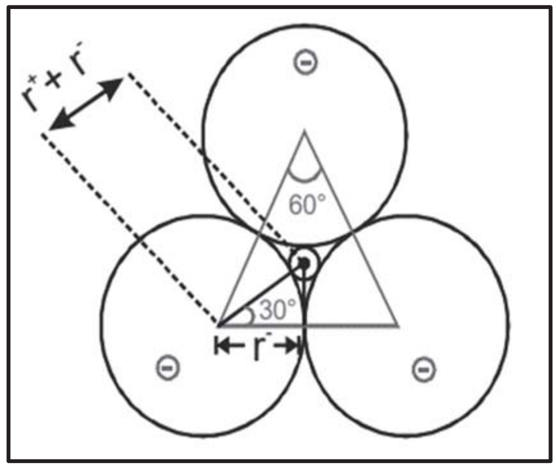
## RADIUS RATOI RULE

Limiting radius ratios play a crucial role in the structure of ionic crystals, where a multitude of cations and anions coexist. Typically, cations are smaller in size compared to anions. The arrangement involves cations being surrounded by anions, and they come into contact with each other. This spatial arrangement aims to achieve maximum stability within the ionic crystal lattice. The stability of the crystal is elucidated in terms of the radius ratio, denoted as the ratio of cation radius (r) to anion radius (R), expressed as $(\frac{r}{R})$. The limiting radius ratio establishes a range within which this ratio may fall, influencing the arrangement of ions in various crystal structures. Clearly, the radius ratio $(\frac{r}{R})$ plays a pivotal role in determining the stable structure of an ionic crystal, with larger cations tending to occupy larger holes (such as cubic) and smaller cations favoring smaller holes (such as tetrahedral).

### (i) Triangular:

All anions touch each other and co-ordination number is 3




$$\cos\theta \frac{r^-}{r^- + r^+}$$

$$\text{Cos } 30° = \frac{\sqrt{3}}{2} = \frac{r^-}{r^- + r^+}$$

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

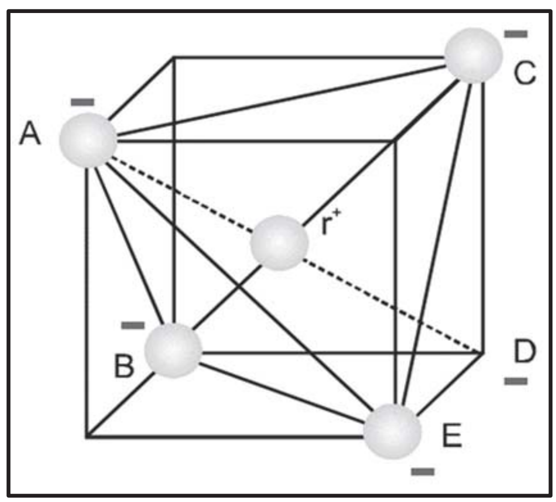
$$\sqrt{3}r^+ = (2-\sqrt{3})\ r^-$$

$$\frac{r^+}{r^-} = \frac{2-\sqrt{3}}{\sqrt{3}} = \frac{2-1.73}{1.73} = \frac{0.27}{1.73} = 0.155$$

$$\text{L.R.R.} = 0.155 = \frac{r^+}{r^-} < 1$$

### (ii) Tetrahedral void:

All anions are in contact with one another, and the coordination number of the cation is 4.




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

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

Triangle ACD –

$AD^2 = Ac^2 + CD^2$

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

$AD = \sqrt{3}\ a$

According to cube diagonal AD

$\because \quad \frac{\sqrt{3}\ a}{2} = r^+ + r^-$

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

Put the value of $a = \sqrt{2}r^-$

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

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

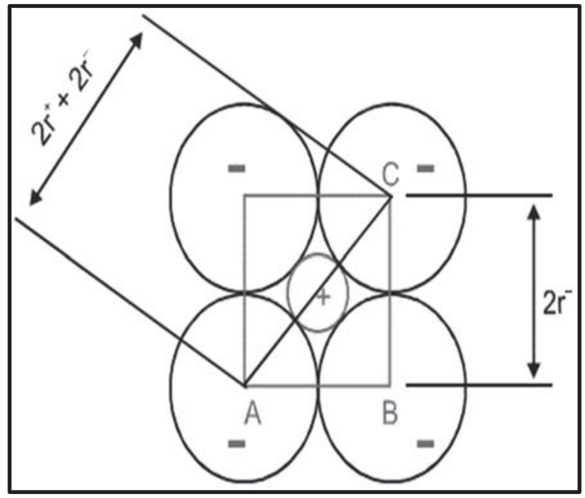
$$\frac{\sqrt{3}}{\sqrt{2}} = \frac{r^+}{r^-} + 1$$

$$\frac{r^+}{r^-} = \frac{\sqrt{3}}{\sqrt{2}} - 1 \rightarrow \frac{r^+}{r^-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = \frac{1.73 - 1.414}{1.414} = 0.225$$

**(iii) Octahedral void:**

All the anions are touch each other and co-ordination number is 6.

$$\text{In } \Delta ABC \; AC^2 = AB^2 + BC^2$$
$$= a^2 + a^2$$
$$AC = \sqrt{2}a$$
$$2r^+ + 2r^- = AC = \sqrt{2}a$$
$$BC = a = 2r^-$$
$$\frac{2r^+ + 2r^-}{2r^-} = \frac{\sqrt{2} \times 2r^-}{2r^-}$$
$$\frac{r^+}{r^-} + 1 = \sqrt{2} \rightarrow \frac{r^+}{r^-} = \sqrt{2} - 1$$
$$= 1.414 - 1 = 0.414$$




**(iv) Cubic void:**

All the anions are in contact with one another, and the coordination 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.

$$\sqrt{3} = \frac{r^+}{r^-} + 1 \rightarrow \frac{r^+}{r^-} = \sqrt{3} - 1 = 1.732 - 1 = 0732$$

The favored orientation of the structure increases with the growth of the radius ratio in the following manner:

$$\text{Plane triangular} \xrightarrow{0.225} \text{Tetrahedral} \xrightarrow{0.414} \text{octahedral} \xrightarrow{0.732} \text{Cubic}$$

**Limiting radius ratio for various types of sites**

| Limiting radius ratio $= \frac{r}{R}$ | Coordination Number of cation | Structural Arrangement (Geometry of voids) | Example |
|---|---|---|---|
| 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 |