

Lecture Notes - Mineralogy - Pauling's Rules

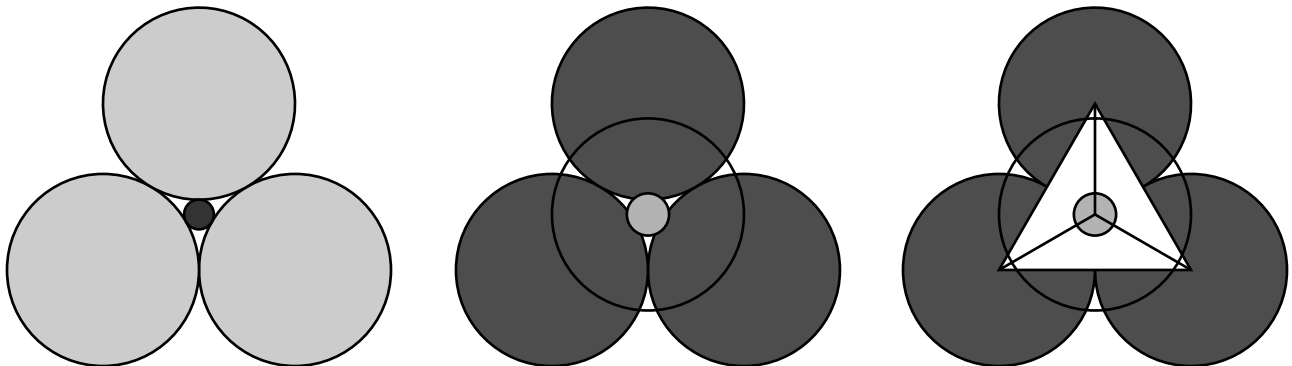
- Oxygen is the major anion in a great many common minerals. Because oxygen has such a large electronegativity, most of the bonds in these minerals have a significantly ionic character. For this reason, Linus Pauling's model and "rules" for ionic crystals (Pauling, 1960, *The Nature of the Chemical Bond*) are very useful in understanding many aspects of the crystal chemistry of minerals.

Rule #1 - A coordinated polyhedron of anions is formed about each cation, the cation-anion distance equaling the sum of their characteristic packing radii and the coordination polyhedron being determined by the radius ratio.

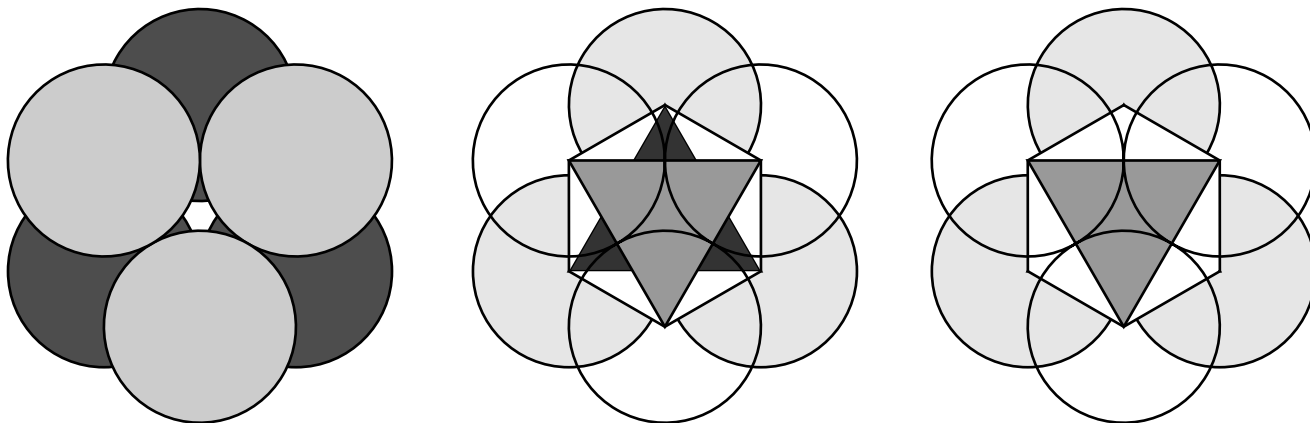
- Pauling's model treats the anions and cations of a crystal as if they were hard spheres packed so tightly together that the spheres are touching. In fact, the arrangement of anions in many minerals is that expected for a cubic or hexagonal closest-packed arrangement of spheres, which suggests that the hard sphere model is a good first approximation. The number of large spheres (anions) that can fit around a small sphere (cation) is called the **anion coordination number** and depends on the relative sizes of the small and large sphere (the **radius ratio**). The coordination number will be the same for a range of radius ratios as follows:

<u>coordination #</u>	<u>anion polyhedron</u>	<u>radius ratios</u>	<u>cation examples (oxides)</u>
3	triangle	0.15-0.22	C
4	tetrahedron	0.22-0.41	Si, Al
6	octahedron	0.41-0.73	Al, Fe, Mg, Ca
8	cube	0.73-1.00	K, Na
12	closest packing	1.00	

If the calculated radius ratio is near a limiting value separating two coordination numbers, the cation commonly can occur in crystallographic sites with either coordination number. Indeed, the radius of a cation depends to some extent on its coordination number. If the centers of the anions that are coordinated to a single cation are connected by lines, these lines outline the edges of a **coordination polyhedron**. Complex ionic crystals structures are more clearly represented by showing the coordination polyhedra, than by trying to show the anions and cations themselves.



Pauling's Rules



Rule #2 - An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an anion equal the charge on that anion.

- The **electrostatic bond strength** of an ionic bond may be defined as the charge on the cation divided by the coordination number of the cation. In effect, the charge on a cation is “shared” equally among all the nearest neighbor anions. The electrostatic attraction of the cation to one anion is reduced if another anion is attracting the cation in another direction. For example, the electrostatic bond strength for the Si-O bond is 1 (+4/4) whereas the Al/O bond has a strength of $\frac{3}{4}$ (+3/4) or $\frac{1}{2}$ (+3/6). In most cases, the sum of the bond strengths for all the bonds to a single oxygen anion is 2. In other words, the -2 charge on the oxygen anion is balanced by a total charge of +2. Pauling’s Rule #2 is also called the principle of local charge balance.

Rule #3 - The sharing of edges and particularly faces by two anion polyhedra decreases the stability of an ionic structure.

- Cations strongly repel one another. When the bonding in a crystal is largely ionic, the crystal is likely to have a structure that keeps the cations as far apart as possible. However, because anions commonly have more than one cation bonded to them, cations are never far apart. Cations will be farthest apart if they share only one anion, *i.e.* their coordination polyhedra share only corners. If two anions are shared, the coordination polyhedra have an edge in common and the cations are closer together. If three anions are held in common, the coordination polyhedra of the two cations share faces and the cations are “unreasonably close.”

Rule #4 - In a crystal containing different cations, those of high valency and small coordination number tend not to share polyhedron elements with one another.

- If a cation has a high valency (charge) and a small coordination number, the electrostatic bond strength for bonds between this cation and its coordinating anions will be relatively large. If the bond strength is more than half the charge on the anion, it is unlikely that that anion will have more than one bond to the same cation with the same coordination number (see Rule #2). For example, bonds between phosphorus (with a charge of +5) and oxygen (in four coordination) would have a strength of $\frac{5}{4}$. Two such bonds to an oxygen anion would “overload” its -2 charge with a positive charge of +2.5.

Rule #5 - The number of essentially different kinds of constituents in a crystal tends to be small.

- Thank goodness! This makes understanding the crystal structures of minerals possible and, in some cases, even easy.
- Consider how all these rules apply to the periclase (MgO) structure we determined last week. Mg has a charge of +2. Using the radii given in Klein and Hurlbut, the radius ratio for Mg^{+2} (0.66) coordinated by O^{-2} (1.40) is 0.66, which indicates that Mg should be in six coordination (octahedral coordination). The bond strength for the Mg-O bonds is $+2/6 = 1/3$. Each O^{-2} is bonded to six Mg^{+2} (*i.e.* each O^{-2} is a corner of six different octahedra) giving exact local charge balance. The structure of periclase can be viewed as layers of Mg-filled oxygen octahedra, all of which share all of their edges (12) with adjacent octahedra.
- Halite (NaCl) has the same structure as periclase. Because Na^{+1} and Cl^{-1} have lower charges than Mg^{+2} and O^{-2} , the electrostatic bond strength for the Na-Cl bonds in halite is $1/6$ rather than the $1/3$ bond strength for Mg-O bonds in periclase. The lower hardness (2.5) of halite relative to periclase (6.0) reflects this difference in bond strength.

NaCl - halite

