THE SOLID STATE

RADIUS RATIO RULE

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Limiting Radius Ratios An ionic crystal contains a large number of cations and anions. Generally, cations are Smaller in size than that of anions. The cations are surrounded by anions and they touch each other. These ions are arranged in space in such a way to produce maximum stability. The stability of the ionic crystal may be described in terms of radius ratio i.e., the ratio of the radius of cation (r) to that of anion (R) is (r/R). The range of (r/R) may be expressed as limiting radius ratio. This value is important to determine the arrangement of the ion in different types of crystals. Evidently radius ratio (r/R) plays a very important role in deciding the stable structure of ionic crystal. Larger cations prefer occupying larger holes (cubic etc.) and smaller cations prefer occupying smaller holes (tetrahedral etc.)

(i) Triangular: All anions touch each other and co-ordination number is 3



(ii) Tetrahedral void: All anions touch each other and co-ordination number of cation is 4.

Face diagonal AC = $\sqrt{2}a = 2r^{-1}$

$$r^{-} = = \frac{a}{\sqrt{2}}$$
 or $a = \sqrt{2}r^{-}$

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(ii) **Octahedral void:** All the anions are touch each other and co-ordination number is 6.





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(iii) **Cubic void:** All the anions are touch each other and co-ordination number is 8.

According to cube diagonal

$$AD = \sqrt{3} a = 2r^+ + 2r$$

$$(a = 2r^- = BC)$$

$$\sqrt{3} \times 2r^- = 2r^+ + 2r^-$$

Dividing by $2r^{-}$ on both sides.

$$\sqrt{3} = \frac{r^+}{r^-} + 1$$
 \longrightarrow $\frac{r^+}{r^-} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$

The preferred direction of the structure with increase in the radius ratio is as follows :

Plane triangular <u>0.225</u> Tetrahedral <u>0.414</u> octahedral <u>0.732</u> Cubic

Limiting radius	Coordination	Structural	Example
ratio $=\frac{r}{R}$	Number of cation	Arrangement	
		(Geometry of voids)	
0.155 - 0.225	3	Plane Trigonal	Boron Oxide
0.225 - 0.414	4	Tetrahedral	ZnS, SiO ₂
0.414 - 0.732	4	Square planaer	-
0.414 - 0.732	6	Octahedral	NaCl, MgO ₂
0.732 - 1.000	8	Cubic	CsCl

Limiting radius ratio for various types of sites