Pauling introduced the idea of defining the percent ionic character possessed by a chemical bond. A covalent bond with equal sharing of the charge density has 0% ionic character, and a perfect ionic bond would of course have 100% ionic character.

One method of estimating the percent ionic character is to set it equal to the ratio of the observed dipole moment to the value of eR, all multiplied by 100. The value of eR is the value of the dipole moment when one charge is completely transferred in the formation of the bond and the resulting ions are spherical.

\[
\text{percent ionic character} = \left( \frac{\mu}{eR} \right) \times 100
\]

Pauling has proposed an empirical relationship which relates the percent ionic character in a bond to the electronegativity difference

\[
\text{percent ionic character} = \left( 1 - e^{-\left(\frac{1}{4}(\chi_A - \chi_B)\right)} \right) \times 100
\]
Table 6.2 Percent Ionic Character of a Single Chemical Bond with Oxygen

<table>
<thead>
<tr>
<th>Difference in electronegativity</th>
<th>Ionic character, %</th>
<th>Difference in electronegativity</th>
<th>Ionic character, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.5</td>
<td>1.7</td>
<td>51</td>
</tr>
<tr>
<td>0.2</td>
<td>1.0</td>
<td>1.8</td>
<td>55</td>
</tr>
<tr>
<td>0.3</td>
<td>2.0</td>
<td>1.9</td>
<td>59</td>
</tr>
<tr>
<td>0.4</td>
<td>4.0</td>
<td>2.0</td>
<td>63</td>
</tr>
<tr>
<td>0.5</td>
<td>6.0</td>
<td>2.1</td>
<td>67</td>
</tr>
<tr>
<td>0.6</td>
<td>9.0</td>
<td>2.2</td>
<td>70</td>
</tr>
<tr>
<td>0.7</td>
<td>12.0</td>
<td>2.3</td>
<td>74</td>
</tr>
<tr>
<td>0.8</td>
<td>15.0</td>
<td>2.4</td>
<td>76</td>
</tr>
<tr>
<td>0.9</td>
<td>19.0</td>
<td>2.5</td>
<td>79</td>
</tr>
<tr>
<td>1.0</td>
<td>22.0</td>
<td>2.6</td>
<td>82</td>
</tr>
<tr>
<td>1.1</td>
<td>26.0</td>
<td>2.7</td>
<td>84</td>
</tr>
<tr>
<td>1.2</td>
<td>30.0</td>
<td>2.8</td>
<td>86</td>
</tr>
<tr>
<td>1.3</td>
<td>34.0</td>
<td>2.9</td>
<td>88</td>
</tr>
<tr>
<td>1.4</td>
<td>39.0</td>
<td>3.0</td>
<td>89</td>
</tr>
<tr>
<td>1.5</td>
<td>43.0</td>
<td>3.1</td>
<td>91</td>
</tr>
<tr>
<td>1.6</td>
<td>47.0</td>
<td>3.2</td>
<td>92</td>
</tr>
</tbody>
</table>


Some examples

CsF \( \chi_{Cs} = 0.7; \chi_{F} = 4.0 \)
\( \chi_{F} - \chi_{Cs} = 3.3 \)
\( > 92\% \) ionic; \(< 8\% \) covalent

Si-O bond: \( \chi_{Si} = 1.8; \chi_{O} = 3.5 \)
\( \chi_{O} - \chi_{Si} = 1.7 \)
51\% ionic, 49\% covalent

ZnS \( \chi_{Zn} = 1.6; \chi_{S} = 2.5 \)
\( \chi_{S} - \chi_{Zn} = 0.9 \)
19\% ionic; 81\% covalent

CCl₄ \( \chi_{C} = 2.5; \chi_{Cl} = 3.0 \)
\( \chi_{Cl} - \chi_{C} = 0.5 \)
6\% ionic; 94\% covalent

Fluorides ionic
Chlorides covalent-ionic
Oxides Silicates covalent
B-group metalloids Sulfides/arsenides covalent-metallic
Metals, alloys metallic-covalent
Can we use the ionic bond to anything useful in modern materials science?


"Ionic Theory is a good starting place for getting some general guidance.... Ionic theory has had a good run (> 50 years) and is still heavily over-emphasized: **SO FAR AS DETAILED CONSIDERATIONS OF CRYSTAL STRUCTURES ARE CONCERNED IT IS TIME IT WAS INTERRED**"

Pauling’s five rules for coordination (ionic) compounds

These rules rationalize crystal structures of minerals.

Prof. Linus Pauling (1901-1994)
Nobel Prize for Chemistry 1954
Nobel Prize for Peace 1962
Rule 1

*Cation coordination and the radius rule.*
A polyhedron of spherical anions is grouped around each cation, such that the number of anions that may surround the cation is a function of the radius ratio, $R = r_{\text{cat}}/r_{\text{an}}$.

Rule 2

*Electrostatic bond strength and the number of polyhedra with a common corner.*
The number of cations that may surround a given anion is limited by the requirement that negative electric charge on anions be satisfied locally or over short range by near cation neighbours. A given anion will be the common corner to several coordination polyhedra, the exact number be limited by the concept of EBS (electronic bond strength), equal to (cation charge)/(cation CN).
Electrostatic bond strength, EBS

An anion will be the common corner of several coordination polyhedra. The exact number is limited by the EBS sum. Assume that the charge of the cation is distributed equally between neighbouring anions.

\[
\begin{align*}
\text{Li}^+/	ext{CN(VI)}: & \quad +1/6 \\
\text{Al}^{3+}/	ext{CN(VI)}: & \quad +1/2 \\
\text{Al}^{3+}/	ext{CN(IV)}: & \quad +3/4 \\
\text{Si}^{4+}/	ext{CN(IV)}: & \quad +1 \\
\text{O}^{2-}: & \quad \Sigma(\text{EBS}) = 2 \\
\text{F}^{-}: & \quad \Sigma(\text{EBS}) = 1
\end{align*}
\]

\[
\begin{align*}
\text{SiO}_2 & \quad \text{Si}^{4+} \text{CN(IV) EBS}=1 \\
& \quad \text{i.e. CN(O^{2-})=II} \\
& \quad \text{Si}^{4+}\text{O}_2^{11} \\
\text{NaCl} & \quad \text{Na}^{+}, \text{CN(VI) EBS}=1/6 \\
& \quad \text{CN(Cl}^{-}) = \text{VI} \\
\text{MgO} & \quad \text{Mg}^{2+}, \text{CN(VI) EBS}=1/3 \\
& \quad \text{CN(O}^{2-}) = \text{VI}
\end{align*}
\]

Rule 3

The rule of polyhedral sharing

The stability of structures with different types of polyhedral linking is vertex-sharing > edge-sharing > face-sharing. The effect is largest for cations with high charge and low coordination number. Especially large when \( r^+/r^- \) approaches the lower limit of the polyhedral stability.
Rule 4

**Independence of polyhedra with small cations of high charge**

Cations with small radius and large charge tend not to share polyhedral elements with one another. (extension of rule 2)

\[
\begin{align*}
C^{4+}/CN(III): & +4/3 \quad P^{5+}/CN(IV): +5/4 \\
Ca^{VI}C^{III}O_3^{III} \quad \text{or} \quad Ca^{VI}[CO_3]^{VI}
\end{align*}
\]

Rule 5

**The rule of parsimony**

A large number of different coordination polyhedra in a given mineral tends to decrease its stability.

**KISS: Keep it simple, stupid**

“The Dalai Lama once said that simplicity is the key to happiness in the modern world. This philosophy can be adapted into the realm of web design and digital interface design.” The expressions "Keep it simple, stupid", "Kill your darlings" and "Less is more" all pinpoint the fact that simplicity is important.”
Rule 5

Many exceptions to this rule…

Tourmaline:
$\text{Na}^{+}\text{Mg}_3^{\text{VI}}\text{Al}_6^{\text{VI}}\text{[Si}_6^{\text{IV}}\text{O}_{18}]\text{[B}^{\text{III}}\text{O}_3\text{]}_3\text{[OH},\text{F}]_4$

Hornblende:
$\text{Na}_{0.5}^{+}\text{Ca}^{\text{VIII}}(\text{Fe}^{2+},\text{Al})_2^{\text{VI}}\text{Fe}_2^{2+}\text{Mg}^{\text{VI}}\text{[Si}_{6.5}^{\text{IV}}\text{Al}_{1.5}^{\text{IV}}\text{O}_{22}]\text{[OH},\text{F}]_2$

Ionic radii

Close packed anions:
14 voids around each sphere:
6 octahedral, 8 tetrahedral
(i.e. 1 octahedral and 2 tetrahedral voids / sphere)

Only 6 of these may be occupied in any given mineral
(given by Paulings 2. rule)
Ionic radii

An ion in vacuum do not have a fixed radius
In crystals: interatomic distance is the sum of the ionic radii

In NaF ... “separated by a zero electron density is a convenient distortion of the truth”

X-ray diffraction for structure determination
X-rays: Wilhelm Conrad Röntgen 1895
Diffraction: Friedrich, Knipping and Laue 1912
W.H. and W.L. Bragg: Krystalstruktur analyse

1901 Physik: **W.C. Röntgen**: Entdeckung der Röntgenstrahlen
1914 Physik: **Max von Laue**: Beugung von Röntgenstrahlen an Kristallen
1915 Physik: **Sir William Henrik Bragg and Sir William Lawrence Bragg**: Analyse von Kristallstrukturen mit Hilfe von Röntgenstrahlen
Ionic radii, empirical

Wasastjerna, 1923
Goldschmidt, 1926
Pauling, 1927
Ahrens, 1952
Fumi and Tosi, 1964
Shannon and Prewitt, 1969
(Table 4.2)

Radii depends on coordination

Electrostatic bond strength diagrams Pauling’s second rule
Implicitly stating that charge is neutralized locally

Group 2A:
Minerals with one unique anion:
Rutile: TiO₂, Flourite: CaF₂
Unique EBS solution

Group 2B:
Two or more anions with different cation environment or with different anions

Group 2C:
Minerals where the same anion (e.g. O²⁻) is surrounded by different cation arrangements which do not satisfy Paulings 2. rule
Pauling Rule 2A group

Rutile: TiO$_2$, Ti$^{4+}$/VI = 2/3

Flourite: CaF$_2$, Ca$^{2+}$/VIII = 1/4

Al$_2$O$_3$?

Spessartine (garnet)
Mn$_3$Al$_2$[SiO$_4$]$_3$
Mn$^{2+}$(VIII) = 1/4,
Al$^{3+}$(VI) = 1/2,
Si$^{4+}$(IV) = 1

I.e. each Oxygen anion is surrounded by:
2 x Mn$^{2+}$, 1 x Al$^{3+}$, 1 x Si$^{4+}$

Is this compatible with the garnet composition?

$12x$ (1O: 2x1/8 Mn, 1/6 Al, 1/4 Si)
Mn$_3$Al$_2$Si$_4$O$_{12}$

Whenever SiO$_4$ is present, the SiO$_4$ polyhedra are independent. One unique anion in the structure....

Olivine (MgFe)$_2$[SiO$_4$]
Oxygen surrounded by: One Si$^{4+}$/IV, three (MgFe)$^{2+}$/VI, 1+3x1/3

Zircon Zr[SiO$_4$]
One Si$^{4+}$/IV, two Zr$^{4+}$/VIII, (1 + 2x1/2)

YPO$_4$ (isostructural with zircon)
One P$^{5+}$/IV = 5/4
two Y$^{3+}$/VIII = 3/8
= 10/8 + 6/8
Pauling Rule 2B group

When SiO₄ tetrahedra share corners, there are more than one type of oxygen ions.

Bridging oxygen: Si⁴⁺/IV = 1

Thortveitite, Sc₂[Si₂O₇]
O1: 2xSi⁴⁺/IV
O2: 1xSi⁴⁺/IV, 2xSc³⁺/VI

Beryl: Al₂Be₃[Si₆O₁₈]
O1: 2xSi⁴⁺/IV
O2: 1xSi⁴⁺/IV, 1xAl³⁺/VI, 1xBe²⁺/IV

Sheet silicates (phyllosilicates):
2-dimensional sheets, Si₂O₅
Talc: Mg₃[Si₄O₁₀](OH)₂
Si⁴⁺ CN(IV), Mg²⁺ CN(VI)

Three types of oxygen:
O1: Bridging oxygen,
O2 in contact with 1 Si and 3 Mg
O3 in OH group, contact 3 Mg
Pauling Rule 2B group

Bastnaesite, CeF[CO₃]

Ce³⁺: radius ratio analysis:
\[ r: 1.14 \text{ Å CN(VIII)}, 1.29 \text{ Å CN(XII)} \]

Radius ratio O²⁻: 0.838 and 0.948

EBS suggests Ce³⁺ CN (IX)

X-ray: Ce³⁺ three F⁻ coplanar
Three oxygen up and down
F⁻ surrounded by three Ce³⁺
O²⁻ surrounded two Ce³⁺ and one C⁴⁺

(Or each CO₃ group surrounded by six Ce³⁺)

Pauling Rule 2C group

In many minerals the nearest neighbour cation arrangement around each anion differ, leading to EBS summations that does not correspond to the anion charge.

This means that neutrality is not satisfied locally, but are spread out over a larger domain.

Diopside (pyroxene), CaMg[Si₂O₆]

Ca⁸⁺Mg⁶⁺[Si₂⁴⁺O₁⁶⁻]

Ca⁸⁺Mg⁶⁺[Si₂⁴⁺O₂⁴⁺O₂⁻]

O₁: Si, 2Mg, Ca: \[ 1 + 2 \times \frac{1}{3} + \frac{1}{4} = 1.916 \]
O₂: Si, Mg, Ca: \[ 1 + \frac{1}{3} + \frac{1}{4} = 1.583 \]
O₃: 2xSi, 2xCa: \[ 2 \times 1 + 2 \times 1/4 = 2.5 \]
Zachariasen’s elaboration of Pauling’s rule 2

EBS is inversely proportional to A-X bond lengths

(single crystal structures of borate minerals)

This is the beginning of more complex bond strength analysis, used for e.g. validating structures, identify missing charges (e.g. hydrogen), identify hydrogen bonding schemes, investigate formal charges etc.
Coordination polyhedra

2 linear
3 trigonal planar
4 tetrahedral
5 pyramidal
6 planar
7 square planar
8 trigonal bipyramidal
9 trigonal prismatic
10 square prismatic
11 octahedral
12 trigonal prismatic
13 cuboctahedral
14 anti-cuboctahedral