CHE 205
General Chemistry

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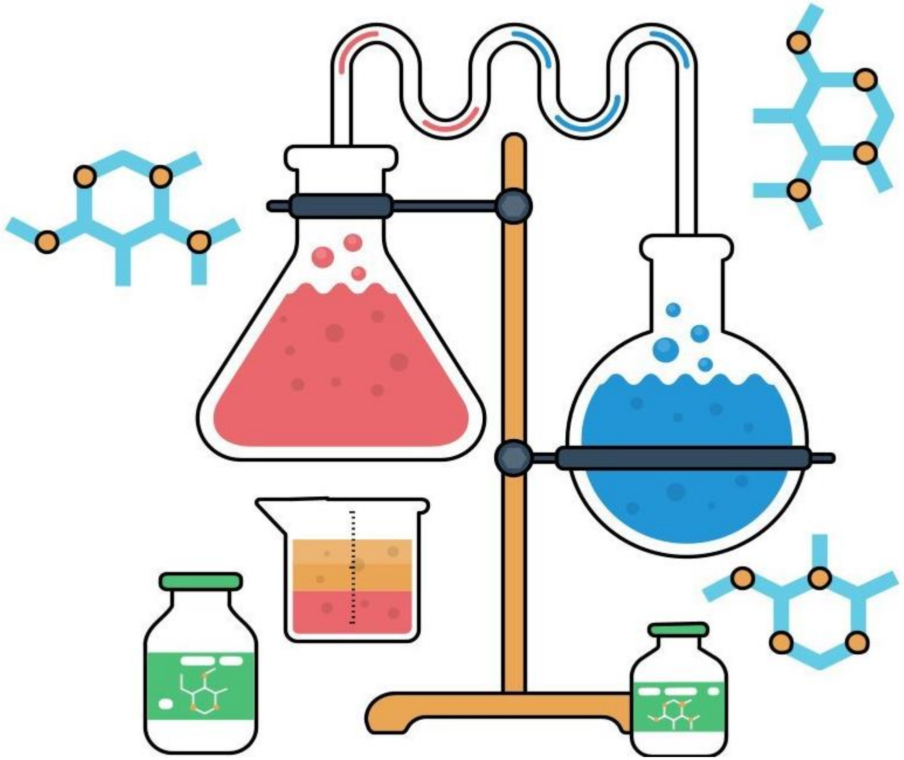
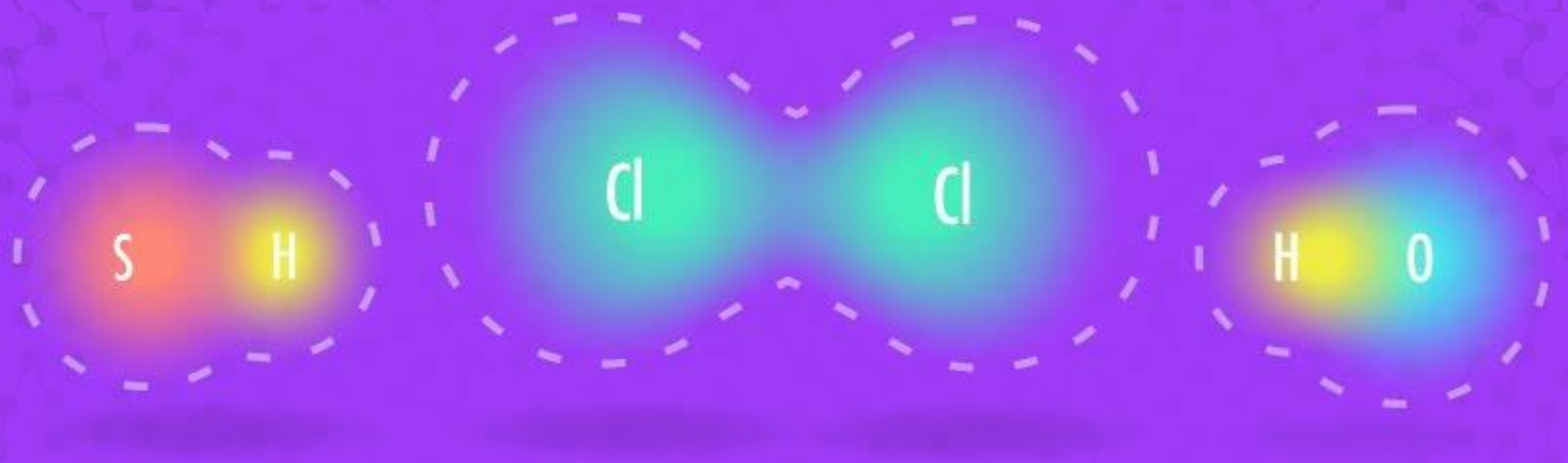


Chapter II: Bonding : General Concepts



Chapter 2

Bonding: General Concepts

Chapter outline

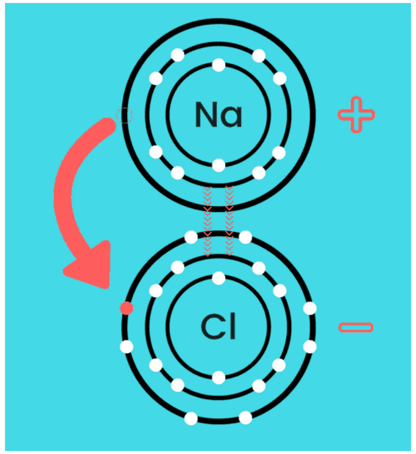
1. Types of Chemical Bonds
2. Electronegativity
3. Bond Polarity and Dipole Moments
4. Ions: Electron Configurations and Sizes
5. The Localized Electron Bonding Model
6. Lewis Structures
7. Exceptions to the Octet Rule
8. Resonance structures
9. Formal charge
10. Molecular Structure: The VSEPR Model

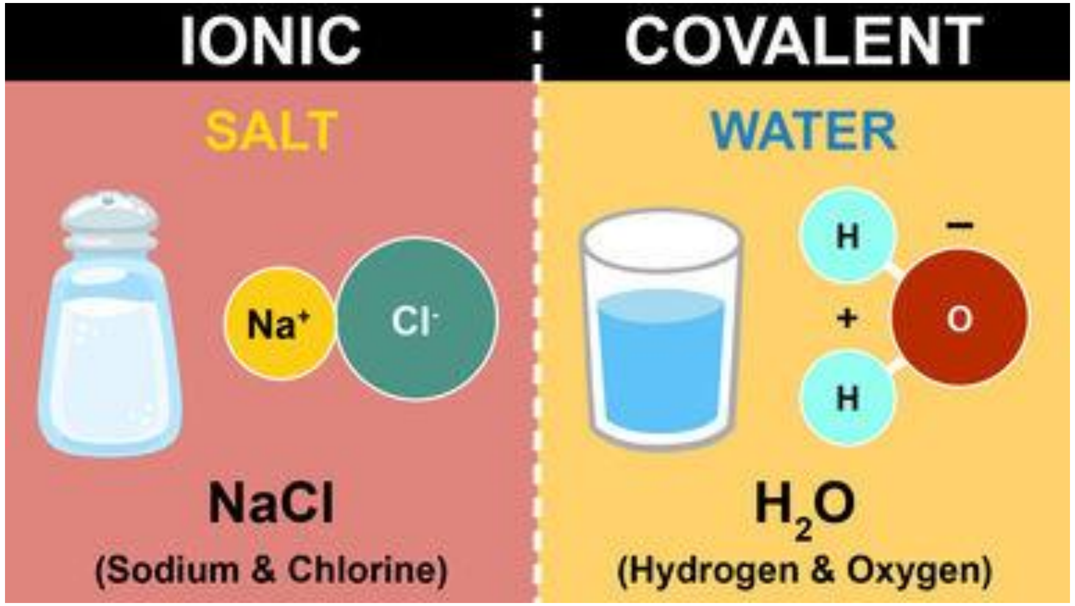
Types of Chemical Bonds

What is a chemical bond?

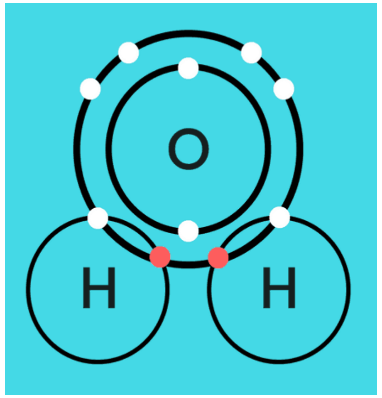
A chemical bond is a lasting attraction between atoms or ions that enables the formation of chemical compounds.

A bond may result from the electrostatic force of attraction between oppositely charged ions as in an **Ionic Bond**.





A bond may be formed through the sharing of electrons between atoms as in a **Covalent Bond**.



Types of Chemical Bonds

Ionic bond: Metal + Non metals

- An ionic compound results when a *metal reacts with a nonmetal*.

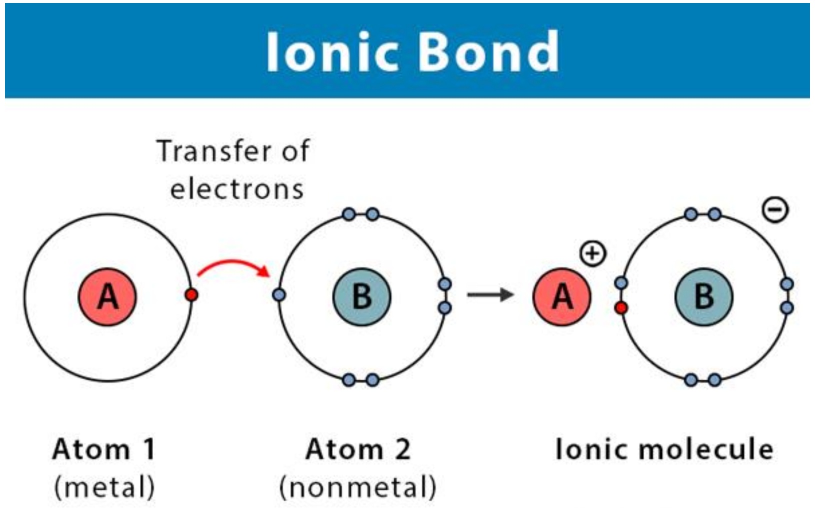
An ionic bond is an electrostatic attraction between two adjacent, oppositely charged ions.

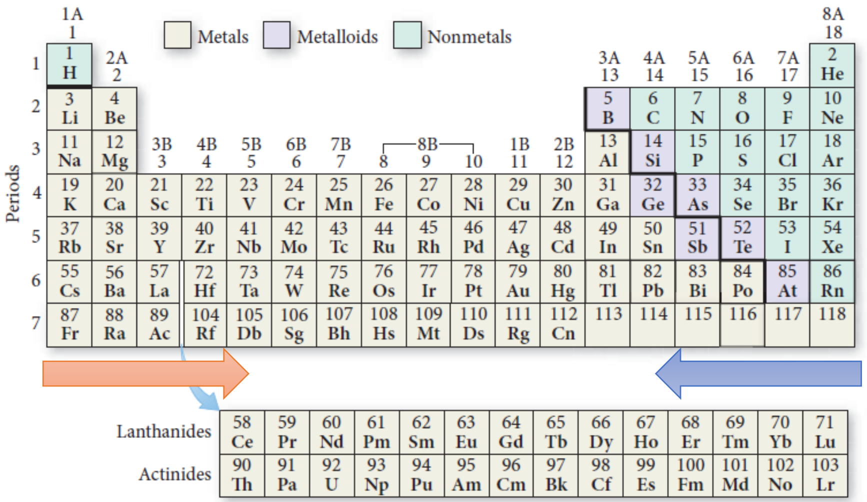
- When sodium and chlorine react to form sodium chloride, electrons are transferred from the sodium atoms to the chlorine atoms to form Na^+ and Cl^- ions, which then aggregate to form solid sodium chloride. *Why does this happen?*

Because the system can achieve the lowest possible energy by behaving in this way.

- Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons.

An ionic compound results when a metal reacts with a nonmetal.





Types of Chemical Bonds

Covalent bond: Non metal + Non metals

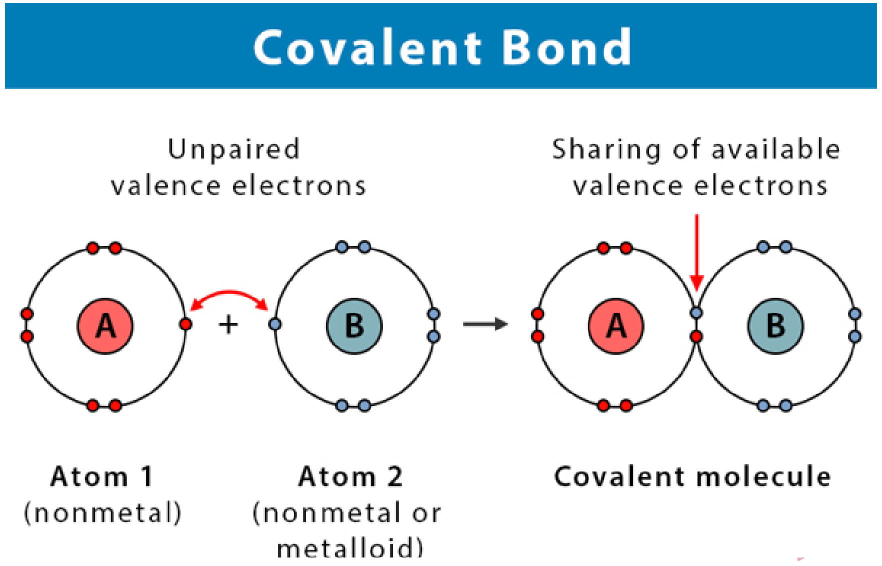
A covalent bond is a bond formed when electrons are shared between two atoms.

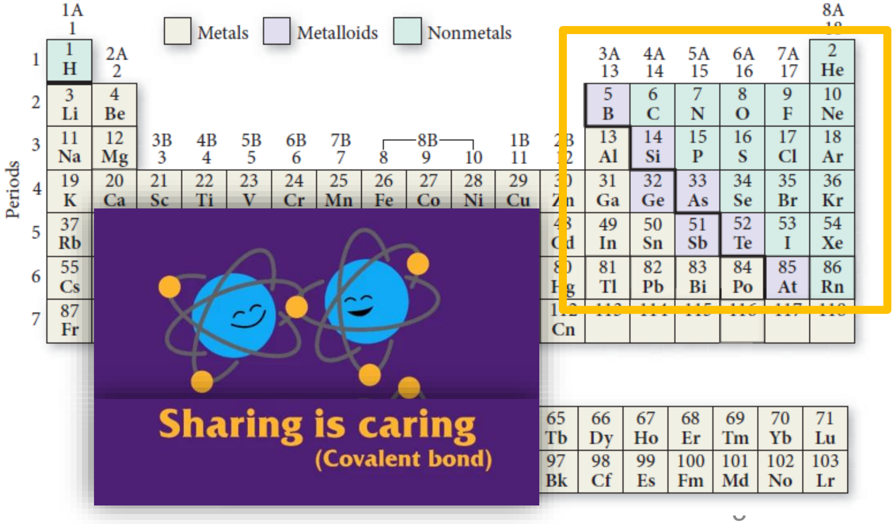
How does a bonding force develop between two identical atoms?

For example, in an H_2 molecule, what conditions will favor bond formation?

The answer lies in the strong tendency in nature for any system to achieve the *lowest possible energy*. A bond will form (that is, the two hydrogen atoms will exist as a molecular unit) if the system can lower its total energy in the process.

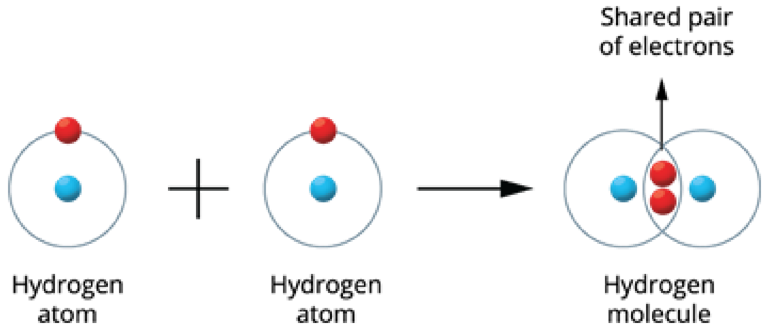
Then, **the hydrogen atoms will position themselves so that the system will achieve the lowest possible energy.**

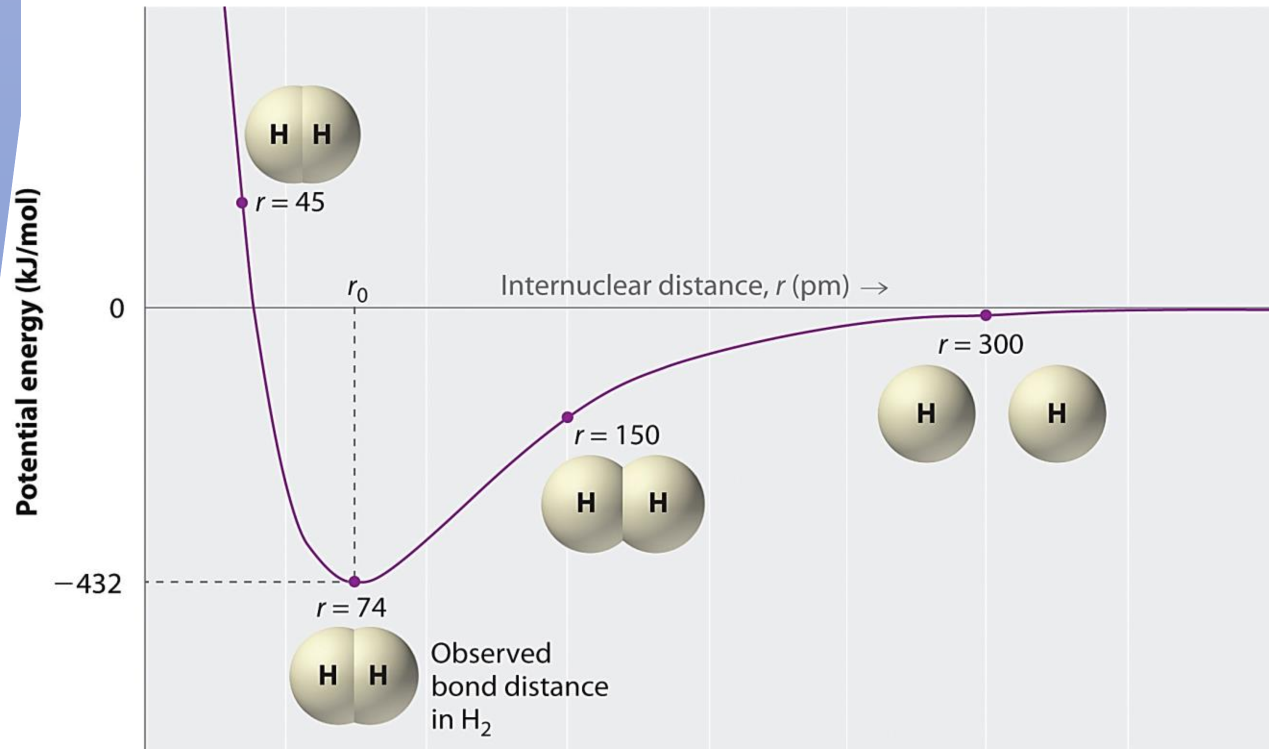




Types of Chemical Bonds

Covalent bond: Non metal + Non metals





- In the H_2 molecule, the electrons reside primarily in the space between the two nuclei, where they are attracted simultaneously by both protons.

- This positioning is precisely what leads to the stability of the H_2 molecule compared with two separated hydrogen atoms.

- When we say that a bond is formed between the hydrogen atoms, we mean that the H_2 molecule is more stable than two separated hydrogen atoms by a certain quantity of energy (the bond energy).

- The type of bonding we encounter in the hydrogen molecule and in many other molecules in which *electrons are shared by nuclei* is called **covalent bonding**.

Types of Chemical Bonds

- In **Ionic bonding**, one or more electrons are transferred to form oppositely charged ions, which then attract each other.
- In **Covalent bonding** two identical atoms share electrons **equally**. The bonding results from the mutual attraction of the two nuclei for the shared electrons.

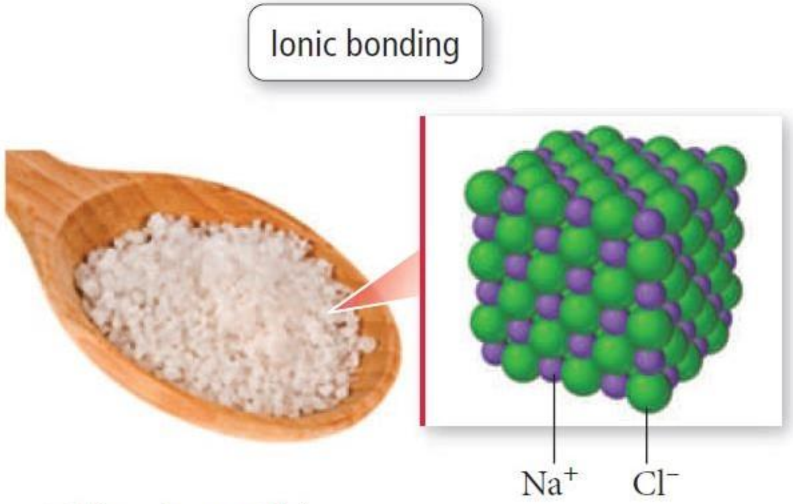


Table salt, NaCl(s)

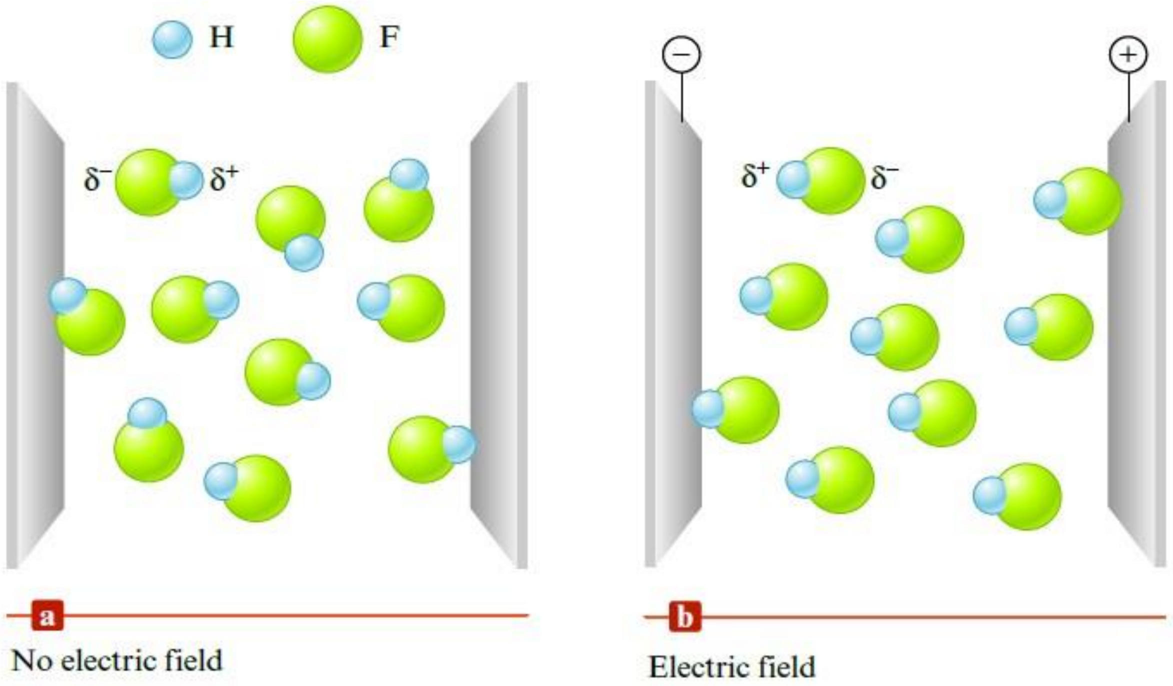
Between these extremes are **intermediate cases** in which the atoms are not so different that electrons are completely transferred but are different enough that **unequal sharing** results, forming what is called a

"Polar covalent bond".

Types of Chemical Bonds

Polar covalent bond

An example of this type of bond occurs in the hydrogen fluoride (HF) molecule. When a sample of hydrogen fluoride gas is placed in an electric field, the molecules tend to orient themselves, with the fluoride end closest to the positive pole and the hydrogen end closest to the negative pole.



The effect of an electric field on hydrogen fluoride molecules. (**a**) When no electric field is present, the molecules are randomly oriented. (**b**) When the field is turned on, the molecules tend to line up with their negative ends toward the positive pole and their positive ends toward the negative pole.

Types of Chemical Bonds

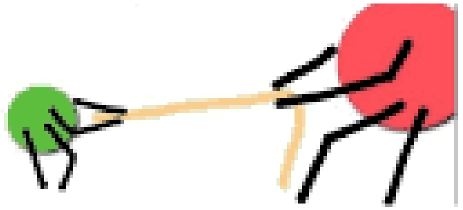
Polar covalent bond

Polar Covalent Bonds

This result implies that the HF molecule has the following charge distribution:

$$\underset{\delta^+}{\mathrm{H}}\text{—}\underset{\delta^-}{\mathrm{F}}$$

δ (lowercase delta) is used to indicate partial charge.



- The polarity of the HF molecule assumes that the **fluorine atom has a stronger attraction for the shared electrons** than the hydrogen atom.

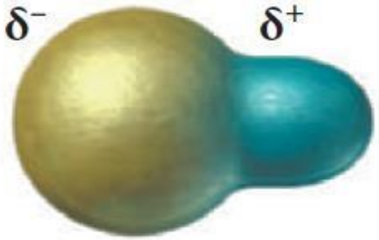
- The partial positive and negative charges on the atoms (bond polarity) in such molecules as HF and H_2O is explained by the ***unequal sharing of electrons*** in the bonds.

Types of Chemical Bonds

Pure (nonpolar) covalent bond

Electrons shared equally

Polar covalent bond

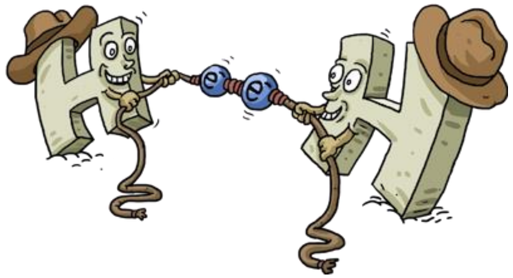


Electrons shared unequally

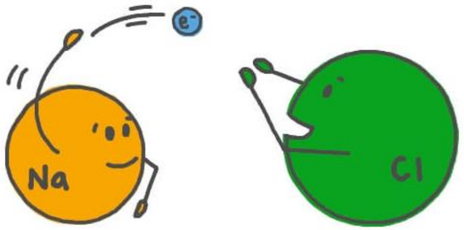
Ionic bond

Electrons transferred

Non-Polar Covalent Bond



Polar Covalent Bond



Electronegativity

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

For example: Fluorine is more *electronegative* than hydrogen because it takes a greater share of the electron density in HF.

In 1939, Linus Pauling quantified electronegativity.

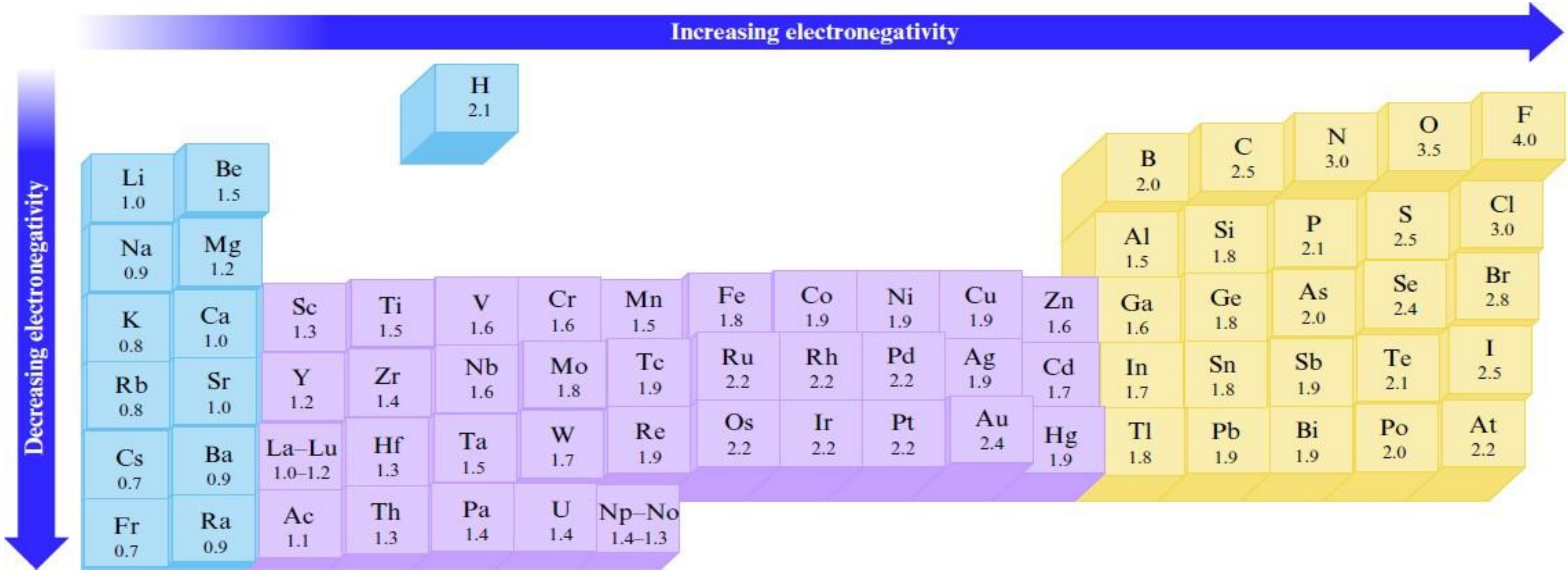
Prof. Linus Pauling
Nobel Prize for Chemistry 1954
Nobel Prize for Peace 1962

Electronegativity in the periodic table:

- Electronegativity generally increases across a period in the periodic table.
- Electronegativity generally decreases down a column in the periodic table.
- Fluorine is the most electronegative element.
- Francium is the least electronegative element (sometimes called the most *electropositive*).

In general, electronegativity is inversely related to atomic size. The larger the atom, the less ability it has to attract electrons to itself in a chemical bond.

Electronegativity



The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.

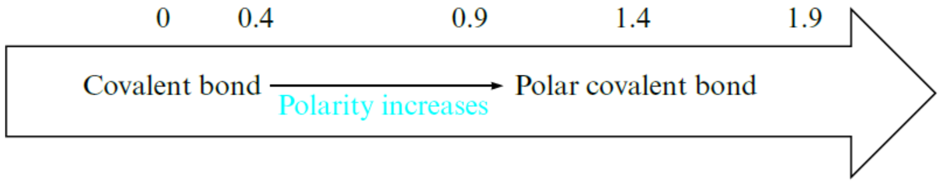
Electronegativity

The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type	
Zero	Covalent	Covalent character
Intermediate	Polar covalent	
Large	Ionic	Ionic character

The polarity of the bond increases as the difference in electronegativity increases. Example:

$$\underset{(2.1)(2.1)}{H-H} < \underset{(2.5)(2.1)}{S-H} < \underset{(3.0)(2.1)}{Cl-H} < \underset{(3.5)(2.1)}{O-H} < \underset{(4.0)(2.1)}{F-H}$$



Electronegativity

The Effect of Electronegativity Difference on Bond Type

Electronegativity Difference (ΔEN)	Bond Type	Example
Small (0–0.4)	Covalent	Cl_2
Intermediate (0.5 -2.0)	Polar covalent	HCl
Large (2.0+)	Ionic	NaCl

Electronegativity

Exercise:

Classify the bond formed between each pair of atoms as covalent, polar covalent, or ionic.

(a) Sr and F (b) N and Cl (c) N and O (d) Br and F

Electronegativities: Sr (1.0), F (4.0), N (3.0), Cl (3.0), O (3.5), Br (2.8)

Solution:

(a) The electronegativity difference is $\Delta EN = 4.0 - 1.0 = 3.0$, so the formed bond is ionic.

(b) $\Delta EN = 3.0 - 3.0 = 0$. So this bond is covalent.

(c) $\Delta EN = 3.5 - 3.0 = 0.5$. So it is a polar covalent bond.

(d) $\Delta EN = 4.0 – 2.8 = 1.2$ So it is a polar covalent bond.

Electronegativity

Exercise:

Which set of elements is arranged in order of increasing electronegativity?

a. O < S < As < Ge

b. Ge < As < S < O

c. S < O < As < Ge

d. As < O < Ge < S

Solution:

b. Ge < As < S < O

Bond Polarity and Dipole Moments

- The degree of polarity in a chemical bond depends on the **electronegativity difference (sometimes abbreviated ΔEN)** between the two bonding atoms.
- The greater the electronegativity difference, the more polar the bond is.
- If two atoms with identical electronegativities form a covalent bond, they share the electrons equally, and the bond is purely covalent or *nonpolar*.

A molecule such as HF that has a center of positive charge and a center of negative charge is said to be **dipolar**, or to have a **dipole moment**. The dipolar character of a molecule is often represented by an arrow pointing to the negative charge center with the tail of the arrow indicating the positive center of charge:

We *quantify the polarity* of a bond with a quantity referred to as the **bond's *dipole moment.***

Bond Polarity and Dipole Moments

- Any diatomic (two-atom) molecule that has a polar bond also will show a molecular dipole moment.

Molecule	ΔEN	Dipole Moment (D)
Cl_2	0	0
ClF	1.0	0.88
HF	1.9	1.82
LiF	3.0	6.33

Dipole Moments of Some Molecules in the Gas Phase

Electronegativity Difference (ΔEN)	Bond Type	Example
Small (0–0.4)	Covalent	Cl_2
Intermediate (0.5 -2.0)	Polar covalent	HCl
Large (2.0+)	Ionic	NaCl

The Effect of Electronegativity Difference on Bond Type

Bond Polarity and Dipole Moments

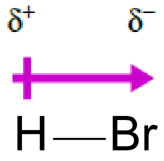
Exercise:

For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HBr and I_2

Electronegativity: Br (2.8), H (2.1), I (2.5)

Solution:

For HBr, the electronegativity of bromine (2.8) is greater than that of hydrogen (2.1). Thus the bromine will be partially negative, and the hydrogen will be partially positive. The HBr molecule has a dipole moment:

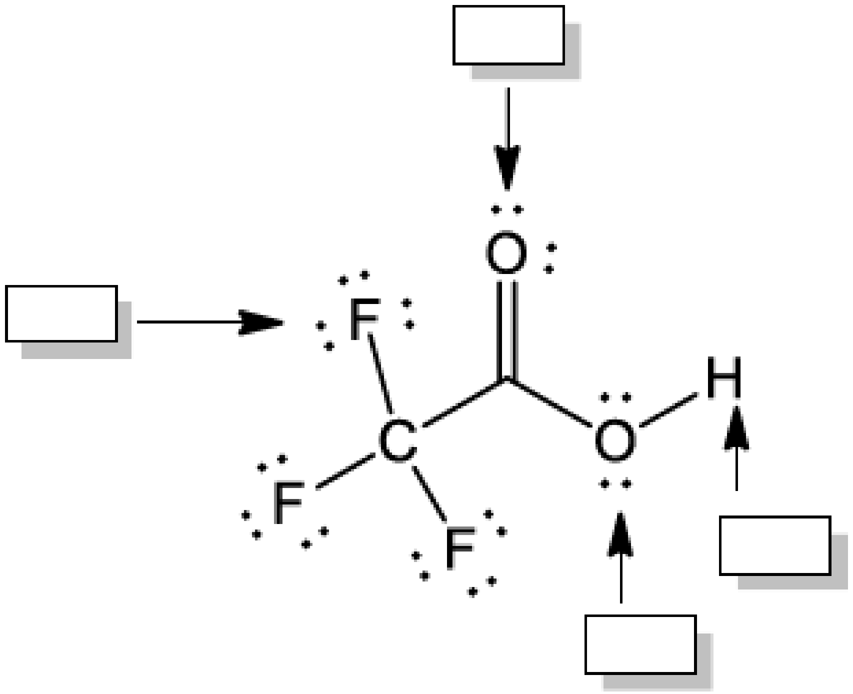


For I_2, The two iodine atoms share the electrons equally. No bond polarity occurs, and the I_2 molecule has no dipole moment.

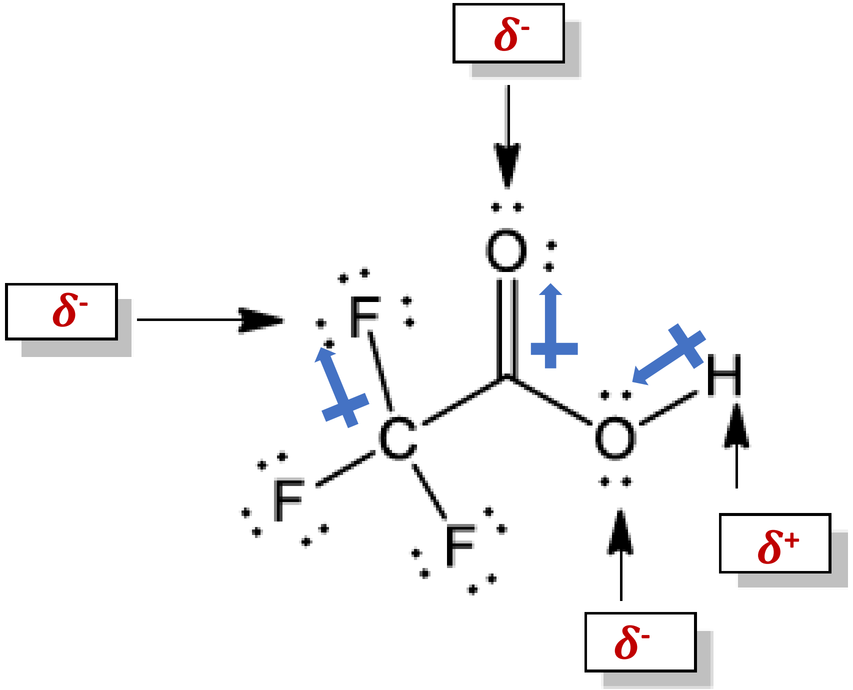
Bond Polarity and Dipole Moments

Exercise:

Add δ^+ or δ^- (partial charges) on the indicated atoms and show the direction of the bond polarities in the following molecule:



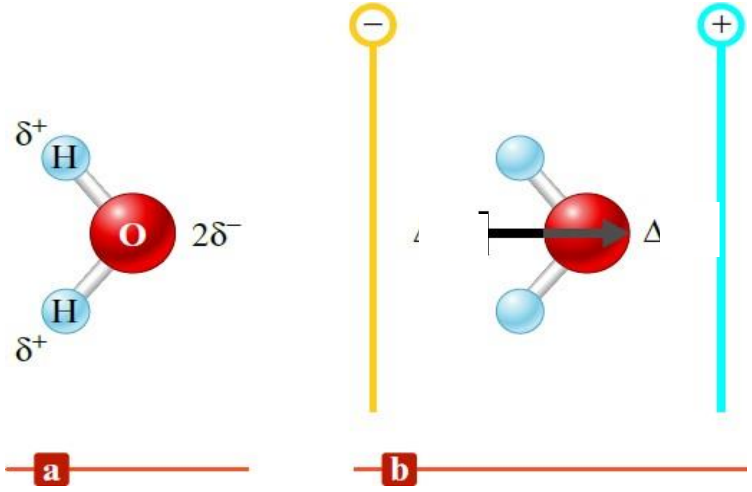
Solution:



Bond Polarity and Dipole Moments

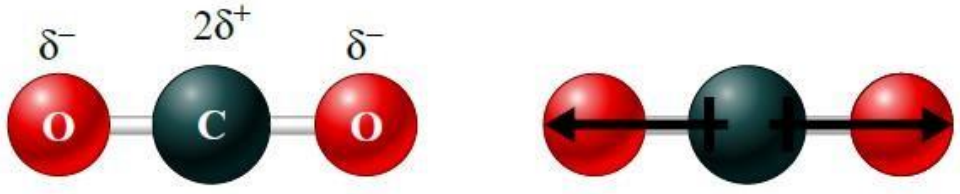
Polyatomic molecules also can exhibit dipolar behavior.

- For example, the oxygen atom in the water molecule has a greater electronegativity than the hydrogen atoms.
- Because of this charge distribution, the water molecule behaves in an electric field as if it has two centers of charge, one positive and one negative. The water molecule has a dipole moment.

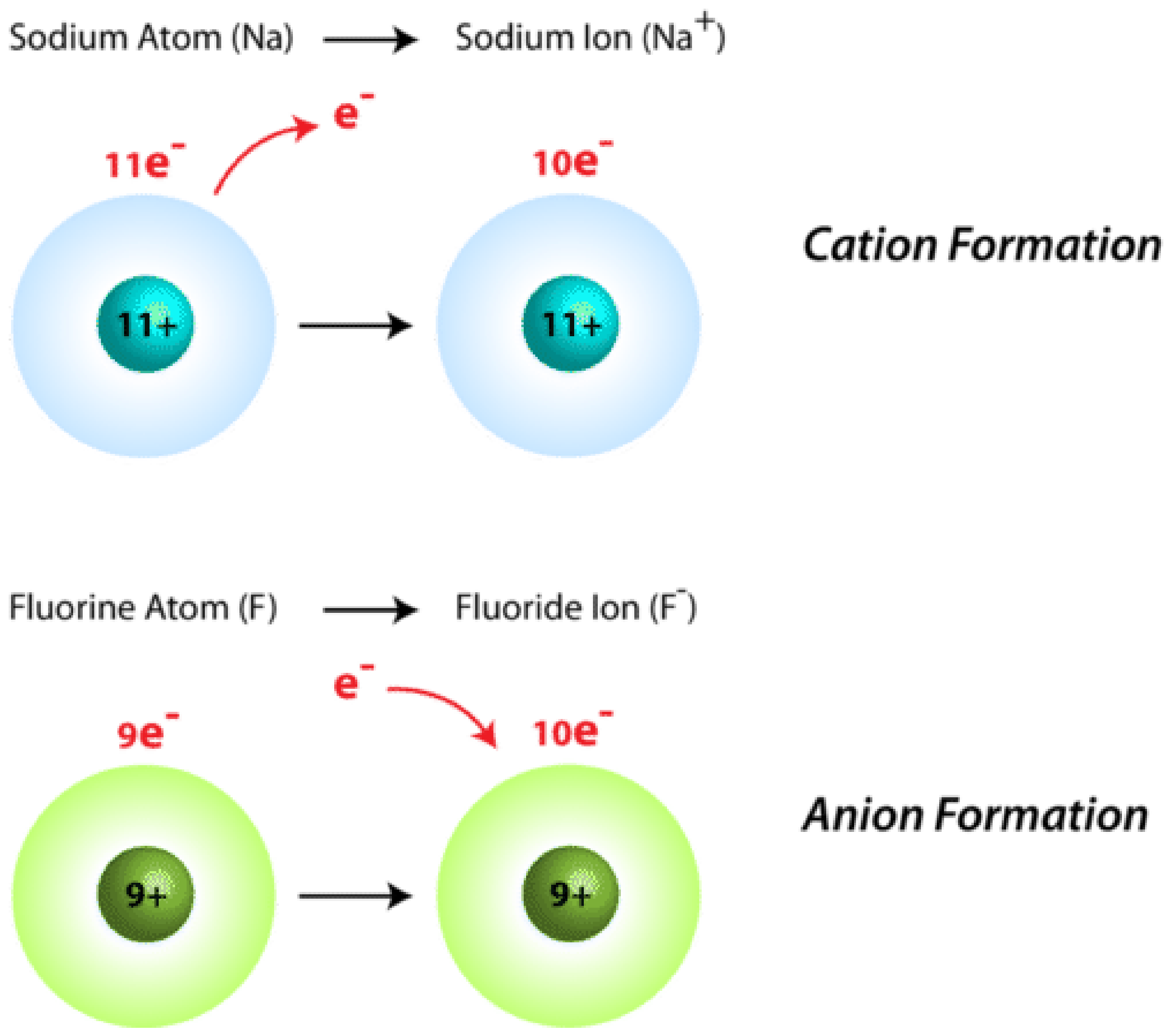


Some molecules have polar bonds but do not have a dipole moment.

- This occurs when the individual bond polarities are arranged in such a way that they cancel each other out.
- An example is the CO_2 molecule, which is a linear molecule. In this case the opposing bond polarities cancel out, and the carbon dioxide molecule does not have a dipole moment.



Ions: Electron Configurations and Sizes



- **Cations** are formed by the loss of one or more electrons from a neutral atom. The charge on a cation is equal to the number of electrons lost.
- **Anions** are formed when a nonmetal atom gains one or more electrons. The charge on an anion is equal to the number of electrons gained.

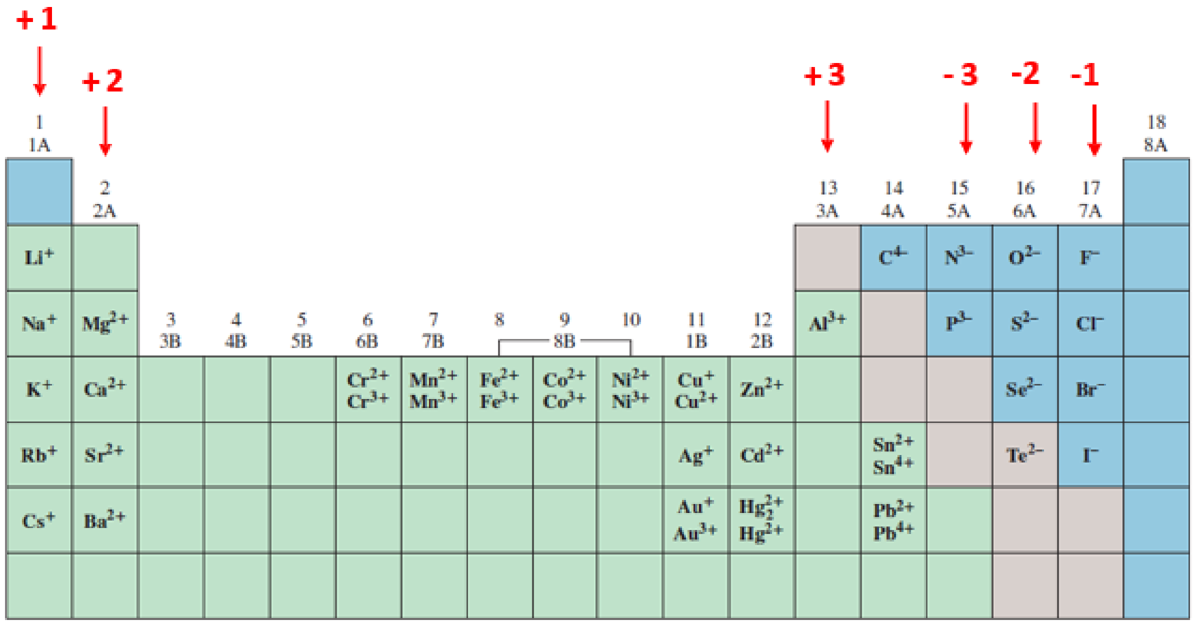
Ions: Electron Configurations and Sizes

In losing electrons to form cations:

- Metals in Group 1A lose one electron.
- Those in Group 2A lose two electrons.
- Those in Group 3A lose three electrons.

In gaining electrons to form anions:

- Nonmetals in Group 7A (the halogens) gain one electron.
- Those in Group 6A gain two electrons.



How losing or gaining electrons will affect the ionic size and electron configuration?

Ions: Electron Configurations and Sizes

- **Anions:** we *add* the number of electrons indicated by the magnitude of the charge of the anion.

$$(F) \text{ is } 1s^2 2s^2 2p^5 \xrightarrow[+1\,e^-]{} (F^-) \text{ is } 1s^2 2s^2 2p^6$$

- **Cations:** we subtract the number of electrons indicated by the magnitude of the charge. For main-group cations, we remove the required number of electrons in the reverse order of filling

$$(Li) \text{ is } 1s^2 2s^1 \xrightarrow[-1\,e^-]{} (Li^+) \text{ is } 1s^2 2s^0 \text{ (or simply } 1s^2)$$

- **Exception** occurs for **transition metal** cations

- 2 e-

V $[Ar]\, 4s^2 3d^3$

V^{2+} $[Ar]\, 4s^0 3d^3$

Transition metals

Ions: Electron Configurations and Sizes

Ions derived from representative elements:

Na $[Ne]3s^1$ Na^+ $[Ne]$

Mg $[Ne]\,3s^2$ Mg^{2+} $[Ne]$

Al $[Ne]3s^23p^1$ Al^{3+} $[Ne]$

*Atoms lose electrons so that **cations** have a **noble gas outer electron configuration***

F $1s^22s^22p^5$ F^- $1s^22s^22p^6$ or $[Ne]$

O $1s^22s^22p^4$ O^{2-} $1s^22s^22p^6$ or $[Ne]$

N $1s^22s^22p^3$ N^{3-} $1s^22s^22p^6$ or $[Ne]$

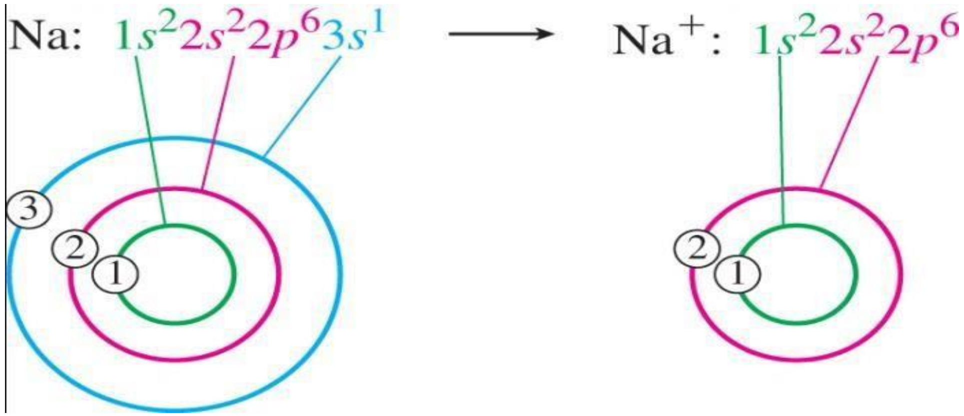
*Atoms gain electrons so that **anions** have **noble gas outer electron configuration***

- **Ions and atoms** that have the **same number of electrons** are called **isoelectronic,** which means the **same ground state electron configuration**.

Ions: Electron Configurations and Sizes

Ion size compared to their corresponding atoms

Cations:



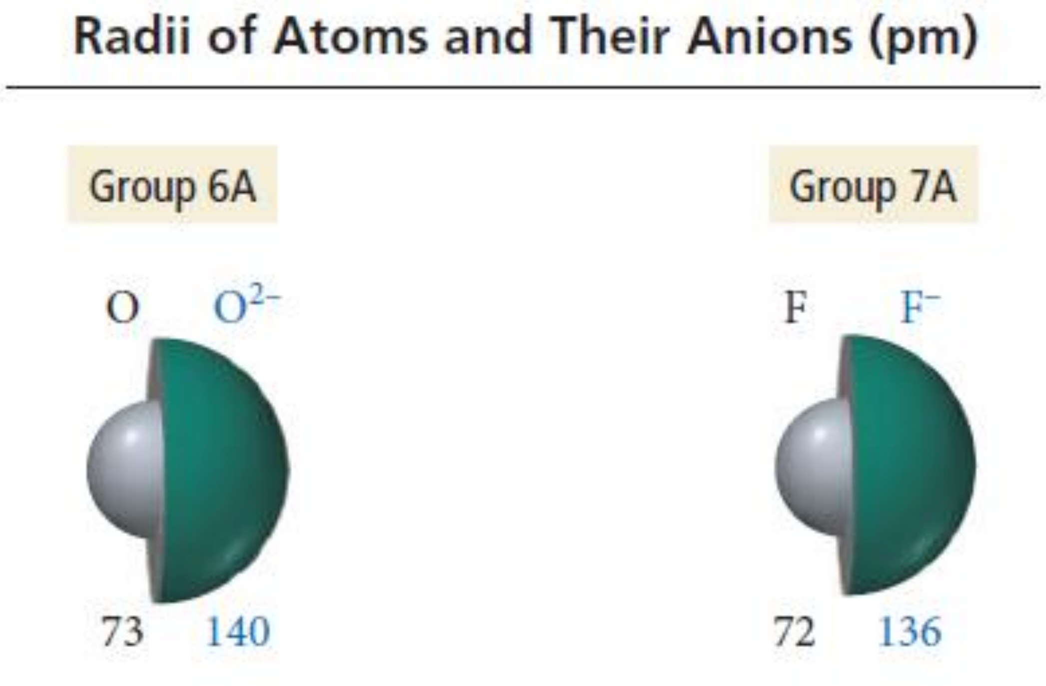
Radii of Atoms and Their Cations (pm)

➢ **Cations are much smaller than their corresponding atoms:** The cation, having lost the outermost electron, has only the core electrons.

Ions: Electron Configurations and Sizes

Ion size compared to their corresponding atoms

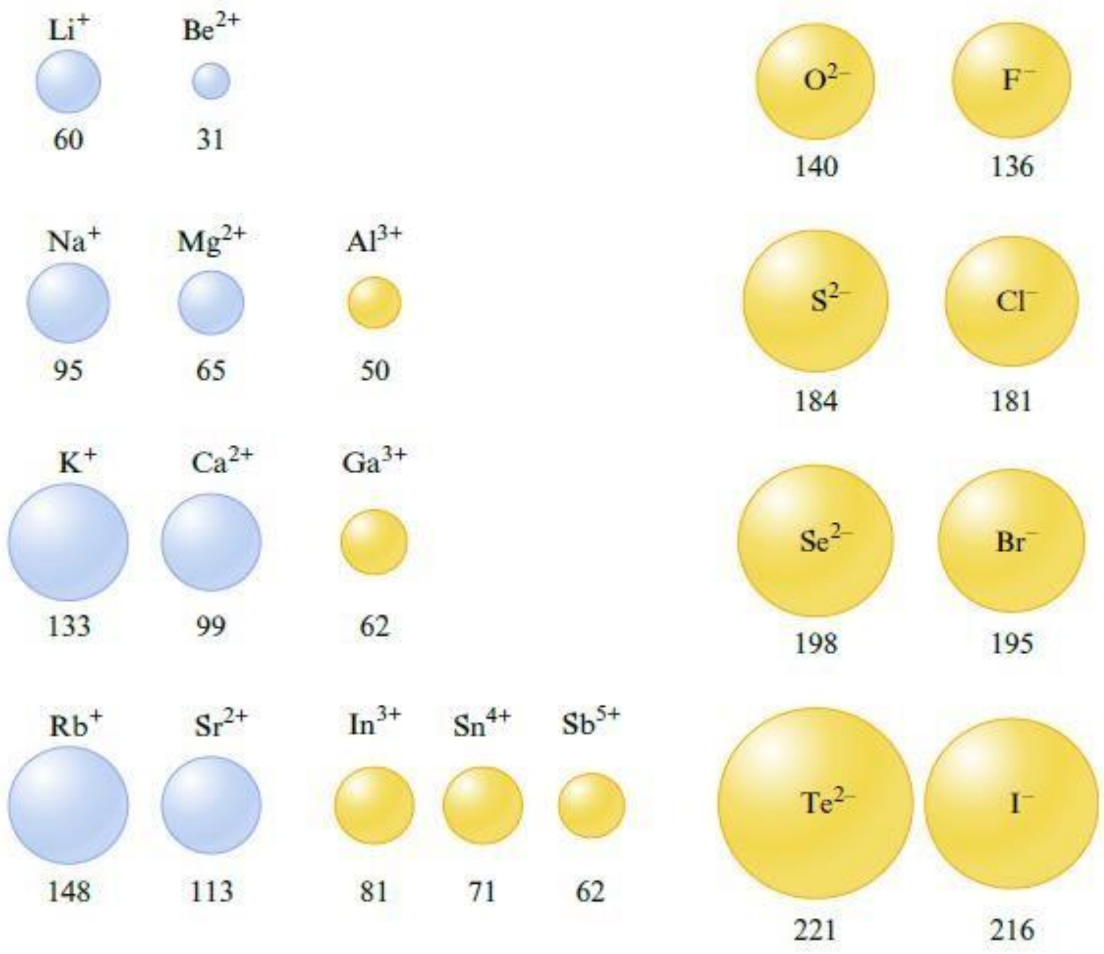
Anions:



- **Anions are much larger than their corresponding atoms.** extra electron increases the repulsions among the outermost electrons.

Ions: Electron Configurations and Sizes

<u>Ions of same charge in the same group:</u> **Size generally increases down a group.**



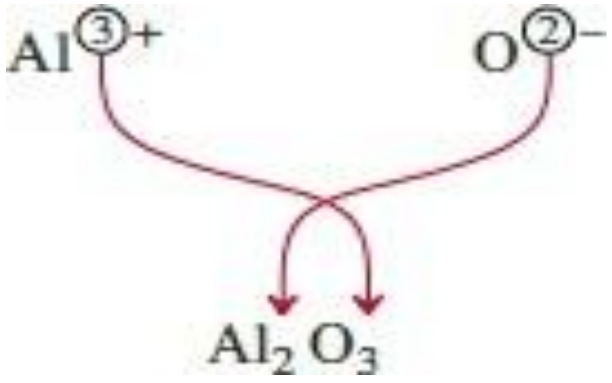
Ions: Electron Configurations and Sizes

ionic compound

How many electrons are transferred?

→ *Think how to achieve noble gas configuration, the most stable configuration*

- Consider the compound formed between **Aluminum and Oxygen.**
- Because aluminum has the configuration [Ne]$3s^2 3p^1$, it loses three electrons to form the Al^{3+} ion and thus achieves the neon configuration.
- Oxygen has to gain two electrons to form the O^{2-} ion and thus achieves the neon configuration.
- Therefore, the Al^{3+} and O^{2-} ions form in this case.
- The **chemical compounds are always electrically neutral (**they have the same quantities of positive and negative charges). Therefore, there must be three O^{2-} ions for every two Al^{3+} ions, and the compound has the formula Al_2O_3.



Ions: Electron Configurations and Sizes

Exercise 1:

Predict the trend in radius of the following ions: Be^{2+}, Mg^{2+}, Ca^{2+}, and Sr^{2+}.

Solution 1:

These ions have the same periodic trend as their atoms because they lost the same number of electrons (2 e-):

$$\mathbf{Be^{2+} < Mg^{2+} < Ca^{2+} < Sr^{2+}.}$$

Ions: Electron Configurations and Sizes

Exercise 2:

The most stable ion iodine (I) can form is:

A. I^+

B. I^-

C. I^{2-}

D. I^{2+}

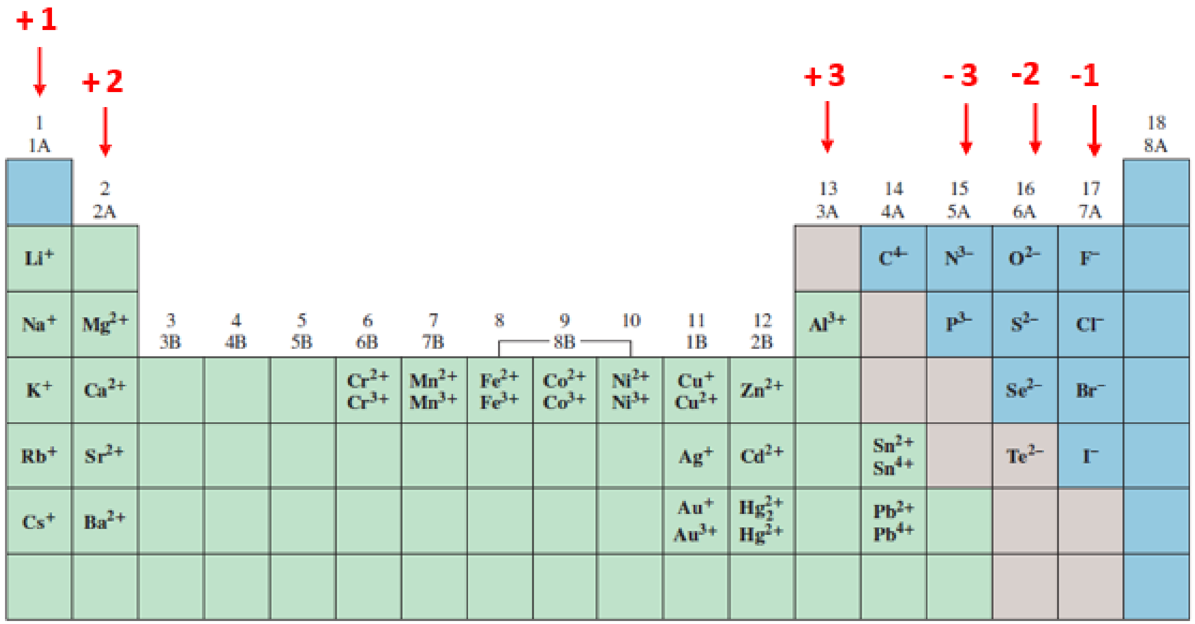
The most stable ion Cs forms is:

A. Cs^+

B. Cs^-

C. Cs^{2-}

D. Cs^{2+}



Ions: Electron Configurations and Sizes

Write the electronic configuration of:

$_{13}Al^{3+}$ $_{14}Si^{4-}$ $_{19}K^{+}$ $_{35}Br^{-}$

$_{13}Al$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

$_{13}Al^{3+}$: $1s^2\ 2s^2\ 2p^6$ or [Ne]

$_{14}Si$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

$_{14}Si^{4-}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or [Ar]

$_{19}K$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

$_{19}K^{+}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or [Ar]

$_{35}Br$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

$_{35}Br^{-}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$ or [Kr]