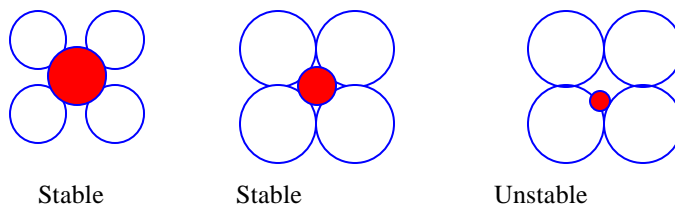


Pauling's Rules (Kingery page:56)

1. A coordination polyhedron of anions is formed about each cation in the structure. The cation-anion distance is determined by the sum of their radii. The coordination number (i.e. the number of anions surrounding the cation), is determined by the ratio of the radii of the two ions. The reason why the radius ratio of two species of ions influences the coordination number is apparent from the figure.



A given coordination number is stable only when the ratio of cation to anion radius is greater than some critical value.

Coordination Number	Disposition of Ions about Central Ion	Range - Ratio of Radius of Cation to Radius of Anion
8	Corners of Cube	≥ 0.732
6	Corners of Octahedron	≥ 0.414
4	Corners of Tetrahedron	≥ 0.225
3	Corners of Triangle	≥ 0.155
2	Linear	≥ 0.000

The first rule focuses attention on the cation coordination polyhedron as the basic building block of an ionic structure. A stable structure must be electrically neutral not only on the macroscopic scale but also at the atomic level. Second rule describes a basis for evaluating local charge neutrality.

2. In a stable structure the total strength of the bonds reaching an anion from all the surrounding cations should be equal to the charge of the cation.

$$\text{Strength of an ionic bond} = \frac{\text{Charge on Cation}}{\text{C.N.}}$$

For example:

- i) Bond Strength for Si is $4/4=1$ because valence of Si is 4 and it has tetrahedral coordination
- ii) Bond Strength for Al is $3/6=1/2$ because valence of Al is 3 and it has octahedral coordination

3. Third rule further concerns the linkage of the cation coordination polyhedra. In a stable structure the corners, rather than the edges and especially the faces, of the coordination polyhedra tend to be shared. If an edge is shared, it tends to be shortened. The basis of this rule is geometrical. The separation of the cations within the polyhedron decreases as the polyhedra successively share corners, edges and faces and the repulsive interaction between cations accordingly increases.

4. Polyhedra formed about cations of low coordination number and high charge tend to be linked by corner sharing.

5. The number of different constituents in a structure tends to be small. This follows from the difficulty of efficiently packing ions, and coordination polyhedra of different sizes, into a single structure.

Zachariasen Rules for the Formation of an Oxide Glass

1. Each oxygen ion should be linked to not more than two cations.
2. The coordination number of oxygen ions about the central cation must be small, 4 or less.
3. Oxygen polyhedra share corners, not edges or faces.
4. At least three corners of each polyhedron should be shared.