

1 Periodic trends

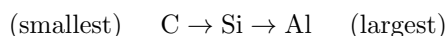
Inside an atom, negatively-charged electrons are attracted to the positively-charged nucleus, but they repel each other. Electrons close to the nucleus can *shield* the outermost electrons from Coulomb forces between the electrons and the nucleus.

Going across a row in the periodic table, each element has one extra electron *and* one extra proton. The additional proton has a strong effect on the electrons, as the number of inner shielding electrons does not change. However, when going down a period, there are more and more shells of electrons with increasing energy and average radius from the nucleus. Therefore, atomic radius decreases from left to right across the rows of the periodic table, and increases from top to bottom.

When atoms become *ionized*, their atomic radius changes as the charge state balance changes. If an atom gains electrons to become negatively charged, it is called an *anion*. If an atom loses electrons to become positively charged, it is called a *cation*. Cations are typically smaller than the neutral version of the atom, while anions are typically larger. An ionic solid contains cations and anions in a ratio that maintains charge neutrality.

Example: Arrange Al, C, and Si in order of increasing atomic radius.

Carbon is in the second period of the periodic table, while Al and Si are in the third: C must be the smallest. Al is in group III, while Si is in group IV, so Al is likely larger than Si due to relatively strong effect of the extra proton Si has.



2 Lewis Dot Diagrams

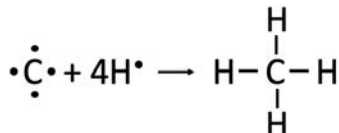
Lewis dot diagrams are a tool used to visualize the valence electrons in atoms. Then, by pairing up electrons, we can visualize possible ways that bonds can be formed between two atoms.

There are a couple of rules of thumb that come in handy when drawing Lewis dot diagrams. The *octet rule* tells us that atoms gain, lose, or share electrons in order to have a full valence shell of 8 electrons (2 for H and He). Also, the number of valence electrons in an atom is equal to the group number. We can generally start by following these steps:

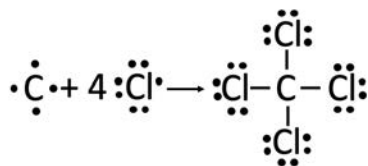
1. Determine the number of valence electrons in each atom in the compound
2. Place a bonding pair between adjacent atoms
3. Starting from terminal atoms, add electrons to form octets

Example: Draw Lewis dot diagrams for the following compounds: CH₄, CCl₄, CO₂, and OH⁻

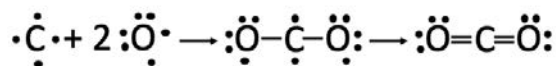
CH₄: C has 4 valence electrons (group IV), while hydrogen just has one. Sharing four electrons between the C and H's yields an octet on the carbon atom and a complete shell of two electrons on the hydrogen. Note that it's often convenient to put the atom that has the most unpaired electrons in the middle.



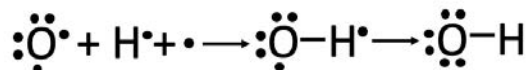
CCl_4 : Again, C has 4 valence electrons, and Cl has 7. Cl can only gain one additional electron to have a full octet, so each Cl only makes one bond. Therefore, we can put C in the middle again and surround it with Cl atoms, and every atom has a full octet.



CO_2 : C has 4 valence electrons, while O has 6. We can start by placing the C in the middle and forming a bond with each O. The structure that results is unstable, because each O is left with an unpaired electron. C also has two unpaired electrons leftover. We can use them to form double bonds between the C and each O without violating the octet rule. Note that each O is left with two lone pairs.



OH^- : Here, the oxygen brings 6 valence electrons and the H brings just one, but there is an additional electron in play because of the structure's overall negative charge. After forming a single bond between the O and the H, we're left with unpaired electrons, so we need to rearrange some more. We can't make a double bond to the hydrogen, as it can only support two electrons. Moving the extra electron to the oxygen to join a lone pair does the trick.



3 Formal charge

Above, we discussed the steps for constructing Lewis dot diagrams: by following these rules, we can determine *stable* electronic configurations of molecules. We can also quantify this stability by calculating the *formal charge*.

$$\text{Formal Charge} = \# \text{ valence } e^- \text{ s} - \left(N + \frac{b}{2}\right)$$

where the number of valence electrons refers to the neutral atom in isolation, N = the number of nonbonding valence electrons and b = the number of valence electrons participating in bonds. Formal charge should be calculated for each atom in the molecule.

Example: Determine the formal charge of CO_2 .

Oxygen: the neutral oxygen atom in isolation has 6 valence electrons. Each oxygen in CO_2 has 4 non-bonding electrons and 4 electrons stored in bonds.

$$\text{Formal Charge (Oxygen)} = 6 - \left(4 + \frac{4}{2}\right) = 0$$

Carbon: the neutral carbon atom in isolation has 4 valence electrons. Each carbon in CO_2 has 8 electrons stored in bonds.

$$\text{Formal Charge (Carbon)} = 4 - \left(\frac{8}{2}\right) = 0$$

MIT OpenCourseWare
<https://ocw.mit.edu/>

3.091 Introduction to Solid-State Chemistry
Fall 2018

For information about citing these materials or our Terms of Use, visit: <https://ocw.mit.edu/terms>.