Bond valence nets and sums

Ram Seshadri

Materials Department, and
Department of Chemistry and Biochemistry
Materials Research Laboratory
University of California, Santa Barbara CA 93106
http://www.mrl.ucsb.edu/~seshadri +++ seshadri@mrl.ucsb.edu

UC SANTA BARBARA
engineering and the sciences

Bond valence nets and sums

Pauling's second rule (electrostatic valence rule):

The electrostatic bond valence of a cation of charge V_+ and coordination (number of anion neighbors) Z_+ is given by: $s_+ = V_+/Z_+$
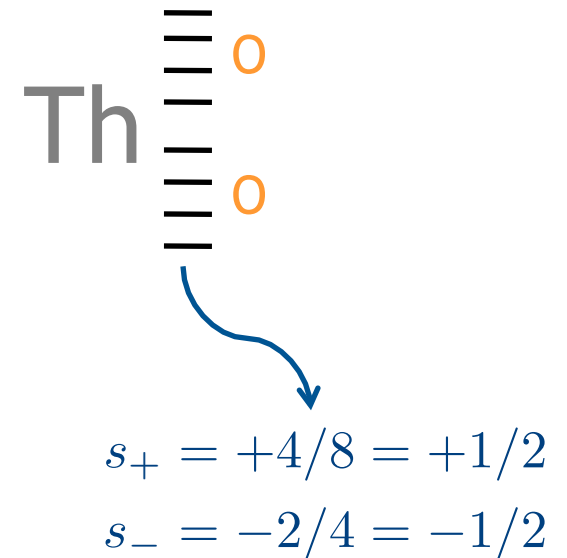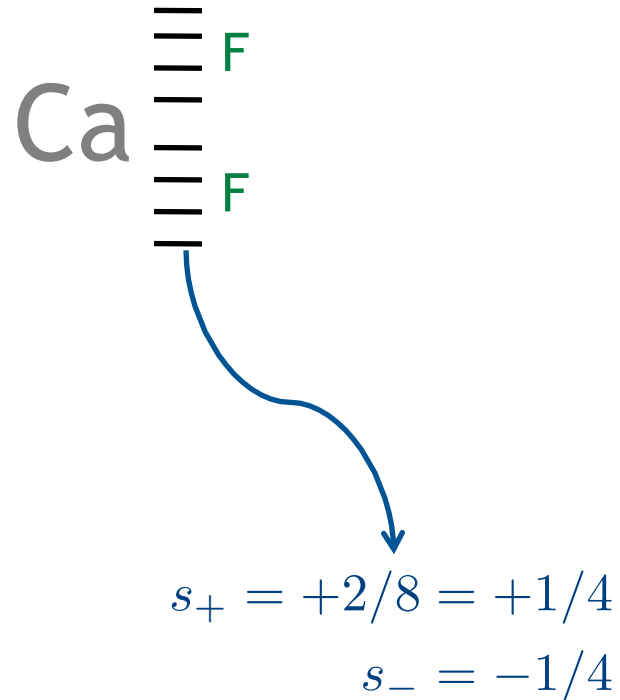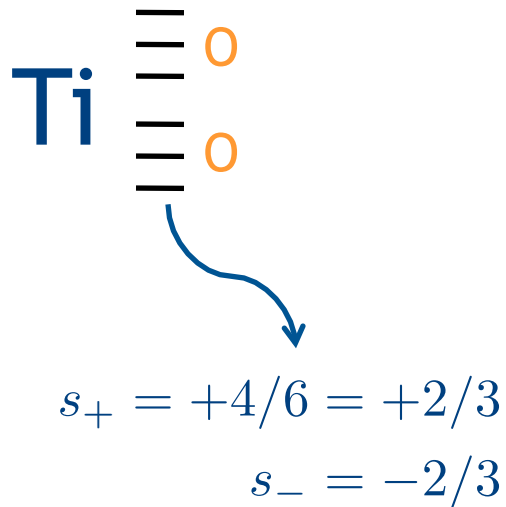
For the anion, similarly, the electrostatic bond valence is: $s_- = V_-/Z_-$

The rule states that the sum of the valence of the cation must equal the sum of the valence of the anion (neglecting signs):

$$\sum |s_-| = \sum |s_+|$$

UC SANTA BARBARA
engineering and the sciences

Bond valence nets and sums

Let us consider some AB_2 structures: rutile TiO_2, and fluorite CaF_2, and ThO_2:

Ti — O
   — O

$$s_+ = +4/6 = +2/3$$
$$s_- = -2/3$$

Ca — F
   — F

$$s_+ = +2/8 = +1/4$$
$$s_- = -1/4$$

Th — O
   — O

$$s_+ = +4/8 = +1/2$$
$$s_- = -2/4 = -1/2$$

Note that the horizontal linkers between ions are not "bonds" in the sense of pairs of electrons, but rather, indications of coordination number: In rutile, the cation is octahedral, in fluorite it is cubic ...

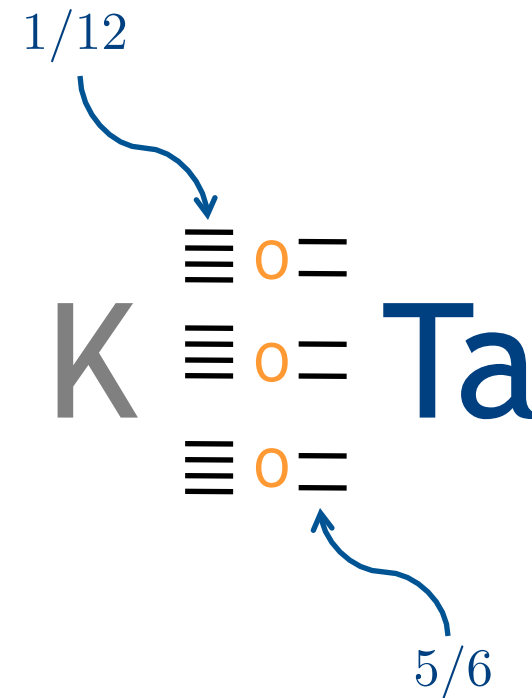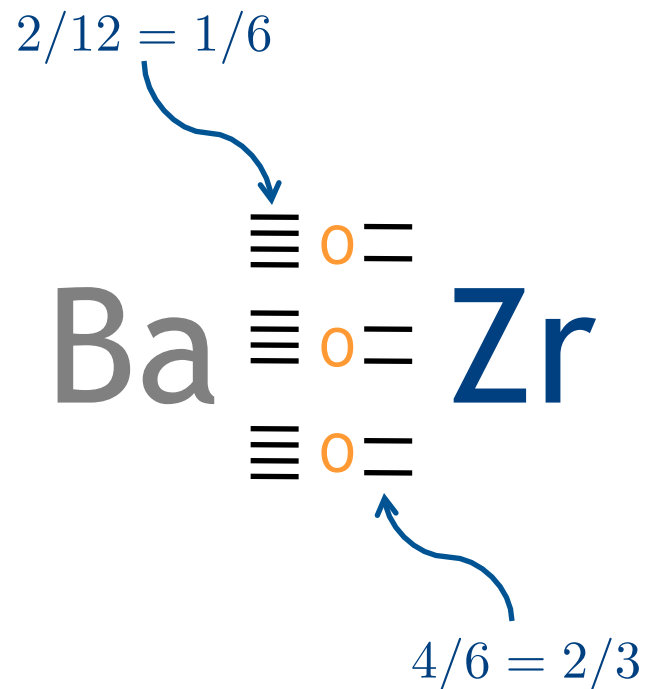We refer to these depictions as bond-valence nets.

Materials 218/Chem 277

Bond valence nets and sums

Bond valence nets (contd.)

Analogies with electrical circuits should be noted: Kirchhoff's junction rule (or nodal rule) for circuits: The principle of conservation of electric charge implies that at any node (junction) in an electrical circuit, the sum of currents flowing into that node is equal to the sum of currents flowing out of that node.

Bond valence nets and sums

Bond valence net of cubic perovskites (example of $BaZrO_3$ and $KTaO_3$).
verify that the values make sense:

$$2/12 = 1/6$$

Ba ≡ O ≡ Zr
   ≡ O ≡
   ≡ O ≡

$$4/6 = 2/3$$

$$1/12$$

K ≡ O ≡ Ta
  ≡ O ≡
  ≡ O ≡

$$5/6$$

UC SANTA BARBARA
engineering and the sciences

Bond valence nets and sums

Bond-strength, bond-length correlations:

Pauling was the first to notice that the bond strength s of a bond relates empirically with the bond length R : Short bonds have high bond strength.

Shannon, Brown, O'Keeffe, Brese and others have parametrized this relationship very effectively for ionic compounds: oxides, fluorides, chlorides *etc.*, using:

$$s = \exp \left(\frac{R_0 - R}{B} \right)$$

Using tabulated values of B (usually 0.37 Å for oxides) and values of R_0 corresponding to the pair of ions forming the bond, the bond valence can be determined for every linker or "bond" between cation and anion.

The sum of the these bonds (the bond valence sum, or BVS) should be equal to the formal oxidation state of the cation or anion respectively.

UC SANTA BARBARA
engineering and the sciences

Bond valence nets and sums

The example of the delafossite $Cu^{1+}Sc^{3+}O_2$: Cu is linear (2 equidistant O neighbors) and Sc is octahedral (6 equidistant O neighbors): The bond valence net is and structures are displayed:

$$Cu \begin{array}{c} - \\ - \end{array} \begin{array}{c} O \equiv \\ O \equiv \end{array} Sc$$
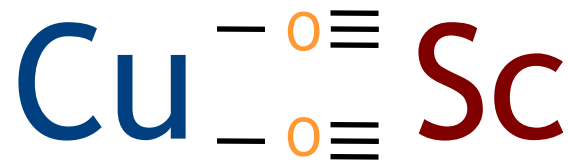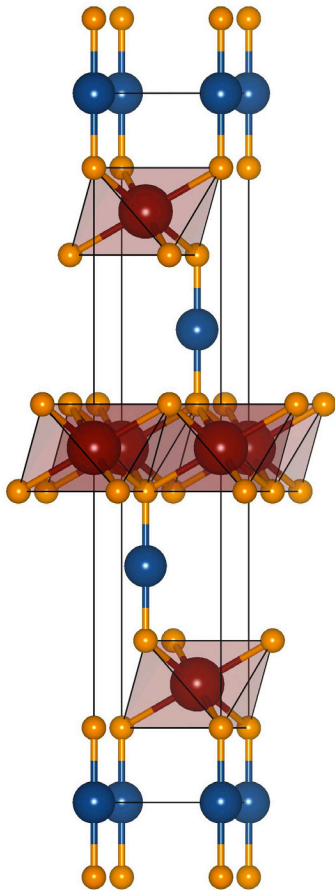
Atom 1	Atom 2	R	R_o	B	s
Cu	O	1.80 Å	1.61 Å	0.37 Å	0.60
Sc	O	2.13 Å	1.85 Å	0.37 Å	0.47

So the BVS for Cu is 2*0.60 = 1.2, and the BVS for Sc is 6*0.47 = 2.8.

Cu is slightly over-bonded and Sc slightly under-bonded !

Materials 218/Chem 277

UC SANTA BARBARA
engineering and the sciences