

Chapter 8: Basic Concepts of Chemical Bonding

8.1 Lewis Symbols and the Octet Rule

- 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 3-D 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
- The number of valence electrons of any representative element is the same as the column number of the element in the periodic table
- Octet rule**: atoms tend to lose or gain electrons until they are surrounded by 8 valence electrons

8.2 Ionic Bonding

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

$$E = k (Q_1 Q_2 / d)$$

E = potential energy of two interacting charged particles

Q_1 and Q_2 = charges on the particles

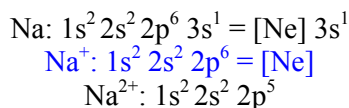
D= distance between the particles

K = constant; $8.99 \times 10^9 \text{ J-m/C}^2$

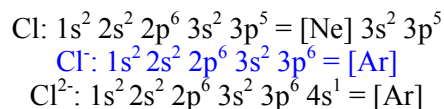
- For a given arrangement of ions, the lattice energy increases as the charges of ions increase and as their radii decrease. The magnitude of lattice energies depends primarily on the ionic charges because ionic radii do not vary over a wide range.

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.



-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



-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 electron 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

8.4 Covalent Bonding

-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

8.5 Bond Polarity and Electronegativity

- 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 from 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

8.6 Drawing Lewis Structure

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*

8.7 Resonance Structures

-**Resonance structures**: aka **resonance forms**; 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.

8.8 Exceptions to the Octet Rule

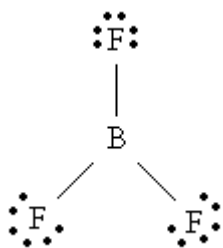
1. Molecules with an odd number of electrons
2. Molecules in which an atom has less than an octet
3. Molecules in which an atom has more than an octet

Odd Number of Electrons

-In a few molecules, such as ClO_2 , NO , and NO_2 , 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, BF_3



-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.

8.9 Strengths of Covalent Bonds

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

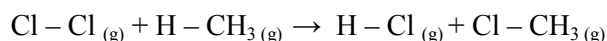
- For polyatomic molecules, we must often utilize average bond energies.
- Bond energy is *always* positive, the greater the bond energy, the stronger the bond
- A molecule with strong bonds generally has less tendency to undergo chemical change than does one with weak bonds

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



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

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

$$\begin{aligned} \Delta H &= [D(\text{Cl} - \text{Cl}) + D(\text{C} - \text{H})] - [D(\text{H} - \text{Cl}) + D(\text{C} - \text{Cl})] \\ &= (242 \text{ kJ} + 413 \text{ kJ}) - (431 \text{ kJ} + 328 \text{ kJ}) \\ &= -104 \text{ kJ} \end{aligned}$$

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 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.