8.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. Lewis electron dot symbols, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of 8 valence electrons in their compounds.

- **Ionic bond**: bond formed on the basis of electrostatic forces that exist between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons
- **Covalent bond**: bond formed between two or more atoms by a sharing of electrons
- **Metallic bond**: bonding in which the bonding electrons are relatively free to move throughout the 3D structure
- **Electron dot symbols**: aka Lewis symbols; simple and convenient way of showing the valence electrons of atoms and keeping track of them in the course of bond formation
- **Octet rule**: atoms tend to lose or gain electrons until they are surrounded by 8 valence electrons

8.2: IONIC BONDING

The amount of energy needed to separate a gaseous ion pair is its bond energy. Forming ionic compounds is usually extremely exothermic. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance.

**Energies of Ionic Bond Formation**

The formation of ionic compounds is very exothermic

Removing an electron from an atom, such as Na, is endothermic because energy needs to be used to overcome the attractive forces within the atom. Adding an electron is the opposite process and releases lots of energy

The principal reason that ionic compounds are stable is the attraction between ions of unlike charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array (lattice)

**Lattice energy**: energy required to separate completely a mole of a solid ionic compounds into its gaseous ions

Large values of lattice energy mean that the ions are strongly attracted to one another

Energy released by the attraction between the ions of unlike charges more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process

\[ E = k \frac{Q_1 Q_2}{d} \]
\[ E = \text{potential energy of two interacting charged particles} \]
\[ Q_1 \text{ and } Q_2 = \text{charges on the particles} \]
\[ D = \text{distance between the particles} \]
\[ K = \text{constant; } 8.99 \times 10^{9} \text{ Jm/C}^2 \]

For a given arrangement of ions, the lattice energy increases as the charges of ions increase and as their radii decrease. The magnitude of lattice energies depends primarily on the ionic charges because ionic radii do not vary over a wide range.

**Electron Configurations of Ions**

Many ions tend to have noble gas electron configurations. This is why Na can have a +1 charge, but not a +2 one. Once an ion has reached noble gas configuration, it wants to stay there.

- Na: \(1s^2 2s^2 2p^6 3s^1 = [\text{Ne}] 3s^1\)
- Na\(^+\): \(1s^2 2s^2 2p^6 = [\text{Ne}]\)
- Na\(^{2+}\): \(1s^2 2s^2 2p^5\)

Similarly, addition of electrons to nonmetals is either exothermic or slightly endothermic as long as electrons are being added to the valence shell. Further addition of electrons requires tremendous amounts of energy; more than is available from the lattice energy.

- Cl: \(1s^2 2s^2 2p^6 3s^2 3p^5 = [\text{Ne}] 3s^2 3p^5\)
- Cl\(^-\): \(1s^2 2s^2 2p^6 3s^2 3p^6 = [\text{Ar}]\)
- Cl\(^{2-}\): \(1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 = [\text{Ar}]\)

The lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only 3 electrons from atoms. Thus we find cations only having charges of +1, +2, or +3.

Because most transition metals have more than 3 electrons beyond a noble gas core, attainment of a noble gas configuration for these ions is usually impossible.

When a positive ion is formed from an atom, electrons are always lost first from the subshell with the largest value of \(n\). Thus, a transition metal always loses the outer \(s\) electrons before it loses electrons from the underlying \(d\) subshell.

**8.3 Sizes of Ions**

Sizes of ions are important in determining both the way in which the ions pack in a solid and the lattice energy of the solid. It is also a major factor governing the properties of ions in solution.

The size of an atom depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the outer-shell electrons reside.

Positive ions are formed by removing 1 or more electrons from the outermost region of the atom. Thus, the formation of
a cation not only vacates the most spatially extended orbitals, it also decreases the total electron-electron repulsions. Hence, cations are smaller than the original atoms from which they came.

The opposite happens when speaking of negative ions. An added electron increases electron-electron repulsions and causes the electrons to spread out more in space.

For ions of the same charge, size increases as we go down a group.

### 8.3: COVALENT BONDING

*The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest.*

Ionic substances are usually brittle with high melting points. They are usually crystalline, meaning that they have flat surfaces that make characteristic angles with one another.

- **Covalent bond**: chemical bond formed by sharing a pair of electrons
- **Lewis structure**: structure that represents bonding using dots for unpaired electrons and lines for bonds

For nonmetals, the number of valence electrons is the same as the group number.

Knowing this, we can predict that an element in Group 7A would need one covalent bond in order to get an octet, an element in Group 6A would need two, and so on.

### Multiple Bonds

- **Single bond**: sharing of one pair of electrons, one covalent bond
- **Double bond**: two shared electrons

Distance between bonded atoms decreases as the number of shared electron pairs increases.

### 8.4: BOND POLARITY AND ELECTRONEGATIVITY

*Bond polarity and ionic character increase with an increasing difference in electronegativity. The electronegativity ($\chi$) of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average.*

- **Bond polarity**: measure of how equally the electrons are shared between the atoms in a chemical bond
- **Nonpolar bond**: one in which the electrons are shared equally between the two atoms
- **Polar covalent bond**: one of the atoms exerts a greater attraction for the electron than the other
Electronegativity

Used to estimate whether a bond will be nonpolar, polar covalent, or ionic

Electronegativity: ability of an atom in a molecule to attract electrons to itself

An atom with a very negative electron affinity and high ionization energy will both attract electrons from other atoms and resist having its electrons attracted away; it will be highly electronegative

Highest electronegativity = 4.0 (Fluorine), lowest = 0.7 (Cesium)

Electronegativity increases form left to right, and usually decreases with increasing atomic number in any one group

Electronegativity and Bond Polarity

Differences in electronegativities:

Nonpolar = 0 – 0.4

Polar covalent = 0.4 – 1.6

Ionic = > 1.6 (> 50% = ionic)

δ⁺ and δ⁻: "delta sign"; represent partial positive and negative charge. The atom with the δ is the more electronegative one

8.5: DRAWING LEWIS STRUCTURES

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families.

1. Sum the valence electrons from all atoms. For an anion, add an electron to the total negative charge. For a cation, subtract an electron.

2. Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond.

3. Complete the octets of the atoms bonded to the central atom.

4. Place any leftover electrons on the central atom, even if doing so results in more than an octet

5. If there are not enough electrons to give the central atom an octet, try multiple bonds

8.6: RESONANCE STRUCTURES

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the
delocalization of electrons within molecules. These structures are written with a double-headed arrow between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures.

**Resonance structures (resonance forms)** are individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. If a molecule (or ion) has two or more resonance structures, the molecule is a blend of these structures. The molecule does not oscillate rapidly between two or more different forms.

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**8.7: EXCEPTIONS TO THE OCTET RULE**

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an **odd number of valence electrons**, (2) When there are **too few valence electrons**, and (3) when there are **too many valence electrons**

1. Molecules with an odd number of electrons
2. Molecules in which an atom has less than an octet
3. Molecules in which an atom has more than an octet

**Odd Number of Electrons**

In a few molecules, such as ClO₂, NO, and NO₂, the number of electrons is odd. In NO for example, there are 5+6 = 11 valence electron. Hence, complete pairing of these electrons is impossible and an octet around each atom cannot be achieved.

**Less Than an Octet**

Second type of exception occurs when there are fewer than eight electrons around an atom in a molecule or ion. Relatively rare situation; most often encountered in compounds of Boron and Beryllium. For example, let’s consider Boron Trifluoride, BF₃

![Boron Trifluoride](image)

There are 6 electrons around the Boron atom. We can form a double bond between Boron and any of the 3 Fluorine atoms (3 possible resonance structures)

However, by doing so, we forced a Fluorine atom to share additional electrons with Boron. This would make the F atom to have a +1 charge, and the Boron atom to have a –1 charge, which is extremely unfavorable.
We then conclude that the structures containing the double bonds are less important than the one illustrated on the right. *Since in this case Boron has only 6 valence electrons, it will react violently with molecules that have an unshared pair of electrons.*

**More Than an Octet**

The octet rule works as well as it does because the representative elements usually employ only an *ns* and three *np* valence shell orbitals in bonding, and these hold eight electrons.

Because elements of the second period have only 2s and 2p orbitals, they cannot have more than an octet of electrons in their valence shells. However, from the third period on, the elements have unfilled *nd* orbitals that can be used in bonding.

Size also plays an important role in determining whether an atom can accommodate more than eight electrons. The larger the central atom, the larger the number of atoms that can surround it. The size of the surrounding atoms is also important. Expanded valence shells occur most often when the central atom is bonded to the smallest and most electronegative atoms.

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**8.8: STRENGTHS OF COVALENT BONDS**

*Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. The bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms.*

**Bond dissociation energy:** aka *bond energy*; enthalpy change, ΔH, required to break a particular bond in a mole of gaseous substance.

For polyatomic molecules, we must often utilize average bond energies.

Bond energy is *always* positive, the greater the bond energy, the stronger the bond

A molecule with strong bonds generally has less tendency to undergo chemical change than does one with weak bonds

**Bond Energies and the Enthalpy of Reactions**

\[ \Delta H = \Sigma \text{(bond energies of bonds broken)} - \Sigma \text{(bond energies of bonds formed)} \]

If \( \Delta H > 0 \), the reaction is endothermic

If \( \Delta H < 0 \), the reaction is exothermic

\[ \text{Cl} \text{– Cl (g)} + \text{H} \text{– CH}_3 \text{(g)} \rightarrow \text{H} \text{– Cl (g)} + \text{Cl} \text{– CH}_3 \text{(g)} \]

Bonds broken: 1 mol Cl – Cl, 1 mol C – H
Bonds made: 1 mol H – Cl, 1 mol C – Cl

\[\Delta H = [D (Cl – Cl) + D(C – H)] [D (H – Cl) + D (Cl – Cl)]\]

= (242 kJ + 413 kJ) – (431kJ + 328 kJ)

= 104 kJ

**Bond Strength and Bond Length**

As the number of bonds between a given element increase, the bond energy increases and the bond length decreases. Hence, the atoms are held more tightly and closely together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger.*

### 8.10 Oxidation Numbers

**Oxidation Numbers:** aka **Oxidation states**; a positive or negative whole number assigned to an element in a molecule or ion on the basis of a set of normal rules; to some degree it reflects the positive or negative character of an atom.

Oxidation numbers do NOT correspond to real charges on the atoms, EXCEPT in the special case of simple ionic substances.

1. *The oxidation form of an element in its elemental form is zero.*
2. *The oxidation number of a monoatomic ion is the same as its charge.* For example, the oxidation number of sodium in Na\(^+\) is +1, and that of sulfur in S\(^2-\) is –2.
3. *In binary compounds (those with two different elements), the element with greater electronegativity is assigned a negative oxidation number equal to its charge in simple ionic compounds the element.* For example, consider the oxidation state of Cl in PCl\(_3\). Cl is more electronegative than P. In its simple ionic compounds, Cl appears as the ion Cl\(^-\). Thus, in PCl\(_3\), Cl is assigned an oxidation number of –1.
4. *The sum of the oxidation numbers equals zero for an electrically neutral compound and equals the overall charge of the ionic species.* For example, PCl\(_3\) is a neutral molecule. Thus, the sum of oxidation number of the P and Cl atoms must equal zero. Because the oxidation number of each Cl in this compound is –1 (rule 3), the oxidation number of P must be +3.

Group 1A elements are +1, Group 2A elements are +2, and Aluminum is +3.

The most electronegative element, F, is always found in the –1 oxidation state. Oxygen is usually in the –2 state, however, it can be –1 in peroxides.

Hydrogen has an oxidation number of +1 when it is bonded to a more electronegative element (most nonmetals), and of –1 when bonded to less electronegative elements (most metals)

**Oxidation Numbers and Nomenclature**

Name of the less electronegative element is given first, followed by the name of the more electronegative element modified to have an –*ide* ending.
Compounds of metals in higher oxidation states tend to be molecular rather than ionic