



# Chemistry Terms (Bonding) & Dot Diagrams

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## 1. TERMS:

- a. **Expanded Valence:** State of affairs when an atom has more than eight electrons around it in a dot diagram; this is only allowed when the atom in question has more than four outer shell orbitals, i.e., when the atom is on or below the row that includes Al to Ar.
- b. **Bond Order:** The net number of bonding pairs of electrons in a bond. Note that the first pair of electrons in a bond is assumed to be involved in sigma bonding. The second and third pairs (if they are in the bond) are assumed to be involved in pi bonding. Thus:
  - 1) single bond = one pair of electrons; sigma bond
  - 2) double bond = two pairs of electrons; sigma bond + one pi bond
  - 3) triple bond = three pairs of electrons; sigma bond + two pi bonds
- c. **Bond Energy:** The energy required to break a bond; as a general rule, for similar bonds the greater the bond order, the greater the bond energy and the shorter the bond length, since stronger bonds are shorter bonds.
- d. **Resonance:** State of affairs when no single dot diagram adequately describes a molecule's bonding; the normal recourse in such cases is to draw several (two or more) dot diagrams and to assert that the true bonding is a blend of them; this does not assert that the bonding is switching back and forth between or among the "resonance forms", but rather that the truth is an averaging of them. Note that this sort of situation can result in fractional bond orders.
- e. **Bond Polarity:** If the two atoms in a bond do not attract electrons equally (and they will not attract electrons equally unless they are equal in electronegativity), then one atom will attract more, and it will become slightly negative, the other atom becoming slightly positive. This slight separation of charge is called polarity, and such bonds are said to be "polar". Greater polarity comes from greater differences in electronegativity, and if atoms are sufficiently different in electronegativity, this polarity difference becomes great enough that the bonding is better described as **ionic** than as **covalent**. Polar covalent then is ionic character introduced into covalent bonding.
- f. **Oxidation State:** The charge an atom would have if all of the bonds were ionic and electrons in each bond were assigned
  - 1) to the more electronegative atom when the atoms in the bond were different, and,
  - 2) half to each atom when the atoms in the bond were the same.
- g. **Formal Charge:** The charge an atom would have if all of the bonds were ionic but electrons in each bond were divided equally between the bonding atoms.

- h. Note that oxidation state and formal charge are two different ways of assigning the electrons in a chemical substance. Both are quite useful, and you must be able to use both methods.
    - 1) In general, of a group of possible dot diagrams, the best one is the one that minimizes formal charge or, if formal charges cannot be made zero for all atoms, the best structure is the one that localizes negative charge on the most electronegative atom present or localizes positive charge on the least electronegative atom present.
    - 2) In general oxidation states indicate the more positive and more negative atoms in a species, and thus give guidance to predicting chemical reactions the species might undergo.
  - i. **Sigma Bond:** Covalent bonds that s-orbitals can form; thus bonds resulting from the head-on overlap of atomic orbitals; one lobe from one orbital overlaps one lobe from another; note that all orbitals can be involved in sigma bonding.
  - j. **Pi Bond:** Covalent bonds that p-orbitals can form but that s-orbitals cannot; thus bonds resulting from the sideways overlap of atomic orbitals; two lobes from one orbital (one + and one – in wave sign) overlap two similar lobes from another; note that s-orbitals can not be involved in pi bonding.
2. In drawing **DOT DIAGRAMS** of molecules, a good guide is to
- a. Predict the arrangement (connectivity of atoms: H and highly electronegative atoms like F or O are usually on the outside of molecules; atoms of lower electronegativity are usually on the inside.
  - b. Count up the number of electrons (dots) in the diagram: add up the outer shell electrons of all the atoms present and add or subtract electrons as appropriate for the charge on the species.
  - c. Put one pair of electrons between each pair of atoms (these are called “bonding pairs”) and put enough electron pairs around each peripheral (outside) atom to give it a complete octet (these are called “lone pairs”); note that H only gets the two in the bond.
  - d. Put any pairs of electrons left over on the central (inside) atom(s) as lone pairs; note that central atoms from the first row of the p-block can at most have eight electrons.
  - e. If the central atom does not at this point have a share in at least eight electrons, change lone pairs on the peripheral atoms to bonding pairs with the central atom sufficient to give the central atom a complete octet; note that this will result in “multiple bonding”, i.e., two or more pairs of electrons joining two atoms.

[NOTE: Some authorities prefer at this point to continue this process until the formal charges in the molecule are minimized. This is a valid procedure, but it gives a slightly different dot diagram. For more information on “formal charge” see above.]