

Life on Earth depends on water – we need water to drink, bathe, cool ourselves off on a hot summer day (Figure 1). In fact, evidence suggests that life on Earth began in the water, more specifically in the ocean, which has a combination of water and salts, most prominently common table salt – sodium chloride. But where do water and these common salts appear on the great organizer of the elements, the periodic table? Well they, and millions of other substances, are not found on the most famous of all chemistry references: the periodic table. Why not? The answer is a simple one.

The periodic table organizes the 118 currently recognized chemical elements, but water and sodium chloride are not elements. Rather, both are substances that are made up of a combination of elements in a fixed ratio. Such fixed ratio combinations of those 118 elements are known as compounds.

In its chemical reactions and physical interactions, sodium chloride doesn't act like the elements that make it up (sodium and chlorine); rather, it acts as a completely different and unique substance. That's a good thing since chlorine is a poisonous gas that has been used as a chemical weapon, and sodium is a highly reactive metal that is mildly explosive with water. So what allows sodium chloride to act in an entirely different way? The answer is that within table salt, sodium and chlorine are joined together by a chemical bond that creates a unique compound, very different from the individual elements that comprise it.

The chemical bond can be thought of as a force that holds the atoms of various elements together in such compounds. It opens up the possibility of millions and millions of combinations of the elements, and the creation of millions and millions of new compounds. In short, the existence of the chemical bonds accounts for the richness of chemistry that reaches far beyond just those 118 building blocks.

When discussing the history of chemistry it's always dangerous to point to the specific origin of an idea, since by its very definition, the scientific process relies upon the gradual refinement of ideas that came before. However, as is the case with a number of such ideas, one can point to certain seminal moments, and in the case of chemical bonding, a famous early 18th century publication provides one such moment.

In his 1704 publication *Opticks*, Sir Isaac Newton makes mention of a force that points to the modern idea of the chemical bond. In Query 31 of the book, Newton describes 'forces' – other than those of magnetism and gravity – that allow 'particles' to interact.

In 1718, while translating *Opticks* into his native language, French chemist Étienne François Geoffroy created an Affinity Table. In this fascinating first look at the likelihood of certain interactions, Geoffroy tabulated the relative affinity that various substances had for other substances, and therefore described the strength of the interactions between those substances.

While Newton and Geoffroy's work predated our modern understanding of elements and compounds, their work provided insight into the nature of chemical interactions. However, it was over 100 years before the concept of the combining power of elements was understood in a more modern sense. In a paper in the journal *Philosophical Transactions* entitled "On a new series of organic bodies containing metals" (Frankland, 1852), Edward Frankland describes the "combining power of elements," a concept now known as valency in chemistry. Frankland summarized his thoughts by proposing what he described as a 'law':

A tendency or law prevails (here), and that, no matter what the characters of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms.

Frankland's work suggested that each element combined with only a limited number of atoms of another element, thus alluding to the concept of bonding. But it was two other scientists who performed the most important contemporary research on the concept of bonding.

In 1916, the American scientist Gilbert N. Lewis published a now famous paper on bonding entitled "The atom and the molecule" (Lewis, 1916). In that paper he outlined a number of important concepts regarding bonding that are still used today as working models of electron arrangement at the atomic level. Most significantly, Lewis developed a theory about bonding based on the number of outer shell, or valence, electrons in an atom. He suggested that a chemical bond was formed when two atoms shared a pair of electrons (later renamed a covalent bond by Irving Langmuir). His "Lewis dot diagrams" used a pair of dots to represent each shared pair of electrons that made up a covalent bond.

Lewis also championed the idea of 'octets' (groups of eight), that a filled valence shell was crucial in understanding electronic configuration as well as the way atoms bond together. The octet had been discussed previously by chemists such as John Newland, who felt it was important, but Lewis advanced the theory.

While still in college, a young chemist by the name of Linus Pauling familiarized himself with Lewis's work and began to consider how it might be interpreted within the context of the newly developed field of quantum mechanics. The theory of quantum mechanics, developed in the first half of the 20th century, had redefined our modern understanding of the atom and so any theory of bonding would be incomplete if it were not consistent with this new theory (see our modules Atomic Theory II: Bohr and the Beginnings of Quantum Theory and Atomic Theory III: Wave-Particle Duality and the Electron for more information).

Pauling's greatest contribution to the field was his book *The Nature of the Chemical Bond* (Pauling, 1939). In it, he linked the physics of quantum mechanics with the chemical nature of the electron interactions that occur when chemical bonds are made. Pauling's work concentrated on establishing

that true ionic bonds and covalent bonds sit at extreme ends of a bonding spectrum, and that most chemical bonds are classified somewhere between those extremes. Pauling further developed a sliding scale of bond type governed by the electronegativity of the atoms participating in the bond.

Pauling's immense contributions to our modern understanding of the chemical bond led to his being awarded the 1954 Nobel Prize for "research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances."

Chemical bonding and interactions between atoms can be classified into a number of different types. For our purposes we will concentrate on two common types of chemical bonds, namely covalent and ionic bonding.

Molecular bonds are formed when constituent atoms come close enough together such that the outer (valence) electrons of one atom are attracted to the positive nuclear charge of its neighbor. As the independent atoms approach one another, there are both repulsive forces (between the electrons in each atom and between the nuclei of each atom), and attractive forces (between the positive nuclei and the negative valence electrons). Some constituents require the addition of energy, called the activation energy, to overcome the initial repulsive forces. But at various distances, the atoms experience different attractive and repulsive forces, ultimately finding the ideal separation distance where the electrostatic forces are reduced to a minimum. This minimum represents the most stable position, and the distance between the atoms at this point is known as the bond length.

As the name suggests, covalent bonding involves the sharing (co, meaning joint) of valence (outer shell) electrons. As described previously, the atoms involved in covalent bonding arrange themselves in order to achieve the greatest energetic stability. And the valence electrons are shared – sometimes equally, and sometimes unequally – between neighboring atoms. The simplest example of covalent bonding occurs when two hydrogen atoms come together to ultimately form a hydrogen molecule, H₂.

The covalent bond in the hydrogen molecule is defined by the pair of valence electrons (one from each hydrogen atom) that are shared between the atoms, thus giving each hydrogen atom a filled valence shell. Since one shared pair of electrons represents one covalent bond, the hydrogen atoms in a hydrogen molecule are held together with what is known as a single covalent bond, and that can be represented with a single line, thus H-H.

There are many instances where more than one pair of valence electrons are shared between atoms, and in these cases multiple covalent bonds are formed. For example, when four electrons are shared (two pairs), the bond is called a double covalent bond; in the case of six electrons being shared (three pairs) the bond is called a triple covalent bond.

Common examples of such multiple bonds are those formed between atoms in oxygen and nitrogen gas. In oxygen gas (O_2), two atoms share a double bond resulting in the structure $O=O$. In nitrogen gas (N_2), a triple bond exists between two nitrogen atoms, $N\equiv N$.

Double covalent bonds are shorter and stronger than comparable single covalent bonds, and in turn, triple bonds are shorter and stronger than double bonds – nitrogen gas, for example, does not react readily because it is a strongly bonded stable compound.

Ionic bonding occurs when valence electrons are shared so unequally that they spend more time in the vicinity of their new neighbor than their original nuclei. This type of bond is classically described as occurring when atoms interact with one another to either lose or gain electrons. Those atoms that have lost electrons acquire a net positive charge and are called cations, and those that have gained electrons acquire a net negative charge and are referred to as anions. The number of electrons gained or lost by a constituent atom commonly conforms with Lewis's valence octets, or filled valence shell principle.

In reality even the most classic examples of ionic bonding, such as the sodium chloride bond, contain characteristics of covalent bonding, or sharing of electrons of outer shell electrons. A common misconception is the idea that elements tend to bond with other elements in order to achieve these octets because they are 'stable' or, even worse, 'happy', and that's what elements 'want'. Elements have no such feelings; rather, the actual reason for bond formation should be considered in terms of the energetic stability arising from the electrostatic interaction of positively charged nuclei with negatively charged electrons.

Substances that are held together by ionic bonds (like sodium chloride) can commonly separate into true charged ions when acted upon by an external force, such as when they dissolve in water. Further, in solid form, the individual atoms are not cleanly attracted to one individual neighbor, but rather they form giant networks that are attracted to one another by the electrostatic interactions between each atom's nucleus and neighboring valence electrons. The force of attraction between neighboring atoms gives ionic solids an extremely ordered structure known as an ionic lattice, where the oppositely charged particles line up with one another to create a rigid, strongly bonded structure.

The lattice structure of ionic solids conveys certain properties common to ionic substances. These include:

High melting and boiling points (due to the strong nature of the ionic bonds throughout the lattice).

An inability to conduct electricity in solid form when the ions are held rigidly in fixed positions within the lattice structure. Ionic solids are insulators. However, ionic compounds are often capable of conducting electricity when molten or in solution when the ions are free to move.

An ability to dissolve in polar solvents such as water, whose partially charged nature leads to an attraction to the oppositely charged ions in the lattice.

Lewis used dots to represent valence electrons. Lewis dot diagrams (see Figure 1) are a quick and easy way to show the valence electron configuration of individual atoms where no bonds have yet been made.

The dot diagrams can also be used to represent the molecules that are formed when different species bond with one another. In the case of molecules, dots are placed between two atoms to depict covalent bonds, where two dots (a shared pair of electrons) denote a single covalent bond. In the case of the hydrogen molecule discussed above, the two dots in the Lewis diagram represent a single pair of shared electrons and thus a single bond.

If ionic bonding and covalent bonding sit at the extreme ends of a bonding spectrum, how do we know where any particular compound sits on that spectrum? Pauling's theory relies upon the concept of electronegativity, and it is the differences in electronegativity between the atoms that is crucial in determining where any bond might be placed on the sliding scale of bond type.

Pauling's scale of electronegativity assigns numbers between 0 and 4 to each chemical element. The larger the number, the higher the electronegativity and the greater the attraction that element has for electrons. The difference in electronegativity between two species helps identify the bond type. Ionic bonds are those in which a large difference in electronegativity exists between two bonding species. Large differences in electronegativity usually occur when metals bond to non-metals, so bonds between them tend to be considered ionic.

When the difference in electronegativity between the atoms that make up the chemical bond is less, then sharing is considered to be the predominant interaction, and the bond is considered to be covalent. While it is by no means absolute, some consider the boundary between ionic and covalent bonding to exist when the difference in electronegativity is around 1.7 – less of a difference tends toward covalent, and a larger difference tends towards ionic. Smaller differences in electronegativity usually occur between elements that are both considered non-metals, so most compounds that are made up from two non-metal atoms are considered to be covalent.

Once differences in electronegativity have been considered, and a bond has been determined as being covalent, the story is not quite over. Not all covalent bonds are created equally. The only true, perfectly covalent bond will be one where the difference in electronegativity between the two atoms within the bond is equal to zero. When this occurs, each atom has exactly the same attraction for the electrons that make up the covalent bond, and therefore the electrons are perfectly shared. This typically occurs in diatomic (two-atom) molecules such as H_2 , N_2 , O_2 , and those of the halogen compounds when the atoms in the bond are identical.