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Bond valence and bond energy

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Abstract

The relationship between bond valence and structural energy has never been fully explored, although several predictive models have assumed some simple relationship between the two. Some of these models relate energy only to bond valence, while others also take into account other factors, such as bond character. We examined periodic trends in bond dissociation energies as a function of their ionicity, covalency, and metallicity, defined in terms of the electronegativity values of the atoms involved. A statistical model was optimized to describe these trends, allowing us to generate rough bond energy vs. bond valence curves. The shapes of these curves vary dramatically as a function of bond character, and are strongly influenced by the lone-pair bond-weakening effect. The curve shapes can be used to rationalize several chemical trends, including the preferred structures of compounds with different bond types, the prevalence of peroxide and persulfide minerals, preferred bond lengths in oxides, and the pK_a values of (hydr)oxy-acids. The last is perhaps the most important, because some valence-based acidity models are in current use, despite the fact that some aspects of their rationale are unclear.

Keywords: Bond valence, energy, ionicity, metallicity, covalency, lone-pair bond-weakening effect, acidity