Ionic Bonding - Pauling's Rules and the Bond Valence Method

Chemistry 754
Solid State Chemistry
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Lecture #14

Pauling’ Rules for Ionic Structures
Linus Pauling, J. Amer. Chem. Soc. 51, 1010 (1929)

1. The Cation-Anion distance is determined by summing ionic radii. The cation coordination environment is determined by radius ratio.

2. The bond valence sum of each ion should equal its oxidation state.

3. Crystals tend to avoid shared polyhedral edges and/or faces. This is particularly true for cations with high oxidation state & low coordination number.

4. In a crystal containing different cations those with large valence and small coord. # tend not to share anions.

5. The number of chemically different coordination environments for a given ion tends to be small.
Pauling’s 1st Rule – Ionic Radii

The Cation–Anion distance is determined by sums of ionic radii. The cation coordination environment is determined by radius ratio.


- There are two sets of radii, “Crystal radii”, are based on the best estimate of the size from accurate X-ray crystallography studies. “Traditional ionic radii” are based on the sizes of oxide and fluoride ions as chosen by Pauling. The crystal radii of the cations are 0.14 Å larger while the crystal radii of the anions are 0.14 Å smaller.

- Ionic radii are most accurate for oxides and fluorides, and for smaller, highly charged (hard) cations in regular coordination environments. The sizes of softer ions are more dependent upon their surroundings, and thus are less transferable.

- Radii are dependent upon both the oxidation state of the ions involved and the coordination number.

Ionic Radii – Notable Trends

There are several trends in ionic radii that should be familiar to you

- The radius increases as you move down a column.
  - Al\(^{3+}\) = 0.675 Å, Ga\(^{3+}\) = 0.760 Å, In\(^{3+}\) = 0.940 Å, Tl\(^{3+}\) = 1.025 Å

- The radius decreases as you move across a period.
  - La\(^{3+}\) = 1.172 Å, Nd\(^{3+}\) = 1.123 Å, Gd\(^{3+}\) = 1.078 Å, Lu\(^{3+}\) = 1.001 Å

- The 4d & 5d metals have similar radii due to the lanthanide contraction.
  - Nb\(^{5+}\) = 0.78 Å, Ta\(^{5+}\) = 0.78 Å, Pd\(^{4+}\) = 0.755 Å, Pt\(^{4+}\) = 0.765 Å

- The cation radius decreases as you increase the oxidation state.
  - Mn\(^{2+}\) = 0.810 Å, Mn\(^{3+}\) = 0.785 Å, Mn\(^{4+}\) = 0.670 Å

- The radius increases as the coordination number increases.
  - Sr\(^{2+}\): CN=6 → 1.32 Å, CN=8 → 1.40 Å, CN=10 → 1.50 Å, CN=12 → 1.58 Å
Pauling's 1st Rule - Radius Ratio

The Cation-Anion distance is determined by sums of ionic radii. The cation coordination environment is determined by radius ratio.

The radius ratio rule is a geometric argument based on the number of anions you can get around a cation. It predicts that as the cation size decreases, its coordination number decreases.

\[
1.00 < \frac{R(\text{cation})}{R(\text{anion})} > 0.732 \\
\text{Cubic (CN=8)}
\]

\[
0.732 > \frac{R(\text{cation})}{R(\text{anion})} > 0.414 \\
\text{Octahedral (CN=6)}
\]

\[
0.414 > \frac{R(\text{cation})}{R(\text{anion})} > 0.225 \\
\text{Tetrahedral (CN=4)}
\]

If the cation radius ↓ as anion radius remains constant, it will lead to unfavorable overlap of anions in order to maintain optimal cation-anion contact.

While this is generally true, the reasons are probably not the simple geometrical ones suggested by Pauling. Furthermore, there are so many exceptions to this rule that it is of marginal significance.

Pauling's 2nd Rule - Bond Valence

The bond valence sum of each ion should equal its oxidation state.

This idea is well known in organic chemistry where each bond has a valence of 1. So that C always has a valence sum of 4 (4 bonds), O always forms 2 bonds, H forms 1 bond, etc.

Pauling took this concept and extended it to inorganic compounds, including extended ionic lattices. Pauling's proposed that the valence of a bond, \( s_{ij} \), could be non-integer, and the sum of the bond valences around each atom, should equal its oxidation state.

\[
V_i = \sum s_{ij}
\]

\( V_i \) = The oxidation state of atom i
\( s_{ij} \) = The valence of the bond between atoms i and j.

If there are \( n \) equivalent bonds around a central atom with valence \( m \), then valence of each bond is equal to:

\[
s_{ij} = \frac{m}{n}.
\]
**Bond Valence – Example 1**

Consider the rutile form of TiO$_2$. What is the valence of the Ti-O bonds?

First let’s calculate the valence of the Ti-O bonds.

\[ V_i = \sum s_{ij} \]

\[ 4 = 6(s_{ij}) \]

\[ s_{ij} = \frac{2}{3} \]

Now use this to determine the coordination number of oxygen.

\[ V_i = \sum s_{ij} \]

\[ 2 = n(2/3) \]

\[ n = 3 \]

**Bond Valence – Example 2**

What is the oxygen coordination in the mineral zircon, ZrSiO$_4$, where Si$^{4+}$ is tetrahedrally coordinated and Zr$^{4+}$ is eight coordinate?

First let’s calculate the valence of the Si-O bonds.

\[ V_i = \sum s_{ij} \]

\[ 4 = 4(s_{ij}) \]

\[ s_{Si-O} = 1 \]

Now let’s calculate the valence of the Zr-O bonds.

\[ V_i = \sum s_{ij} \]

\[ 4 = 8(s_{ij}) \]

\[ s_{Zr-O} = \frac{1}{2} \]

Now let’s determine the coordination number of oxygen.

\[ V_i = n_1 s_{Si-O} + n_2 s_{Zr-O} \]

\[ 2 = n_1(1) + n_2(1/2) \]

\[ n_1 = 1 \quad n_2 = 2 \]
Pauling’s 3rd Rule
The presence of shared edges and particularly shared faces decreases the stability of a structure. This is particularly true for cations with large valences and small coordination number.

When polyhedra share a common edge or face it brings the cations closer together, thereby increasing electrostatic repulsions.

<table>
<thead>
<tr>
<th>Cation-Cation Distance</th>
<th>Corner</th>
<th>Edge</th>
<th>Face</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedra</td>
<td>2 M-X</td>
<td>1.16 M-X</td>
<td>0.67 M-X</td>
</tr>
<tr>
<td>Octahedra</td>
<td>2 M-X</td>
<td>1.41 M-X</td>
<td>1.16 M-X</td>
</tr>
</tbody>
</table>

Pauling’s 4th Rule
In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedron elements with each other.

The logic behind this rule comes in part from the bonding preferences of the anion. Consider the following example. CaWO₄ has the scheelite structure where the W⁶⁺ ions are tetrahedrally coordinated. The valence of the W-O bond is:

\[ V_i = \Sigma s_{ij} \rightarrow 6 = 4(s_{\text{W-O}}) \rightarrow s_{\text{W-O}} = 1.5 \]

If you were to propose a structure where two WO₄ tetrahedra shared a corner the shared oxygen would be bound to 2 W⁶⁺ ions. Its valence is:

\[ V_O = 2 s_{\text{W-O}} \]
\[ V_O = 2(1.5) = 3 \]

This is clearly too high and a violation of the second rule. This effect is exacerbated as the cation valence increases its coordination number decreases, because \( s_{ij} \) increases.
Pauling’s 5th Rule

The number of chemicaly different coordination environments for a given ion in a crystal tends to be small. (Rule of Parsimony)

We have already discussed how ionic forces favor high symmetry and regular coordination environments. This is a generalization of this concept.

Quantitative Bond Valence Method

A powerful advance on Pauling’s bond valence method is to quantitatively link the bond valence to the bond distance (rather than the oxidation state). While a number of scientists have helped in this endeavor the principle driving force has largely been I.D. Brown from McMaster University.1,2 The bond valence is calculated using the following relationship:

\[ s_{ij} = \exp \left( \frac{(R_{ij} - d_{ij})}{b} \right) \]

Where \(d_{ij}\) is the distance between atoms \(i\) and \(j\), \(R_{ij}\) is the empirically determined distance for a given cation-anion pair, and \(b\) is also an empirical value generally set equal to 0.37. Values of \(R_{ij}\) that give bond valence sums near the oxidation state have been tabulated.3,4,5

Uses of the Bond Valence Method

1. To examine experimental structures for accuracy, determine oxidation states, or identify bonding instabilities.
2. To locate light atoms (i.e. H or Li) that are hard to find by X-ray diffraction methods by examining the valences of the surrounding atoms.
3. To predict bond distances, as an alternative to ionic radii. This can be done by inverting the equation:

\[ d_{ij} = R_{ij} - b\ln(s_{ij}) \]

Advantages over ionic radii include
- Independent of coordination number
- Can handle unsymmetrical coordination environments

Bond Valences & Structural Analysis

FeTiO\textsubscript{3} (Ilmenite)  
- **Bond Distances**
  - Fe-O = 3\times2.07, 3\times2.20
  - Ti-O = 3\times1.88, 3\times2.09

- **Bond Valence Sums**
  - Fe = 3\times0.40 + 3\times0.28 = 2.04
  - Fe = 3\times0.84 + 3\times0.48 = 3.96
  - O = 0.40 + 0.28 + 0.84 + 0.48 = 2.00

Al\textsubscript{2}O\textsubscript{3}OH (Diaspore)  
- **Bond Distances**
  - O\textsubscript{1}-Al = 1.85, 1.85, 1.86
  - O\textsubscript{2}-Al = 1.97, 1.97, 1.98

- **Bond Valence Sums**
  - Al = 2.75
  - O\textsubscript{1} = 1.60
  - O\textsubscript{2} = 1.16
**Bond Valences Predictively**

Two types of Oxide ions -
- Bridging - $\text{\textsuperscript{II}}\text{O}$
- Terminal - $\text{\textsuperscript{I}}\text{O}$

Pauling’s 2\textsuperscript{nd} rule gives the expected bond valences
- $\text{Cr}-\text{\textsuperscript{II}}\text{O} \rightarrow s_{ij} = 1.0$
- $\text{Cr}-\text{\textsuperscript{I}}\text{O} \rightarrow s_{ij} = 2.0$

Inverting the bond valence calculation we can estimate distances
- $\text{Cr}-\text{\textsuperscript{II}}\text{O} \rightarrow 1.79$ Å
- $\text{Cr}-\text{\textsuperscript{I}}\text{O} \rightarrow 1.54$ Å

The observed bond distances are
- $\text{Cr}-\text{\textsuperscript{II}}\text{O} \rightarrow 1.75$ Å
- $\text{Cr}-\text{\textsuperscript{I}}\text{O} \rightarrow 1.57$ Å

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**α-MoO\textsubscript{3}**

Space Group = P-1
Chains of edge-sharing octahedra
Mo-O Bond distances = 1.67, 1.73, 1.95, 1.95, 2.25, 2.33

**β-MoO\textsubscript{3}**

Sp. Group = P2\textsubscript{1}/n
Corner sharing octahedra
Mo-O Bond distances =
- Mo(1) 1.65, 1.79, 1.81, 2.09, 2.12, 2.20
- Mo(2) 1.80, 1.87, 1.91, 1.92, 2.01, 2.23
\(-\text{MoO}_3\) A closer look

The Mo\(^{6+}\) ions shift away from the shared edges.

\[
\begin{align*}
\text{d} &= 1.948 \text{ Å} \\
\text{s} &= 0.90 \\
\text{d} &= 2.332 \text{ Å} \\
\text{s} &= 0.32 \\
\text{d} &= 1.671 \text{ Å} \\
\text{s} &= 1.90
\end{align*}
\]

Bond Valence Sums

\[
\begin{align*}
\text{Mo} &= 2 \times 0.90 + 1.90 + 0.32 + 1.60 + 0.40 = 6.02 \\
\text{IO} &= 1.90 \\
\text{IIIO} &= 1.60 + 0.40 = 2.00 \\
\text{IIIIO} &= 0.90 + 0.90 + 0.32 = 2.12
\end{align*}
\]

Distorted Coordination Environments

\[
\begin{align*}
\text{Ca}^2+ (CN=12) &\quad r = 1.48 \text{ Å} \\
\text{Ca}^2+ (CN=8) &\quad r = 1.26 \text{ Å} \\
\text{Ca}^2+ (CN=6) &\quad r = 1.14 \text{ Å} \\
\text{O}^2- (CN = 2) &\quad r = 1.21 \text{ Å} \\
\text{O}^2- (CN = 6) &\quad r = 1.26 \text{ Å}
\end{align*}
\]

How far should the tilting go? Can you tell from the ionic radii of \text{Ca}^{2+} and \text{O}^{2-}?
Distorted Coordination Environments

Ca–O Distances

<table>
<thead>
<tr>
<th></th>
<th>Ca–O Valences</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 2.36 \text{ Å}$</td>
<td>$1 \times 0.345$</td>
</tr>
<tr>
<td>$2 \times 2.37 \text{ Å}$</td>
<td>$2 \times 0.336$</td>
</tr>
<tr>
<td>$1 \times 2.46 \text{ Å}$</td>
<td>$1 \times 0.264$</td>
</tr>
<tr>
<td>$2 \times 2.62 \text{ Å}$</td>
<td>$2 \times 0.171$</td>
</tr>
<tr>
<td>$2 \times 2.65 \text{ Å}$</td>
<td>$2 \times 0.157$</td>
</tr>
</tbody>
</table>

$V_{\text{ca}} = 1.94$

Structure Prediction Using Bond Valences

**SPuDS** is a software program developed for predicting crystal structures of cubic and distorted AMX$_3$ & A$_2$MM'X$_6$ perovskites. It optimizes the structure based on the idea of rigid octahedra and the bond valence method through the following steps.

1. Vary the M–X bond length, $d$, in order to optimize the valence of the octahedral cation(s).
2. Vary the octahedral tilting in order to optimize the valence of the A-site cation(s).


http://www.chemistry.ohio-state.edu/~mlufaso/spuds/