

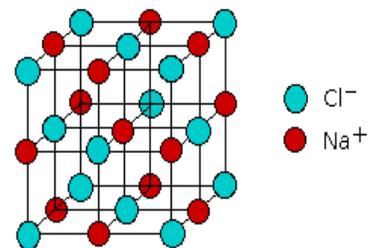
CLASSICAL MODELS OF THE CHEMICAL BOND

By classical, we mean models that do not take into account the quantum behavior of small particles, notably the electron. These models generally assume that electrons and ions behave as point charges which attract and repel according to the laws of electrostatics. Although this completely ignores what has been learned about the nature of the electron since the development of quantum theory in the 1920's, these classical models have not only proven extremely useful, but the major ones also serve as the basis for the chemist's general classification of compounds into "covalent" and "ionic" categories.

The ionic model

Ever since the discovery early in the 19th century that solutions of salts and other electrolytes conduct electric current, there has been general agreement that the forces that hold atoms together must be electrical in nature. Electrolytic solutions contain ions having opposite electrical charges; opposite charges attract, so perhaps the substances from which these ions come consist of positive and negatively charged atoms held together by electrostatic attraction.

It turns out that this is not true generally, but a model built on this assumption does a fairly good job of explaining a rather small but important class of compounds that are called ionic solids.



The most well known example of such a compound is sodium chloride, which consists of two interpenetrating lattices of Na^+ and Cl^- ions arranged in such a way that every ion of one type is surrounded (in three dimensional space) by six ions of opposite charge.

One can envision the formation of a solid NaCl unit by a sequence of events in which one mole of gaseous Na atoms lose electrons to one mole of Cl atoms, followed by condensation of the resulting ions into a crystal lattice:

$\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$	+494 kJ	ionization energy
$\text{Cl(g)} + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$	-368 kJ	electron affinity
$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$	-498 kJ	lattice energy
$\text{Na(g)} + \text{Cl(g)} \rightarrow \text{NaCl(s)}$	-372 kJ	Sum: Na-Cl bond energy

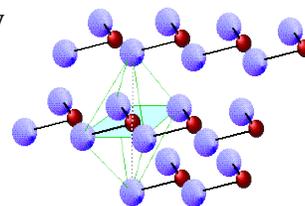
Note: positive energy values denote endothermic processes, while negative ones are exothermic.

Since the first two energies are known experimentally, as is the energy of the sum of the three processes, the lattice energy can be found by difference. It can also be calculated by averaging the electrostatic forces exerted on each ion over the various directions in the solid, and this calculation is generally in good agreement with observation, thus lending credence to the model.

The sum of the three energy terms is clearly negative, and corresponds to the liberation of heat in the net reaction (bottom row of the table), which defines the Na–Cl “bond” energy.

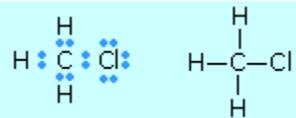
The ionic solid is more stable than the equivalent number of gaseous atoms simply because the three-dimensional NaCl structure allows more electrons to be closer to more nuclei. This is the criterion for the stability of any kind of molecule; all that is special about the “ionic” bond is that we can employ a conceptually simple electrostatic model to predict the bond strength.

The main limitation of this model is that it applies really well only to the small class of solids composed of Group 1 and 2 elements with highly electronegative elements such as the halogens.



Although compounds such as CuCl_2 dissociate into ions when they dissolve in water, the fundamental units making up the solid are more like polymeric chains of covalently-bound CuCl_2 molecules that have little ionic character.

Shared-electron (covalent) model



This model originated with the theory developed by G.N.

Lewis in 1916, and it remains the most widely-used model of

chemical bonding. It is founded on the idea that a pair of electrons shared between two atoms can create a mutual attraction, and thus a chemical bond.

Usually each atom contributes one electron (one of its valence electrons) to the pair, but in some cases both electrons come from one of the atoms. For example, the bond between hydrogen and chlorine in the hydrogen chloride molecule is made up of the single 1s electron of hydrogen paired up with one of chlorine's seven valence (3p) electrons. The stability afforded by this sharing is thought to derive from the noble gas configurations (helium for hydrogen, argon for chlorine) that surround the bound atoms.

The origin of the electrostatic binding forces in this model can best be understood by examining the simplest possible molecule. This is the hydrogen molecule ion H_2^+ , which consists of two nuclei and one electron.

First, however, think what would happen if we tried to make the even simpler molecule H_2^{2+} . Since this would consist only of two protons whose electrostatic charges would repel each other at all distances, it is clear that such a molecule cannot exist; something more than two nuclei are required for bonding to occur.

In H_2^+ we have a third particle, the electron. The effect of this electron will depend on its location with respect to the two nuclei. If the electron is in the space between the two nuclei (the binding region in the

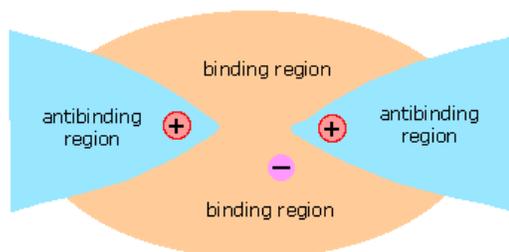
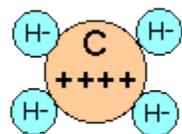


diagram), it will attract both protons toward itself, and thus toward each other. If the total attraction energy exceeds the internuclear repulsion, there will be a net bonding effect and the molecule will be stable. If, on the other hand, the electron is off to one side (in an antibinding region), it will attract both nuclei, but it will attract the closer one much more strongly, owing to the inverse-square nature of Coulomb's law. As a consequence, the electron will now actively work against bonding by helping to push the two nuclei apart.

Polar covalent model

A purely covalent bond can only be guaranteed when the electronegativities (electron-attracting powers) of the two atoms are identical. When atoms having different electronegativities are joined, the electrons shared between them will be displaced toward the more electronegative atom, conferring a polarity on the bond which can be described in terms of percent ionic character. The polar covalent model is thus a generalization of covalent bonding to include a very wide range of behavior.

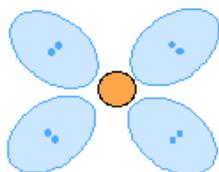
Coulombic model



This is an extension of the ionic model to compounds that are ordinarily considered to be non-ionic. Combined hydrogen is always considered to exist as the hydride ion H^- , so that methane can be treated as if it were $C^{4+} H^{-4}$.

This is not as bizarre as it might seem at first if you recall that the proton has almost no significant size, so that it is essentially embedded in an electron pair when it is joined to another atom in a covalent bond. This model, which is not as well known as it deserves to be, has surprisingly good predictive power, both as to bond energies and structures.

VSEPR model



The “valence shell electron repulsion” model is not so much a model of chemical bonding as a scheme for explaining the shapes of molecules. It is based on the quantum mechanical view that bonds represent electron clouds— physical regions of negative electric charge that repel each other and thus try to stay as far apart as possible. We will explore this concept in much greater detail in a later unit.

Source: <http://www.chem1.com/acad/webtext/chembond/cb02.html>