B.Sc. (Honours) Part-I
Paper-I
Topic: octet rule

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Subject-Chemistry

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OCTET RULE

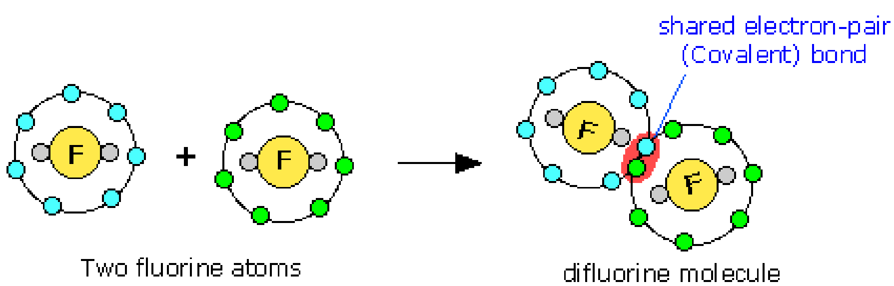
At the time Lewis began developing his ideas in 1902, it was widely believed that chemical bonding involved electrostatic attraction between ion-like entities. This seemed satisfactory for compounds such as NaCl that were known to dissociate into ions when dissolved in water, but it failed to explain 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 posses 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.

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, s2p6) is achieved when two fluorine atoms (s2p5) 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.

Validity of 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 s2 rather than s2p6. 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".

Exceptions to the Octet Rule

- An ion, atom, or a molecule containing an unpaired valence electron is called a free radical. These species disobey the octet rule. However, they are very unstable and tend to spontaneously dimerize.
- Since the first shell can only accommodate two electrons, elements such as lithium, helium, and hydrogen obey the duet rule instead of the octet rule. For example, lithium can lose an electron to have a stable configuration in which the valence shell holds two electrons.
- Due to the presence of a d-orbital, the transition elements do not obey the octet rule. The valence shells of these atoms can hold 18 electrons.
- Aromatic compounds involve a delocalization of pi electrons. These electrons obey Huckel's rule