

THE OCTET RULE

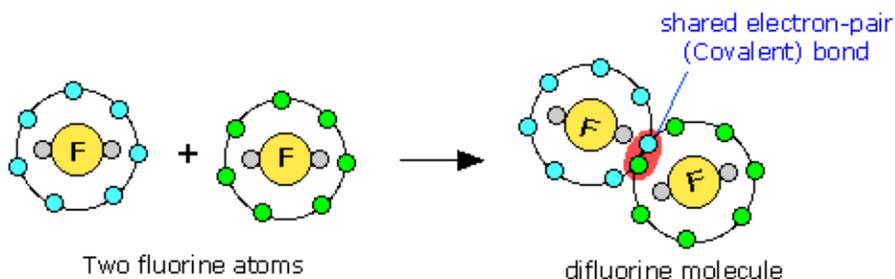
At the time Lewis began developing his ideas in 1902, it was widely believed that chemical bonding involved electrostatic attraction between ion-like entities. This seemed satisfactory for compounds such as NaCl that were known to dissociate into ions when dissolved in water, but it failed to explain the bonding in non-electrolytes such as CH₄. Atomic orbitals had not yet been thought of, but the concept of “valence” electrons was known, and the location of the noble gases in the periodic table suggested that all except helium possess eight valence electrons. It was also realized that elements known to form simple ions such as Ca²⁺ or Cl⁻ do so by losing or gaining whatever number of electrons is needed to leave eight in the valence shell of each. Lewis sought a way of achieving this octet in a way that did not involve ion formation, and he found it in his shared electron-pair theory published in 1916.

Present-day shared electron-pair theory is based on the premise that the s²p⁶ octet in the outermost shells of the noble gas elements above helium represents a particularly favorable configuration.

This is not because of any mysterious properties of octets (or of noble gas atoms); it simply reflects the fact that filling an existing s-p valence shell is energetically more favorable than placing electrons in orbitals of higher principal quantum number. The sharing of electrons in this way between atoms means that more electrons are effectively “seeing” more nuclei, which you should remember is always the fundamental energetic basis of bond formation.

"Noble gas" valence electron configurations

The idea that the noble-gas configuration is a particularly favorable one which can be achieved through formation of electron-pair bonds with other atoms is known as the octet rule.



Noble gas configuration (in this case, that of neon, s^2p^6) is achieved when two fluorine atoms (s^2p^5) are able to share an electron pair, which becomes the covalent bond. Notice that only the outer (valence shell) electrons are involved.

Lewis' idea that the electrons are shared in pairs stemmed from his observation that most molecules possess an even number of electrons.

This paired sharing also allows the formulas of a large number of compounds to be rationalized and predicted—a fact that led to the widespread acceptance of the Lewis model by the early 1920s.

Scope of the Octet Rule

For the lightest atoms the octet rule must be modified, since the noble-gas configuration will be that of helium, which is simply s^2 rather than s^2p^6 . Thus we write LiH as Li:H, where the electrons represented by the two dots come from the $2s$ orbital of lithium and the $1s$ orbital of hydrogen.

The octet rule applies quite well to the first full row of the periodic table (Li through F), but beyond this it is generally applicable only to the non-transition elements, and even in many of these it cannot explain many of the bonding patterns that are observed. The principal difficulty is that a central atom that is bonded to more than four peripheral atoms must have more than eight electrons around it if each bond is assumed to consist of an electron pair. In these cases, we hedge the rule a bit, and euphemistically refer to the larger number of electrons as an “expanded octet”.

These situations tend to occur in atoms whose d orbitals are energetically close enough to the most highly-occupied s^2p^6 orbitals that they can become involved in electron-sharing with other atoms.

In spite of the octet rule's many exceptions and limitations, the shared electron-pair model is the one that chemists most frequently employ in their day-to-day thinking about molecules. It continues to serve as a very useful guiding principle and can be a good starting point for more sophisticated theories.

Source: <http://www.chem1.com/acad/webtext/chembond/cb03.html>