geometries.

Note: This ‘bond geometry’ (directionality) effect generally means that covalent solids are more open (less dense) than ionic solids, where packing of ions can be more efficient.
**Electronegativity**: determines the extent of bond ionicity/covalency
\( \chi \sim \) ability of an atom in a molecule to attract electrons to itself
- high \( \chi \), readily attracts electrons
- low \( \chi \), readily gives up electrons

large \( \Delta \chi \) between two atoms \( \rightarrow \) highly ionic bond
small \( \Delta \chi \) between two atoms \( \rightarrow \) more covalent bond

Electronegativity of different elements - note decreases as you go down rows, and increases as you go left to right on Periodic Table

Empirical relationship between \( \Delta \chi \) and the 'fraction of ionic character' in a diatomic bond:

\[
\text{Ionic character} = 1 - \exp(-0.25(\chi_A - \chi_B)^2)
\]

Li(\( \chi = 0.9 \))-F(\( \chi = 4.1 \)): LiF (\( \Delta \chi = 3.2 \)): 92% ionic
Si(\( \chi = 1.8 \))-C(\( \chi = 2.5 \)): SiC (\( \Delta \chi = 0.7 \)): 12% ionic

Note about Pauling: one of two to win two Noble Prizes: one in chemistry for his ideas of the nature of the chemical bond, one in Peace for agitating about nuclear weapon tests. Just missed a third for the structure of DNA - got to the double-helix structure just after Watson and Crick. (See Watson's *The Double Helix*).

John Bardeen is the other to get two Noble Prizes, both in Physics (Solid-state semiconducting transistor and theory for superconductivity).

Other types of Bonds:

- **van der Waal's**: short-range, dipolar interactions.
  - Very weak (\(-r^{-6}\))
  - Important for organics, ceramic colloids/particles

- **metallic bonds**: valence electrons freely shared by all atoms; continuous energy bands of completely delocalized electrons....
• **hydrogen bonds**: hydrogen involved in a highly polar bond bears a partial positive charge that can interact electrostatically with another negative (or electron rich) atom: \( \text{O-H}^{\delta+} \cdots \text{O}^{\delta-} \)
  • important for ceramic processing, understanding glass corrosion, etc.

**Bonding Summary (for inorganic materials):**

<table>
<thead>
<tr>
<th>Ionic</th>
<th>Covalent</th>
<th>Metallic</th>
<th>Van der Waal's</th>
</tr>
</thead>
<tbody>
<tr>
<td>strong, hard</td>
<td>strong, hard</td>
<td>variable</td>
<td>weak, soft</td>
</tr>
<tr>
<td>high melting points</td>
<td>high melting points</td>
<td>variable</td>
<td>low melting points</td>
</tr>
<tr>
<td>fairly high density</td>
<td>low densities</td>
<td>high densities</td>
<td>high densities</td>
</tr>
<tr>
<td>high coordination #</td>
<td>low coordination #</td>
<td>very high coord. #</td>
<td>high coordination #</td>
</tr>
</tbody>
</table>

**Brief Review of Pauling's Rules**

Empirical relationships between ion properties (size and valence) and crystal packing/structures.

**Rule 1:** Predict anion coordination polyhedron from the radius ratio: \( \frac{r_{\text{cation}}}{r_{\text{anion}}} \)
  • Based on geometries of hard spheres
  • Calculate the *minimum* ratio possible for each coordination polyhedron

![](image)

\((r_c/r_a)_{\text{min}}\) is calculated from the various geometries of packed spheres:

<table>
<thead>
<tr>
<th>Geometry</th>
<th>((r_c/r_a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal</td>
<td>≥0.155</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>≥0.225</td>
</tr>
<tr>
<td>Octahedral</td>
<td>≥0.414</td>
</tr>
<tr>
<td>Cubic</td>
<td>≥0.732</td>
</tr>
</tbody>
</table>

• Trumped (in many cases) by bond hybridization geometries; directionality from partially covalent bonding will stabilize structures with higher or lower CN.

Kingery Fig 2-21
showing various coordination polyhedra
Rule 2: Predict anion CN from valences and cation CN

- Electrostatic Bond Strength ≈ valence/CN
- Anion Valence ≈ Sum of E.B.S. contributed by neighboring cations

\[
\frac{\text{Cation Charge} \ e}{\text{Cation CN}} = \frac{\text{Anion Charge} \ e}{\text{Anion CN}}
\]

- e.g., TiO\textsubscript{2}: from Pauling’s 1\textsuperscript{st} law: \(r_{Ti^{4+}}/r_{O^{2-}}\approx 0.61/1.40=0.44\)
- \(\text{CN(Ti}^{4+})=6\)

\[
\frac{Ti^{4+} \ \text{Charge} \ e}{Ti^{4+} \ \text{CN}} = \frac{4}{6} = \frac{O^{2-} \ \text{Charge} \ e}{O^{2-} \ \text{CN}} = \frac{2}{O^{2-} \ \text{CN}}, \text{O}^{2-} \ \text{CN} = 3
\]

Rule 3: Stable structures prefer that cations are kept far apart (avoid cation-cation repulsion).

- Neighboring polyhedra will share corners before edges and faces.

Kingery Fig. 2-22
showing corner-, edge-, face-sharing

- Note reactivity of silica-w; unstable, edge-shared tetrahedra:

Rule 4: Stable crystals have minimum number of structural sub-units

- simpler structures have lower energies
- difficult to pack coordination polyhedra of different sizes
- ‘Parsimony is Preserved’.