3.091 Solid State Chemistry: Week 4

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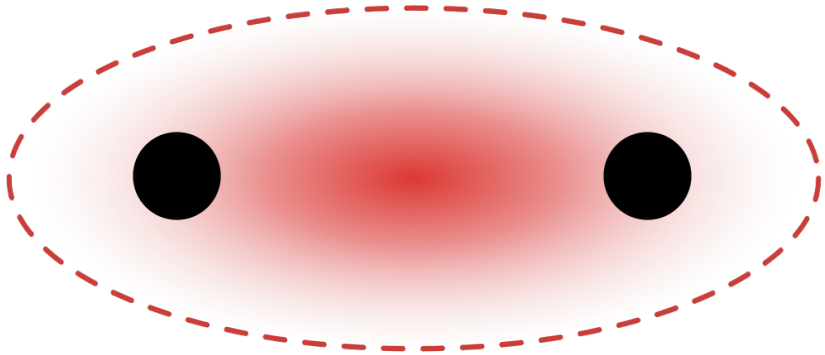
Progress Update

Over the past week I have been introduced to:

1. Covalent bonding.
2. Formal charge.
3. The Pauling formula (polar covalent bonds and energies)
4. Cohesive energy of a network covalent solid.
5. Homonuclear bonding energy.
6. Dipole moments.
7. Ionic character.
8. Bond order.
9. Molecular orbital diagrams.

Covalent Bonding

Covalent bonding is defined as the sharing of electrons between 2 atoms. Consider H_2. Each hydrogen has a singular electron in the $1s$ orbital to start. The atomic orbitals then overlap to release some energy (remove potential energy from the system) and form a molecular orbital as seen below.

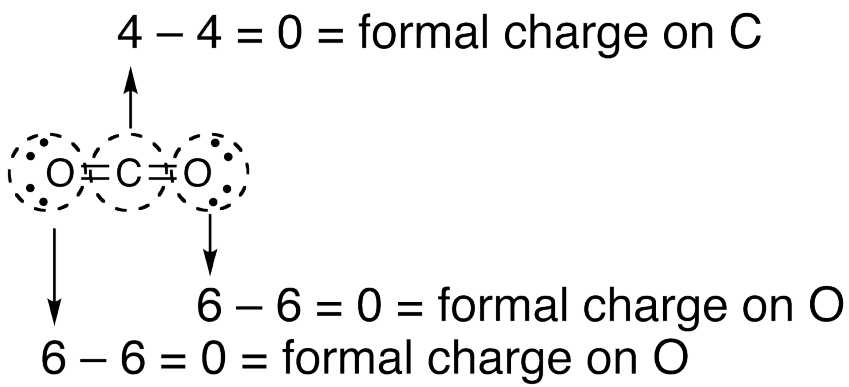


Covalent bonds aren't strictly covalent, and may have additional charge more towards one atom than the other, in the case of non-homonuclear bonds.

Formal charge

The formal charge is the mathematically ideal charge on a bonded atom, described by the formula

$$\text{Formal Charge} = \text{valence electrons in free atom } e^- - \text{non-bonding } e^- - \frac{1}{2}\,\text{bonding } e^-$$



Homonuclear bonding energy

Homonuclear bonding energy is the energy contained in a bond between 2 atoms of the same element. It trends to be constant along a single row across all periods (with the exception of the first row), and decreases as one goes down the rows.

The Pauling Formula

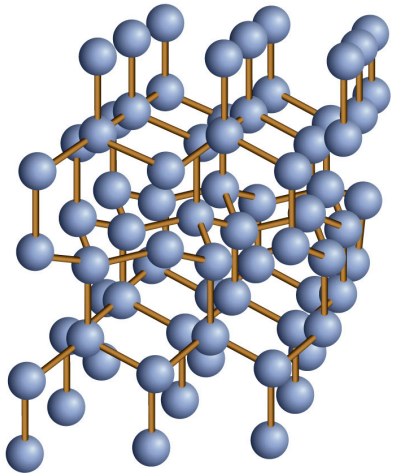
The Pauling formula estimates the energy of a heteronuclear covalent bond by summing the ionic and covalent contributions:

$$E_{AB} = \sqrt{E_{AA} \cdot E_{BB}} + 96.3 \text{ kJ/mol } (X_A - X_B)^2$$

Where E_{AA} is the homonuclear bonding energy of A and X_A is the electronegativity (unitless) of A.

Cohesive energy of a network covalent solid

The cohesive energy of a covalent solid, like a silicon crystal seen here,



approximately follows the formula

$$E_c = 1/2\, z\, E_b$$

where E_b is the bonding energy and z is the coordination number.

Quick ideas

Two quick ideas, each with an associated formula

1. Dipole Moment - The dipole moment describes how offset from the center the average electron position is. In a homonuclear bond, the dipole moment is zero. In a 3 atom molecule like CO_2, it is also zero due to bonds being equal throughout. Dipole moment is defined as $D = qr$
2. Bond order - defined by the bonding and anti-bonding e^- associated with a bond; $BO = \frac{1}{2}$ (bonding e^- − anti-bonding e^-)

Ionic character

Ionic character approximates what percentage of a bond is ionic in nature, and can be approximated via 2 formulae:

$$\text{percent ionic} = \frac{\text{experimental dipole moment}}{\text{fully ionic dipole moment}}$$

$$\text{Pauling percent ionic} = 1 - e^{(-\frac{(X_A - X_B)^2}{4}}$$

Molecular orbital diagrams

Consider O_2: