Two parameters, radii and the electron attracting power of atoms or ions, determine the bonding, structure, and reaction of elementary substances and compounds. Much effort has been devoted to finding numerical values for these two factors applicable to all materials. It is hoped that the chemical properties of a known compound, and of a still non-existent new material, can be predicted with a combination of suitable numerical values. Firstly, geometrical factors will be described.

| Atomic Radii (pm) | H 32 | Li 123 Be 89 | B 82 C 77 N 75 O 73 F 72 | Na 154 Mg 136 | Al 118 Si 111 P 106 S 102 Cl 99 | K 203 Ca 174 Sc 144 Ti 132 V 122 Cr 118 Mn 117 Fe 116 Co 115 Ni 117 Cu 125 Zn 126 Ga 122 Ge 120 As 117 Se 114 Br 118 Rb 216 Sr 191 Y 162 Zr 145 Nb 130 Mo 127 Tc 125 Ru 125 Rh 128 Pd 134 Ag 148 Cd 144 In 144 Sn 140 Sb 136 Te 133 I 133 | Cs 235 Ba 198 La 169 Hf 144 Ta 134 W 128 Re 126 Os 127 Ir 130 Pt 134 Au 149 Hg 148 Tl 147 Pb 146 |

### Atomic and Ionic Radii

The electron density in atoms gradually approaches, but never reaches, zero as the distance from the nucleus increases. Therefore, strictly speaking the radius of an atom or ion is indeterminable. However, it is possible to determine the bond distance between atomic nuclei experimentally. Atomic radii determined experimentally are one of the most important atomic parameters describing the structural chemistry of compounds. It is reasonable to define the metal radius of a bulk metal as half of the distance between metal atoms. Half of the distance between atoms is defined also as the covalent radius of a covalent elementary substance (Table \(\PageIndex{1}\)).

| Ionic Radii (pm) | Li\(^+\) (4) 59 Be\(^{2+}\) (4) 27 B\(^3+\) (4) 11 N\(^3+\) (6) 16 O\(^2-\) (6) 140 F\(^-\) (6) 133 | Na\(^+\) (6) 102 Mg\(^{2+}\) (6) 72 Al\(^3+\) (6) 54 P\(^3+\) (6) 44 S\(^2-\) (6) 184 Cl\(^-\) (6) 181 | K\(^+\) (6) 138 Ca\(^{2+}\) (6) 100 Ga\(^3+\) (6) 62 As\(^3+\) (6) 58 Se\(^2-\) (6) 198 Br\(^-\) (6) 196 | Rb\(^+\) (6) 152 Sr\(^{2+}\) (6) 118 In\(^3+\) (6) 80 Te\(^2-\) (6) 221 I\(^-\) (6) 220 | Cs\(^+\) (6) 167 Ba\(^{2+}\) (6) 135 Ti\(^3+\) (6) 89 |
Since the cations and anions of different elements in an ionic compound are bonded by electrostatic interactions, the bond distance is the sum of ionic radii assigned to the cation and anion. The standard ionic radius of one species is fixed first and is then subtracted from the distance between ions to decide the radius of the partner ion. As the standard, the radius of $O^{2-}$ ion in a number of oxides is set to 140 pm (1 pm = $10^{-12}$ m) (R. D. Shannon). Cationic radii in oxides are the difference between the bond distance and 140 pm. After cation radii in oxides are decided, other anion radii can be calculated by subtraction of the cation radii from the distances between the atoms in ionic compounds. By applying such methods to many ionic compounds, ionic radii have been compiled in such a way that experimental and calculated values are generally consistent (Table \(\PageIndex{2}\)).

Even ionic compounds have some covalent contribution and it is not expected that calculated and experimental bond distances will agree exactly. Even if the ionic radius assigned to a standard ion is changed, we can still compile a set of ionic radii that are consistent across many compounds. Other examples of the proposed radii of $O^{2-}$ ion are 132 pm (V. M. Goldschmidt) or 60 pm (J. C. Slater). We must also be mindful that the cation-anion distances of the same ion pair become larger as the coordination number of opposite ions increases. Therefore, in any discussion of the structural features of ionic compounds from a viewpoint of ionic radii, a set of the ionic radii calculated using the same standard radius for the compounds with the same coordination number should be used.

Exercise \(\PageIndex{2}\)

Which ionic radius is larger, Cs\(^+\) or F\(^-\) ?

**Answer**

Cs\(^+\) (167 pm) > F\(^-\) (133 pm). The anion radius is not always larger.

The metal and covalent radii, also called the atomic radii, become smaller in the same period of the periodic table as the group of the element goes to the right and then increase again in the next period. The lanthanide contraction is responsible for the 5th period (4d) elements having almost the same atomic radii as those of the 6th period (5d) ones. In the periodic table, the lanthanide elements are inserted before the 5d elements. The atomic radii of lanthanide elements decrease noticeably as the effective nuclear charge increases because the screening effects of the 4f orbitals of lanthanide elements are weak due to their orbital shapes. Consequently, the atomic radii of the elements following lanthanides are very similar to those of the 4d elements.

### Lattice enthalpy

Although the stability of a crystal at constant temperature and pressure depends on the Gibbs free energy change of the crystal’s formation from its constituent ions, the stability of a crystal is determined mostly by the enthalpy change alone since the lattice formation is very exothermic, and the entropy term is negligibly small (refer to Section 3.1). Lattice enthalpy, \(\Delta H_L\), is defined as the standard enthalpy change of the reaction in which an ionic crystal decomposes into gaseous ions (s is solid, g is gas and L is lattice).

\[
MX(s) \rightarrow M^{+}(g) + X^{-}(g) \quad \Delta H_L
\]
Lattice enthalpy is indirectly calculated from the values of the enthalpy change at each stage using a Born-Haber cycle (Figure \(\PageIndex{1}\)). Namely, a closed cycle is formed using enthalpy data; standard enthalpy of formation \(\Delta H_f\) of an ionic crystal from elements, sublimation enthalpy of an elementary solid, or atomization enthalpy \(\Delta H_{atom}\) corresponding to the dissociation enthalpy of a gaseous elementary molecule, the ionization enthalpy \(\Delta H_{ion}\), which is the sum of the ionization enthalpy of cation formation and electron acquisition enthalpy of anion formation. Lattice enthalpy is calculated using the relation that enthalpy change in a cycle is zero.

\[
\Delta H_{atom}^{0} + \Delta_{ion}^{0} - \Delta H_{L}^{0} - \Delta H_{f}^{0} = 0
\]

The total Coulomb potential energy that exists between the ions in an ionic crystal consisting of ions A and B should be the sum of the individual Coulomb potential energies \(V_{ab}\). Since the locations of the ions in the crystal lattice are decided by the structure type, the total Coulomb potential between all ions is calculated by setting the distance between the ions to \(d\). A is the Madelung constant that is characteristic of each crystal type (Table \(\PageIndex{3}\)).

\[
V = N_A \frac{e^2}{4 \pi \epsilon_0} \left(\frac{z_A z_B}{d}\right) \times A
\]

\(N_A\) is Avogadro's constant and \(z_A\) and \(z_B\) are the electric charges of the cation and anion. The electrostatic interaction between contiguous ions is the strongest, and the Madelung constant generally becomes larger as the coordination number increases. Because the electrical charges have opposite signs, the potential becomes negative, indicating the stabilization that accompanies the formation of a crystal lattice from well dispersed, gaseous phase ions. Although it is generally true that the lowest electrostatic potential leads to the most stable structure, this is not strictly correct since there are also other interactions to consider.

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**Madelung constant**

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Table \(\PageIndex{3}\)
Madelung constants

<table>
<thead>
<tr>
<th>Structural type</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock-salt</td>
<td>1.748</td>
</tr>
<tr>
<td>Cesium chloride</td>
<td>1.763</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>1.638</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>1.641</td>
</tr>
<tr>
<td>Fluorite</td>
<td>2.519</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.408</td>
</tr>
</tbody>
</table>

The second largest factor that contributes to the lattice enthalpy is the van der Waals force, and dispersion forces or the London interaction is the main origin of this force. It is an attractive interaction between electric dipoles, which is inversely proportional to the 6th power of the distance \(d\) between ions. The van der Waals force is very small.

\[
V = -\frac{N_{A} C}{d^{6}}
\]

The value of the constant \(C\) is a function of each compound. Since it is at most 1% of the Coulombic force, it may be safely neglected in the calculation of lattice enthalpy.

(d) Structure of metal crystals

If we imagine metal atoms as being hard balls, when densely packed in two dimensions each ball will be in contact with six other balls (A). When another layer of this 2 dimensional arrangement is placed on top of the first, the packing will be densest and the structure most energetically stable when the metal atoms are placed on top of the hollows (B) of the first layer. When a 3rd layer is placed on top of the 2nd layer, there are two possibilities. Namely, the 3rd layer (A) overlaps with the 1st layer (A) or the 3rd layer (C) overlaps with neither (A) nor (B). The ABAB...-type packing is called hexagonally close-packed (hcp) (Figure \(\PageIndex{2}\)), and the ABCABC...-type is called cubic close-packed (ccp) (Figure \(\PageIndex{3}\)). In both cases, each ball is surrounded by 12 balls, that is, it is 12-coordinated. The coordination polyhedron of hcp is anti-cubooctahedron,
and that of ccp is cuboctahedron. When the lattice is sliced in different planes, the unit lattice of ccp appears to be a face-centered cubic lattice (fcc), containing a ball at each cubical apex and on the center of each face (Figure \(\PageIndex{4}\)). The unit lattice of hcp is a rhombohedral prism in which two balls are located in the positions shown in (Figure \(\PageIndex{5}\)). There are several different modes of piling up layers other than the normal hcp and ccp, and many examples are known.
The lattice with another ball at the center of a cubic lattice consisting of eight balls is the body centered cubic lattice (bcc), and some metals assume this mode of packing. The ratio of space occupation in a bcc lattice is smaller than that of close-packed ones but the difference is not large. Although the central ball is formally 8-coordinated, it is essentially 14-coordinated since there are a further six balls only 15.5% more distant than the first eight balls. However, because of the smaller ratio of space occupation, bcc appears relatively rarely and pure metals tend to adopt hcp or ccp.

In both hcp and ccp, the cavities among the balls are either the $O_h$ holes enclosed octahedrally by six balls or the $T_d$ holes enclosed tetrahedrally by four balls (Figure 6). ($O_h$ and $T_d$ are the symmetry symbols used in group theory.) In ionic solids, if the anions are in hcp or ccp arrangements, cations enter into either of these cavities.
Ionic Crystal

In ionic crystals, such as metal halides, oxides, and sulfides, metal cations and anions are aligned alternately, and the solid is bound together mainly by electrostatic bonding. Many metal halides dissolve in polar solvents, e.g. sodium chloride NaCl dissolves in water; whereas metal oxides and sulfides, in which there is a significant contribution of covalent bonding, are usually insoluble even in the most polar of solvents. The fundamental structure of ionic crystals is that larger ions (usually anions) are close-packed and smaller ions (usually cations) enter into the octahedral or tetrahedral cavities between them. Ionic crystals are classified into several typical structures according to the kinds of cations and anions involved and their ionic radii. Each structure type is called by the name of the typical compound, just as the rock salt structure representing the structures of not only NaCl (rock salt) but also various other compounds. Representative structure types of solid compounds and examples belonging to each type are shown in Table (PageIndex(4)).

<table>
<thead>
<tr>
<th>Crystal type</th>
<th>Coordination number</th>
<th>Examples of compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock-salt</td>
<td>(6,6)</td>
<td>LiCl, NaCl, KBr, Rbl, AgCl, MgO, NiO, InP</td>
</tr>
<tr>
<td>Cesium chloride</td>
<td>(8,8)</td>
<td>CsCl, CsBr, Csl, CuZn</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>(4,4)</td>
<td>ZnS, CdS, HgS, CuCl, GaP</td>
</tr>
<tr>
<td>Fluorite</td>
<td>(8,4)</td>
<td>CaF₂, SrF₂, CdF₂, ZrO₂, UO₂</td>
</tr>
<tr>
<td>Rutile</td>
<td>(6,3)</td>
<td>TiO₂, SnO₂, RuO₂, NiF₂</td>
</tr>
<tr>
<td>Cadmium iodide</td>
<td>(6,3)</td>
<td>CdI₂, Col₂, Mg(OH)₂</td>
</tr>
<tr>
<td>Rhenium oxide</td>
<td>(6,2)</td>
<td>ReO₃, WO₃, Sc(OH)₃</td>
</tr>
<tr>
<td>Perovskite</td>
<td>(6,2)</td>
<td>CaTiO₃, BaTiO₃, SrTiO₃</td>
</tr>
</tbody>
</table>
**Rock-salt structure** Sodium chloride NaCl is a typical compound in which Cl⁻ anions are arranged in ccp and Na⁺ cations occupy all the octahedral holes (Oh holes) (Figure \(\PageIndex{7}\)). Each Na⁺ cation is surrounded by six Cl⁻ anions. The same structure results even if the positions of anions and cations are exchanged. In the case of the reversed structure, each Cl⁻ anion is surrounded by six Na⁺ cations. Namely, each ion is 6-coordinated and it is convenient to describe the structure as the (6,6)-structure. The number of ions in a unit lattice is calculated by summing up the ions shown in Figure \(\PageIndex{7}\). Since there is one ion inside the lattice, the ions on the faces of the lattice are shared by 2, on the edges by 4, and on the corners by 8 lattices, a net of 4 Cl ions belonging to the unit lattice of NaCl is obtained by multiplying the numbers of ions inside the lattice by 1, on the faces by 1/2, on the edges by 1/4 and on the corners by 1/8. The number of Na ions in the unit lattice is also 4 and the ratio of Cl and Na ions agrees with the formula NaCl.

![Rock-salt structure](image)

Figure \(\PageIndex{7}\): - Rock-salt structure.

**Cesium chloride structure** Cesium chloride, CsCl, is a typical example of the structure shown in Figure \(\PageIndex{8}\). There is a Cs⁺ ion at the center and eight Cl⁻ are located at the eight corners of the cube. Conversely, even if a Cl⁻ comes to the center and eight Cs⁺ come to the corners, the number of each ion in the unit lattice is the same. Thus, this is referred to as the (8, 8)-structure. Since there is one Cs⁺ and one Cl⁻ ion belonging to this unit lattice, it coincides with the formula CsCl.
**Zinc blende structure** Zinc blende has the composition ZnS and its unit lattice is shown in Figure (PageIndex{9}). $S^{2-}$ anions are arranged in ccp and $Zn^{2+}$ cations occupy half of the tetrahedral holes (Td holes). In this arrangement, each cation is coordinated by four anions, and each anion by four cations. Hence, this is a (4, 4)-structure. There are both four $Zn^{2+}$ and $S^{2-}$ ions belonging to this unit lattice and the atomic ratio coincides with the formula of ZnS.

**Fluorite structure** The composition of fluorite is CaF$_2$. Since the number of $F^{-}$ is twice that of $Ca^{2+}$, all the tetrahedral holes of $Ca^{2+}$ arranged in ccp are occupied by $F^{-}$, as shown in Figure (PageIndex{10}). There are four $Ca^{2+}$ and eight $F^{-}$ ions and the number of ions is 4 times the formula. The anti-fluorite structure exchanges the cations and anions, and is exemplified by potassium oxide $K_2O$, etc.
Radius ratio

Generally, the total Coulombic potential energy $E_c$ of the univalent ionic compound MX is expressed by the following formula.

$$E_c = - \frac{N_A e^2}{4 \pi \epsilon_0 R} A$$

$N_A$ is the Avogadro constant, $A$ the Madelung constant and $R$ the distance between ions. According to this formula, a structure with a larger $A / R$ ratio is more stable. The Madelung constant of an MX compound increases with increasing coordination number. On the other hand, it is advantageous to lower the coordination number and to reduce $R$ in the case of small $M$, rendering contact between $M$ and $X$ more difficult. In an ionic crystal, the ratio of $r_M$ and $r_X$ with the anions contacting each other and also with the cations depends on the coordination number.

In a partial structure consisting only of anions, the anions form a coordination polyhedron around a cation. The anionic radius $r_X$ is one half of the distance of the edge of the polyhedron and the distance from the cation center to an apex of the polyhedron is the sum of the anion and cation radii $r_X + r_M$. The coordination polyhedron of the CsCl structure is a cube, the NaCl structure an octahedron, and the ZnS structure a tetrahedron. The distance from the center of each polyhedron to an apex is $\sqrt{3} r_X$, $\sqrt{2} r_X$, $\frac{\sqrt{6}}{2} r_X$. Therefore, the ratios of the cationic and anionic radii $r_M / r_X$ are $\frac{\sqrt{3} r_X - r_X}{r_X} = \sqrt{3} - 1 = 0.732$ for CsCl, $\frac{\sqrt{2} r_X - r_X}{r_X}$...
It has been explained that the coordination number decreases when these radius ratios are smaller than the given values since cations and anions do not come into contact with each other, causing instability. On the other hand, the coordination number increases for larger cations, increasing the radius ratio. However, the relation between a coordination number and a radius ratio is not simple. For example, halides of alkali metals adopt the NaCl structures at normal temperatures except cesium chloride CsCl, cesium bromide CsBr and cesium iodide CsI. It is not possible to assume structure types from the radius ratios even in the case of simple ionic compounds like alkali metal halides. However, the qualitative trend that smaller cations have smaller coordination numbers is generally correct.

Figure \(\PageIndex{11}\): - The radius ratio \(r_M / r_X\) of cations and anions.

**Variation of the solid structure expression**

Many solid-state inorganic compounds have complicated three-dimensional structures. Different structural illustrations for the same compound help our understanding of its structure. In the case of complicated inorganic compounds, drawing bond lines between atoms, as in most organic compounds, causes confusion. The anions in many metal oxides,
sulfides, or halides form tetrahedra or octahedra around the central metal cations. Although there is no bond between anions, the structures are greatly simplified if they are illustrated by the anion polyhedra sharing apexes, edges, or faces. In such illustrations, cationic metal atoms are usually omitted. As has been mentioned, ionic solid structures can be thought of as a close packed arrays of anions.

Figures 2.12 and 2.13 illustrate these three representations for molecular phosphorus pentoxide $\text{P}_2\text{O}_5$ ($= \text{P}_4\text{O}_{10}$) and molybdenum pentachloride $\text{MoCl}_5$ ($= \text{Mo}_2\text{Cl}_{10}$). Polyhedral representations are much easier to understand for the structures of large molecules or solid-state compounds formed by an infinite number of atoms. However, the bond line representation is suitable for molecular compounds such as the above examples.

Figure 2.12: Three expressions for the structure of $\text{P}_4\text{O}_{10}$.

Figure 2.13: Three expressions for the structure of $\text{Mo}_2\text{Cl}_{10}$.