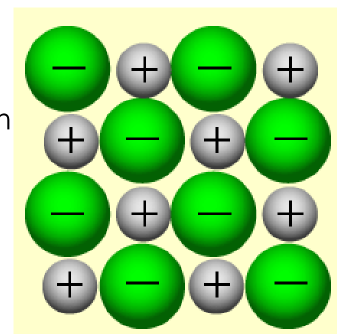
Chemistry continued…

1. Review: J.J. Thomson's Plum Pudding model and ionic vs. molecular bonding

In Unit 6, we examined the interactions between positively charged objects (top tape), negatively charged objects (bottom tape), and neutral objects (foil and paper strips). To explain that objects can become charged, J.J. Thomson proposed that atoms have smaller mobile particles in them. Evidence from his Cathode Ray experiments showed that these smaller mobile particles, later called electrons, are negatively charged. For an atom to be neutral, there must be the same number of positive charges to counter balance the negative charges of electrons. Thomson had no experimental evidence to show where in the atom the positive charges would be. He hypothesized that the interior of an atom was a positive cloud with no mass. It is the attraction between the positive cloud and the negative electrons that holds electrons inside the atom.

However, atoms of different elements have different abilities to attract electrons. We call this electronegativity. Metal elements have free moving electrons that make metals good conductors of electricity. This suggests that the positive charges in metal atoms attract electrons weakly (low electronegativity). On the other hand, nonmetal elements are poor conductors, suggesting strong attraction (high electronegativity) between the positive charges and electrons. This limits the movement of the electrons between atoms. Because of this difference in electronegativity, a metal atom is more likely to form a positive ion (cation) when electrons are transferred to a nonmetal atom due to the higher attraction (higher electronegativity) from the positive charges in the nonmetal atom. The nonmetal atom becomes a negative ion (anion). Thus, the bonding between metal atoms and nonmetal atoms is ionic, as shown by the diagram to the right. If the difference in electronegativity between atoms is not enough to cause electrons to move from one atom to another, i.e., two nonmetal atoms such as H and Cl, these atoms bond together to form neutral HCl molecules, as illustrated in the diagram on the left. However, the slight difference in electronegativity between H and Cl causes uneven distribution of electrons within the molecule, with the H end of the molecule partially positive (δ+) and the Cl end partially negative (δ-). Thus we call HCl a polar molecule.



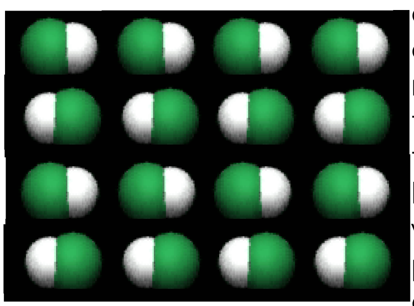


Table 6.2

Electronegativity Values for Selected Elements

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 1.9		

(Recall the tug-of-war analogy we used in describing this situation.)

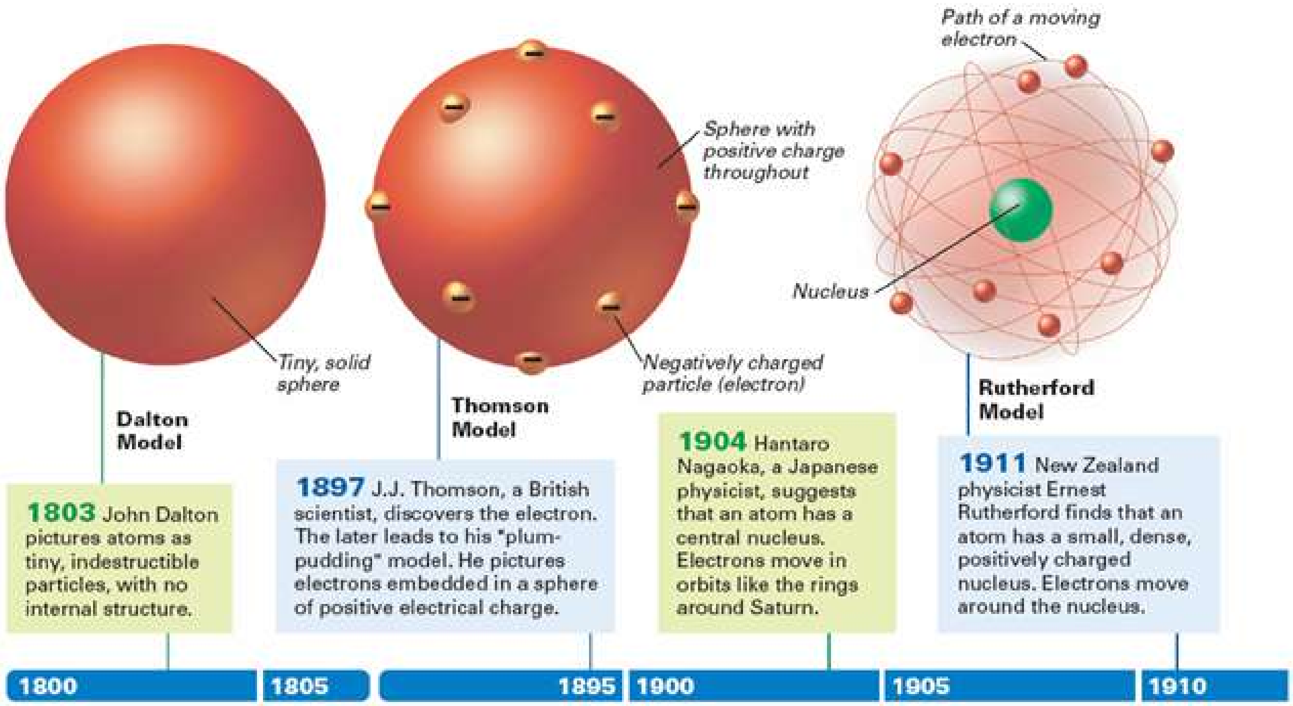
A numerical scale of 0 – 4 has been used to compare the electronegativity of main group elements, as shown in the table to the right.

Intermolecular forces: For polar molecules, the δ+ end of one molecule weakly attracts the δ- end of another molecule. This weak attraction between polar molecules is call dipole-dipole interaction – one of the intermolecular forces that plays a vital role in biological systems.

2. Atomic models beyond Thomson's Plum Pudding Model

Over ten years after J.J. Thomson proposed his Plum Pudding model of an atom, Ernest Rutherford, a former student of Thomson's, proposed a nuclear model of an atom based on evidence collected from his famous gold foil experiment. (Check out the detailed explanation of his experiment at the following link. http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/ruther14.swf) Rutherford suggested that the positive charges in an atom are concentrated in a very small but dense center of the atom that he called a nucleus. Almost all the mass of the atom is also in the nucleus. Without any evidence to show where electrons are in the atom, Rutherford hypothesized that electrons are moving around the nucleus. Thus, according to Rutherford's model, atoms are made of mostly empty space. Later, based on the experimental work by Henry Moseley, James Chadwick and others, scientists proposed that the nucleus is made of positively charged protons and neutral neutrons. Both protons and neutrons have mass, with neutrons slightly more massive than protons. The number of protons in the nucleus must be the same as the number of electrons so that the atom is neutral.

A comparison of the Dalton, Thomson, and Rutherford models is shown in the diagram below.

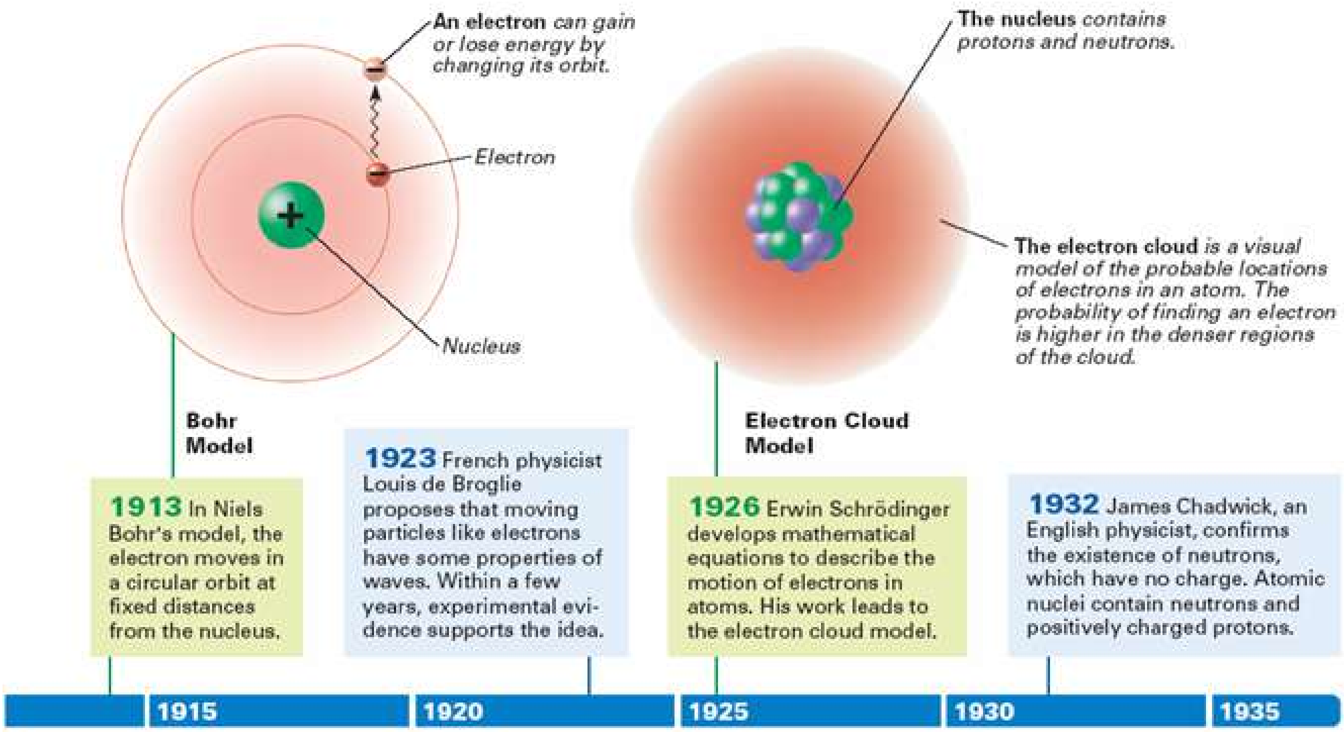


Meanwhile, other scientists, including Niels Bohr, Louis de Broglie, Werner Heisenberg, Erwin Schrodinger and others, took interests in studying the electrons of an atom. Bohr took the idea of quantized (discreet packets, or amounts) energy from Max Plank and Albert Einstein and calculated the energy levels for the electrons outside the nucleus. He proposed a model of an atom with electrons moving in circular orbits around the nucleus like the planets orbit the sun. Electrons in orbits closer to the nucleus are more attracted by the positive protons in the nucleus, therefore have less energy. (Recall in Unit 3 and Unit 7, we generalized that the more attracted the particles are to each other, the closer the particles are, therefore the less potential energy is stored.) The farther away from the nucleus, the more energy electrons have. However, Bohr's model could only explain the experimental results of hydrogen atoms which has only one electron in each atom. All the other elements have multiple electrons in their atoms. So a better atomic model was needed to explain experimental observations of all atoms.

Eventually, based on the work of many scientists, a modern quantum atomic model emerged. In this model, electrons do move around the nucleus with protons and neutrons in it. However, electrons do not have fixed orbits. Instead, electrons behave not only as discrete particles, but also as waves. (Recall in physics, we talked about light and other electromagnetic radiations as waves.) This is kind of hard for us to imagine. A cartoon video at the following link explains the basic idea of the dual property of electrons. http://www.youtube.com/watch?v=x_tNzeouHC4

Because of this particle-wave property of electrons, the actual location of an electron at any given moment cannot be determined. Based on the energy of an electron, we can only know the probability of finding an electron in a given space outside the nucleus. Generally speaking, low energy electrons are mostly likely to appear in the space close to the nucleus while high energy electrons are more likely to appear in the space farther away from the nucleus. The outermost electrons of an atom have highest energy and are most "active". We call these electrons **valence electrons**. These electrons are the ones primarily involved in chemical bonding, which will be discussed in the next section.

The comparison of Bohr model and the quantum model of a single-electron atom is shown in the figure below. In the quantum model, the map of the probable locations of the electron is usually called an electron cloud.

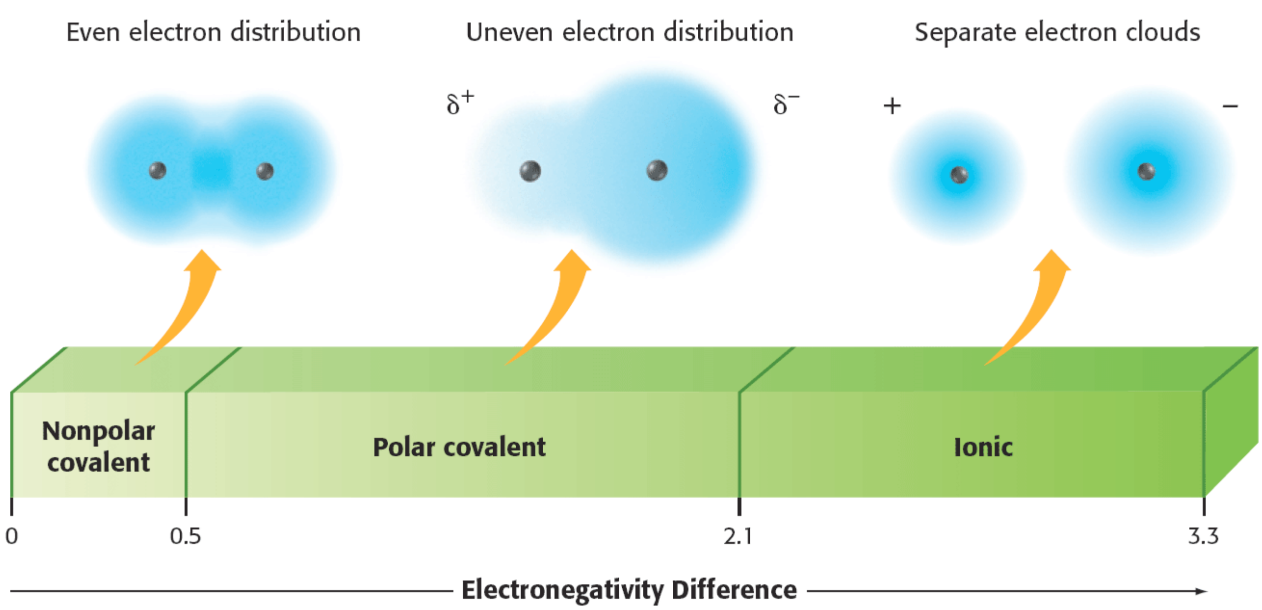


3. An evolved view on bonding based on the quantum atomic model

As discussed in the previous section, high energy valence electrons are farther away from the nucleus. They are less attracted by the positive nucleus. Further more, they are also repelled by the inner electrons, those electrons closer to the nucleus. As a result, valence electrons are more likely to "jump" to another atom when the nucleus of the other atom exerts much more attraction for these electrons than their own nucleus. This is the case of ionic bonding between metal atoms and nonmetal atoms, as was discussed in the Thomson model. For example, in the compound NaCl, the significant difference in electronegativity between Na (0.9) and Cl (3.0) causes the transfer of the only valence electron of the Na atom to the Cl atom, thus forming Na^+ and Cl^- in this ionic compound.

In the case of molecular compounds, which are made of all nonmetal atoms, valence electrons are not able to completely "jump" from one atom to another because both nonmental elements have high electronegativity. The difference in electronegativeity between them is not enough for the electron to be attracted completely into the other. Let's still use H and Cl as an example. The electronegativity of Cl is 3.0, while for H it is 2.1. The valence electron of H and one of the valence electrons of Cl are mostly found in the region between the two nuclei, in other words, the electron clouds overlap. This kind of electron sharing between nonmetal atoms is called covalent bonding. Since Cl has higher electronegativity than H, the most probable location of finding these two valence electrons is closer to Cl than H, thus a polar covalent bond.

The following diagram illustrates the difference between nonpolar covalent, polar covalent and ionic bonds based on the difference in electronegativity between the two atoms.

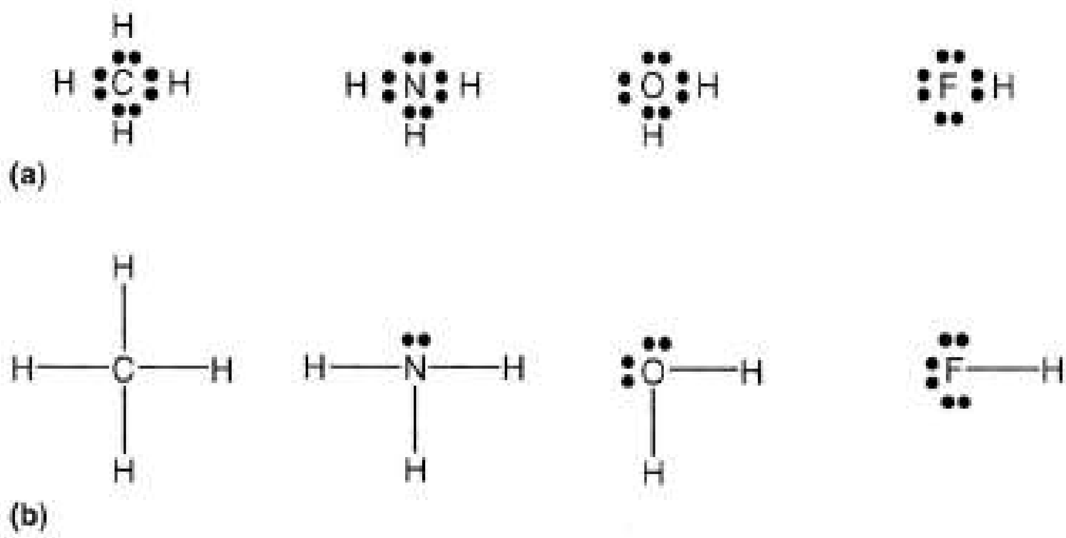


4. The electron Pair and the Rule of Eight: An empirical model of chemical bonding

Through 19th century, long before J.J. Thomson discovered the electron, scientists already knew that chemical bonding, the force holding atoms together in molecules, is electrical in nature. From the composition of large amount of compounds known by that time, scientists also found patterns in the number of bonds that an atom of some elements usually forms in molecules. This characteristic number of bonds of each element is called its ***valence***. For example, carbon has a valence of four, meaning a carbon atom usually forms four bonds in a molecule, as in methane, CH_4, or carbon tetra chloride, CCl_4.

In the attempt to explain the valences of elements and the formulas of a large number of molecules, Gilbert N. Lewis, an extraordinary American chemist, proposed two rules for the electrons in chemical bonds in his famous and revolutionary paper in 1916. Here is a summary of Lewis' rule of two (the electron pair) and rule of eight (the octet rule) by Gillespie and Robinson in their article published in the Journal of Computational Chemistry, Vol. 28, No. 1, 2006.

"…inspired by the fact that the vast majority of stable molecules have an even number of electrons, he proposed that the electrons in a molecule are paired together and that a chemical bond consists of a pair of electrons shared between two atoms. In this way he was able to simply explain valences and the formulas of a very large number of molecules. By "shared" he meant that a single pair of electrons could be considered to occupy the valence shells of both the bonded atoms. He noted that this concept also led to the great majority of atoms in molecules, except hydrogen, having a valence shell of eight electrons and in particular four pairs, that is to say a noble gas valence shell, just as is found in the outer shell of many stable ions such as Na^+, Al^{3+}, and Cl^-. He called this the rule of eight."



Lewis used dots to represent electrons in his 2D drawing of molecules in showing how atoms sharing electrons. Examples of Lewis dot structure are shown in the diagram above. In (a), all electrons are drawn as dots. But notice that some electron pairs are shared between two atoms but others are not. To distinguish these two kinds of electron pairs, a line replaces the two dots to represent the shared electron pair (bonding pair) while dots are still used to represent the unshared pairs (lone pairs), as shown in (b).

It is important to recognize that Lewis' rule of two and rule of eight were completely based on empirical observations. They are not fundamental laws of nature that should have no exceptions. Although the concept of electron pair is still valid in the current quantum mechanic model of chemical bonding, Lewis himself admitted that there are exceptions to the rule of eight, such as BCl_3, PCl_5 and SF_6 molecules. These molecules have less or more than four pairs of electrons in the valence shell of the central atom.