Chapter 8
The Basics of Chemical Bonding

Chemistry, 7th Edition
International Student Version

Brady/Jespersen/Hyslop

Chapter in Context

- Describe the necessary conditions for bond formation
- Examine the factors involved in ionic bonding
- Write electron configurations of ions
- Write Lewis symbols for atoms and ions
- Describe covalent bonds, the octet rule, and multiple bonds
- Understand the energetics of bond formation

Chapter in Context, cont'd

- Learn trends in electronegativity
- Examine how electronegativity affects bond polarity and the reactivity of elements
- Draw Lewis structures of molecules
- Calculate and use formal charges
- Draw and understand resonance structures
- Classify organic compounds and identify functional groups

Chemical Bonds

- Attractive forces that hold atoms together in complex substances
- Molecules and ionic compounds

Why study?

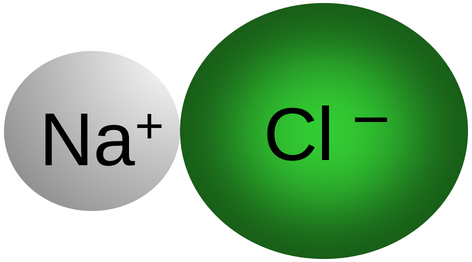
- Changes in these bonding forces are the underlying basis of chemical reactivity
- During reaction
  - Break old bonds
  - Form new bonds

Two Classes of Bonds

- **Covalent bonding**
  - Occurs in molecules
  - Sharing of electrons
- **Ionic Bonding**
  - Occurs in ionic solid
  - Electrons transferred from one atom to another
  - Simpler
  - We will look at this first

Ionic Bonds

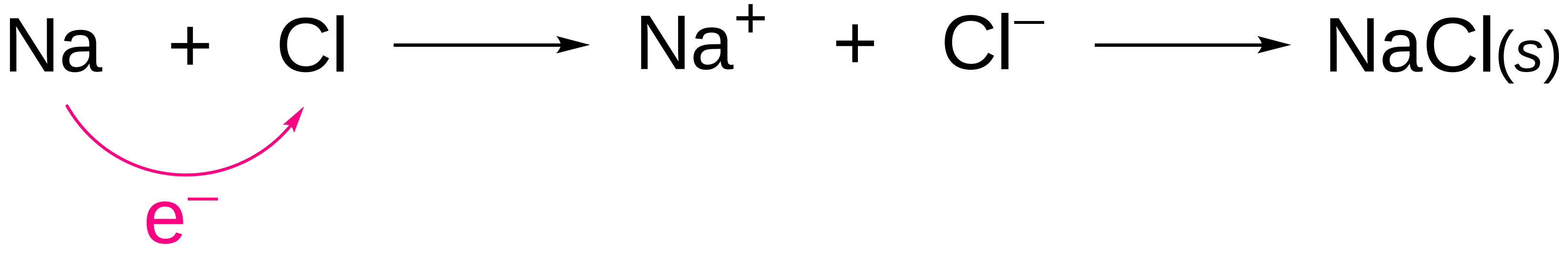
- Result from attractive forces between oppositely charged particles



- Metal - nonmetal bonds are ionic because:
  - Metals have
    - Low ionization energies
    - Easily lose electrons to be stable
  - Non-metals have
    - Very exothermic electron affinities
  - Formation of lattice stabilizes ions

Ionic Compounds

- Formed from metal and nonmetal



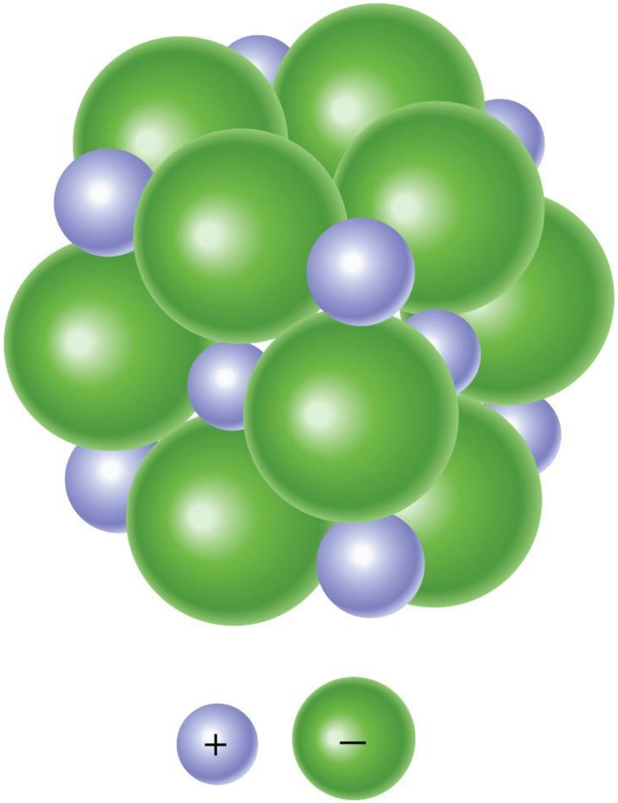
$$Na + Cl \longrightarrow Na^+ + Cl^- \longrightarrow NaCl(s)$$

- **Ionic Bond**
  - Attraction between + and – ions in ionic compound
- Why does this occur? Why is e^- transferred?
  - Why Na^+ and not Na^{2+} or Na^-?
  - Why Cl^- and not Cl^{2-} or Cl^+?

Ionic Compounds

Ionic crystals:

- Exist in 3-dimensional array of cations and anions called a **lattice structure**



Ionic chemical formulas:

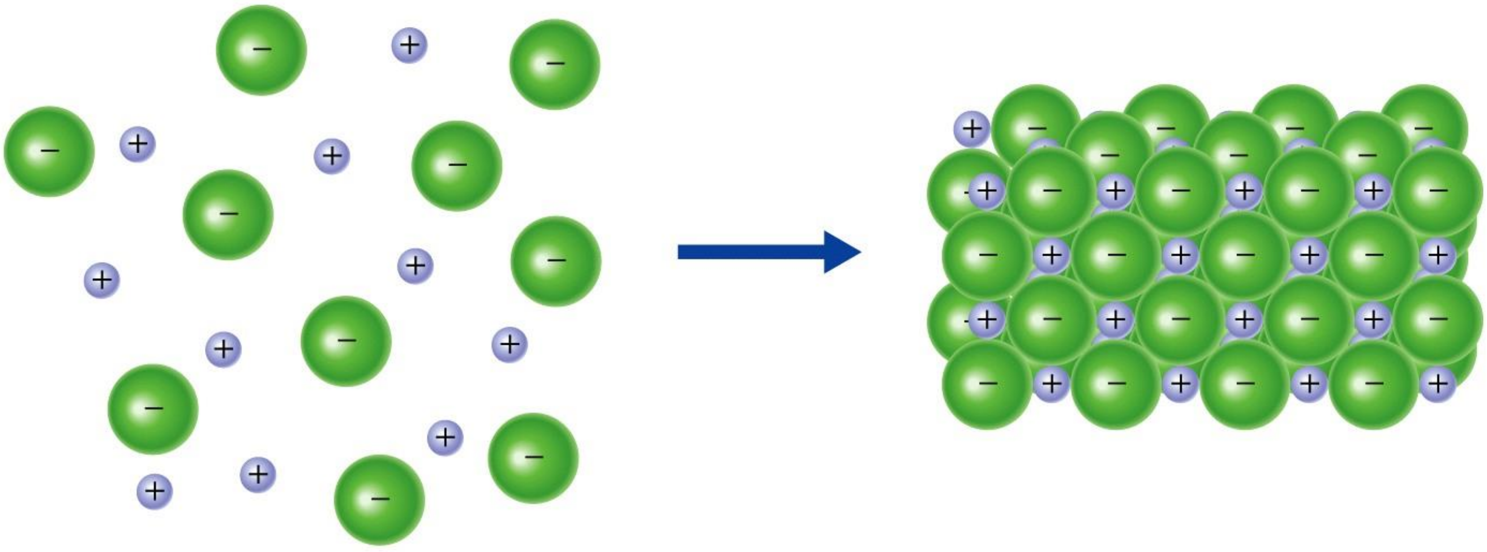
- Always written as empirical formula
- Smallest whole number ratio of cation to anion

Energetics

- Must look at energy of system to answer these questions
- For any stable compound to form from its elements
  - Potential energy of system must be lowered.
  - Net decrease in energy $\Delta H_f^\circ < 0$ (negative)
- What are factors contributing to energy lowering for ionic compound?
  - Use Hess's Law to determine
  - Conservation of energy
  - Envision two paths

Lattice Energy

- Amount that PE of system decreases when one mole of solid salt is formed from its gas phase ions
- Energy released when ionic lattice forms



1 mol Na^+ and 1 mol Cl^-
(gaseous ions from NaCl)

1 mol NaCl
(solid, crystalline NaCl)

Two Paths to Evaluate Energy

1. Single step

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$ $\Delta H_f^\circ = -411.1$ kJ/mol

2. Stepwise path

$Na(s) \rightarrow Na(g)$ $\Delta H_f^\circ(Na, g) = 107.8$ kJ/mol

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ $\Delta H_f^\circ(Cl, g) = 121.3$ kJ/mol

$Na(g) \rightarrow Na^+(g) + e^-$ IE(Na) = 495.4 kJ/mol

$Cl(g) + e^- \rightarrow Cl^-(g)$ EA(Cl) = –348.8 kJ/mol

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ $\Delta H_{lattice} = -787$ kJ/mol

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$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$ $\Delta H_f^\circ = -411$ kJ/mol

Lattice Energy

- Always $\Delta H_{\text{Lattice}} = - =$ exothermic
- $\Delta H_{\text{Lattice}}$ gets more exothermic (larger negative value) as ions of opposite charge are brought closer together
- Ions tightly packed with opposite charged ions next to each other

$$\Delta H_{\text{Lattice}} \propto \frac{q_+ q_-}{d}$$

- Any increase in PE due to ionizing atoms is more than met by decrease in PE from formation of crystal lattice. Even for +2 and –2 ions
- Therefore, forming ionic solids is an overall exothermic process and they are stable compounds

Your Turn!

Assuming that the separation between cations and anions in the lattice is nearly identical, which species would have the greatest lattice energy?

A. sodium chloride

B. calcium chloride

C. calcium nitride ⟵ Highest charges (+2 and -3)

D. sodium oxide

E. calcium oxide

Your Turn!

Which combination below will have the most negative lattice energy?

A. Low-charge ions separated by large distances

B. Low-charge ions separated by small distances

C. High-charged ions separated by large distances

D. High-charged ions separated by small distances

As q increases, ΔH ***increases***

$$\Delta H_{\text{Lattice}} \propto \frac{q_+ q_-}{d}$$

As d increases, ΔH ***decreases***

Why do Metals form Cations and Nonmetals form Anions?

Metal

- Left hand side of Periodic Table
- **IE small** and positive
  - Little energy required to remove electrons
- **EA small** and negative or positive
  - Not favorable to attract an electron to it
- Least expensive, energy-wise, to form cation

Nonmetal

- Right hand side of Periodic Table
- **IE large** and positive
  - Difficult to remove e^-
- **EA large** and negative
  - But easy to add e^-
  - Exothermic—large amount of energy given off
  - PE of system decreases
- Least expensive, energy-wise, to form anion

Electron Configurations of Ions

Review of electron configurations:

Follow Aufbau ordering

Electron configuration based on "filling" an atom with electrons. Follows order in the periodic table

- Reflect electron energy level

Electron configuration based on increasing values of *n* and then in any given energy level by increasing values of ℓ. Helpful format for explaining how ions form

Electron Configurations of Ions

- How electronic structure affects types of ions formed

e.g.,

Na $\mathbf{1s^2 2s^2 2p^6 3s^1 = [Ne]\,3s^1}$

Na^+ $\mathbf{1s^2\, 2s^2 2p^6 = [Ne]}$

$IE_1 =$ 496 kJ/mol small not too difficult

$IE_2 =$ 4563 kJ/mol large ~10 x larger very difficult

- Can remove first electron, as doesn't cost too much
- Can’t remove second electron, as can't regain lost energy from lattice
- Thus, Na^{2+} doesn’t form

Electron Configurations of Ions

e.g.,	Ca	[Ar] $4s^2$	
	Ca^{2+}	[Ar]	
IE_1	small = 590 kJ/mol	not too difficult	
IE_2	small = 1140 kJ/mol	not too difficult	
IE_3	large = 4940 kJ/mol	too difficult	

- Can regain by lattice energy ~2000 kJ/mole if +2, –2 charges
- But third electron is too hard to remove
- Can't recoup required energy through lattice formation
- Therefore Ca^{3+} doesn't form

Electron Configurations of Ions

- Stability of noble gas core above or below the valence electrons effectively limits the number of electrons that metals lose
- Ions formed have noble gas electron configuration
    - True for anions and cations

e.g., Cl $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^5 = [Ne]3s^2\ 3p^5}$

Cl⁻ $\mathbf{1s^2 2s^2 2p^6 3s^2 3p^6 = [Ar]}$

- Adding another electron
    - Requires putting it into next higher ***n*** shell
- Energy cost too high

Electron Configurations of Ions

e.g.,

O $1s^2 2s^2 2p^4$

O^- $1s^2 2s^2 2p^5$

O^{2-} $1s^2 2s^2 2p^6$ = [Ne]

EA_1 = –141 kJ/mol

EA_2 = +844 kJ/mol

EA_{net} = +703 kJ/mol

endothermic

- Energy required to form cation is more than made up for by the increase in $\Delta H_{Lattice}$ caused by higher –2 charge

Electron Configurations of Ions

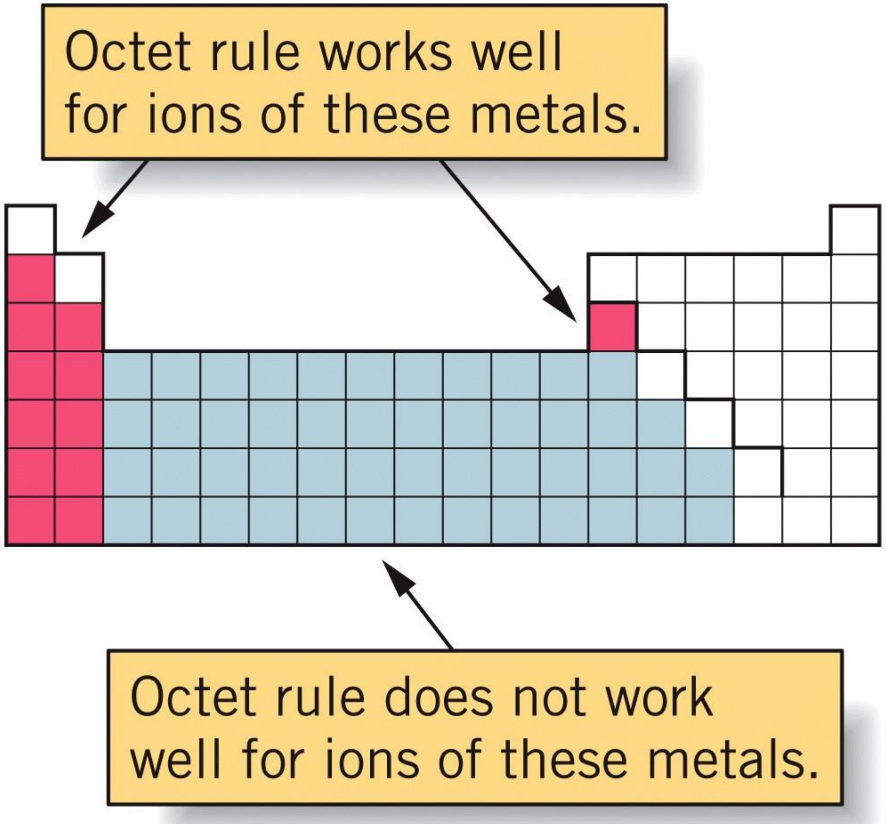
Generalization:

- When ions form
  - Atoms of most representative elements (***s*** and ***p*** block)
  - Tend to gain or lose electrons to obtain nearest Noble gas electron configuration
  - Except He (two electrons), all noble gases have eight electrons in highest ***n*** shell

Octet Rule

- Atoms tend to gain or lose electrons until they have achieved outer (valence) shell containing octet of eight electrons

Octet Rule


Octet rule works well for ions of these metals.

Octet rule does not work well for ions of these metals.

- Works well with
  - Group 1A and 2A metals
  - Al
  - Non-metals
- H and He can't obey
  - Limited to 2 electrons in the *n* = 1 shell
- Doesn't work with
  - Transition metals
  - Post transition metals

Your Turn!

What is the correct electron configuration for Cs and Cs^+?

A. [Xe] $6s^1$, [Xe]

B. [Xe] $6s^2$, [Xe] $6s^1$

C. [Xe] $5s^1$, [Xe]

D. [Xe] $6s^1$, [Xe] $6s^2$

E. [Xe] $6p^2$, [Xe] $6p^1$

Your Turn!

What charges are aluminum, phosphorus, sulfur, strontium, and rubidium most likely to have when they become ions?

A. -3, +3, +2, -2, -1, respectively

B. -5, -3, -2, +2, +1, respectively

C. +3, -3, -2, +2, +1, respectively

D. +13, +3, -2, +2, +2, respectively

E. +3, +5, -2, -2, +1, respectively

Transition Metals

- First electrons are lost from outermost *s* orbital
- Lose electrons from highest *n* first, then ℓ

e.g., Fe $[Ar]\ 3d^6 4s^2$

Fe^{2+} $[Ar]\ 3d^6$ loses 4*s* electrons first

Fe^{3+} $[Ar]\ 3d^5$ then loses 3*d* electrons

- Extra stability due to half-filled *d* subshells
- **Consequences**
  - M^{2+} is a common oxidation state as two electrons are removed from the outer ***ns*** shell
  - Ions of larger charge result from loss of ***d*** electrons

Post Transition Metals

e.g.,

Sn $[Kr]\ 4d^{10}5s^{2}5p^{2}$

Sn^{2+} $[Kr]\ 4d^{10}5s^{2}$

- Neither has noble gas electron configuration
- Have emptied 5*p* subshell

  Sn^{4+} $[Kr]\ 4d^{10}$

- Does have empty 5*s* subshell

Transition Metals

- Not easy to predict which ions form and which are stable
- But ions with exactly filled or half-filled ***d*** subshells are extra stable and therefore tend to form

- Mn^{2+} **[Ar]3*d*^{5}**
- Fe^{3+} **[Ar]3*d*^{5}**
- Zn^{2+} **[Ar]3*d*^{10}**

Predicting Cation Configurations

Consider Bi, whose aufbau configuration is: [Xe]$6s^2\,4f^{14}\,5d^{10}\,6p^3$. What ions are expected?

Rewrite configuration: [Xe]$4f^{14}\,5d^{10}\,6s^2\,6p^3$

Bi^{3+} and Bi^{5+}

Consider Fe, whose aufbau configuration is: [Ar]$4s^2\,3d^6$. What ions are expected?

Rewrite configuration: [Ar]$3d^6\,4s^2$

Fe^{2+} and Fe^{3+}

Predicting Anion Configurations

Non-metals gain electrons to become isoelectronic with next larger noble gas

O: $[\mathrm{He}]2s^2 2p^4 + 2\ e^- \rightarrow$? O^{2-} : $[\mathrm{He}]2s^2\ 2p^6$

N: $[\mathrm{He}]2s^2 2p^3 + 3\ e^- \rightarrow$? N^{3-} : $[\mathrm{He}]2s^2\ 2p^6$

Your Turn!

What are the correct electron configurations for Cu and Cu^{2+} ?

A. [Ar] $3d^94s^2$, [Ar] $3d^9$
B. [Ar] $3d^{10}4s^1$, [Ar] $3d^84s^1$
C. [Ar] $3d^{10}4s^1$, [Ar] $3d^9$
D. [Ar] $3d^94s^2$, [Ar] $3d^{10}4s^1$
E. [K] $3d^94s^2$, [Ar] $3d^9$

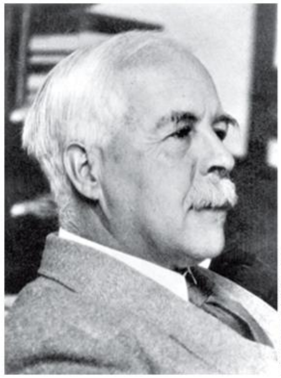
- Filled and half-filled orbitals are particularly stable

Your Turn!

What are the correct electron configurations for zirconium(II) and zirconium(IV) ions?

A. [Kr] $5d^2$ [Kr] $4d^1$
B. [Ar] $4d^2 5s^2$ [Ar] $5s^2$
C. [Kr] $4d^2$ [Kr]
D. [Kr] $4d^6 5s^2$ [Kr] $4d^6$
E. [Rb] $4d^2$ [Rb]

Lewis Symbols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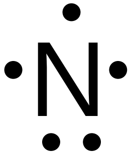
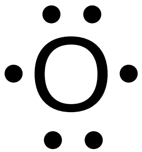
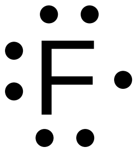
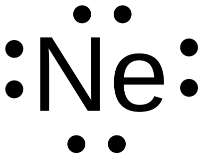
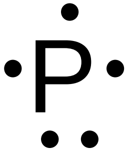
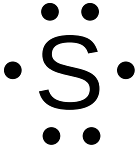
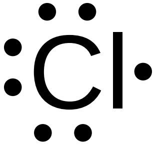
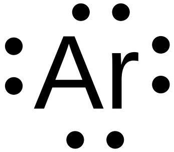
- Electron bookkeeping method
- Way to keep track of *e*–' s
- Write chemical symbol surrounded by dots for each *e*–

Group #	**1A**	**2A**	**3A**	**4A**
Valence *e*–'s	**1**	**2**	**3**	**4**
***e*– conf'n**	ns^1	ns^2	ns^2np^1	ns^2np^2
	$\mathrm{H}\cdot$	$\cdot\mathrm{He}\cdot$		
	$\mathrm{Li}\cdot$	$\cdot\mathrm{Be}\cdot$	$\cdot\overset{\cdot}{\mathrm{B}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$
	$\mathrm{Na}\cdot$	$\cdot\mathrm{Mg}\cdot$	$\cdot\overset{\cdot}{\mathrm{Al}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{Si}}}\cdot$

Lewis Symbols

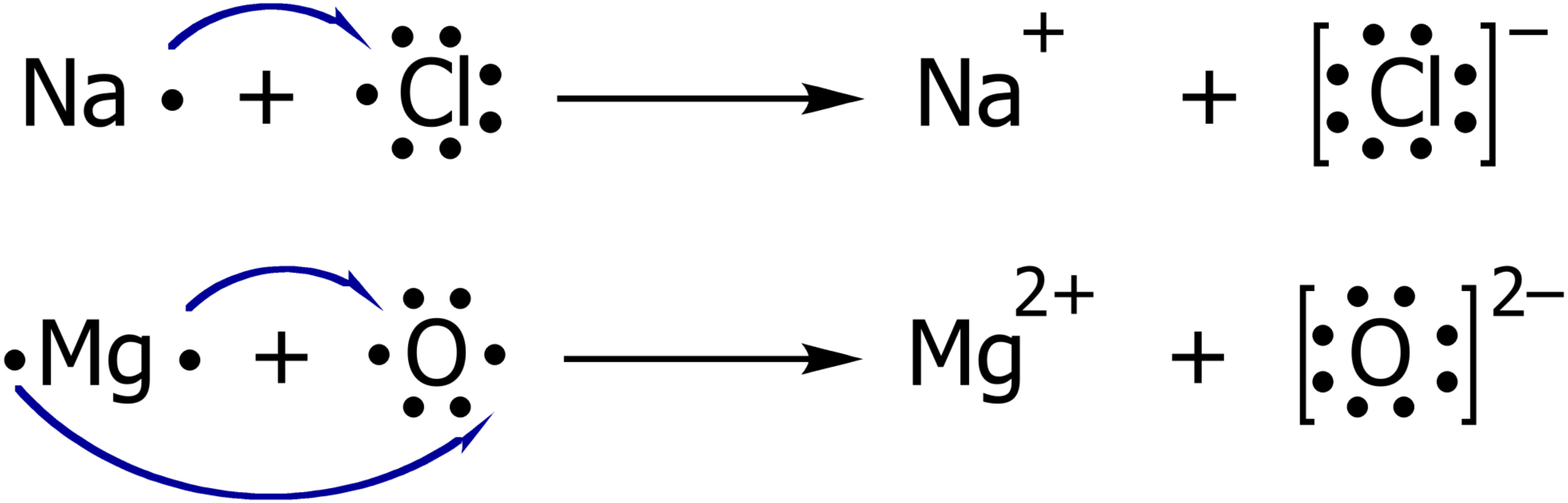
Group #	**5A**	**6A**	**7A**	**8A**
Valence e⁻'s	**5**	**6**	**7**	**8**
e⁻ conf'n	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
				
				
				

For the representative elements

Group number = number of valence *e*⁻'s

Lewis Symbols

- Can use to diagram electron transfer in ionic bonding



Covalent Compounds

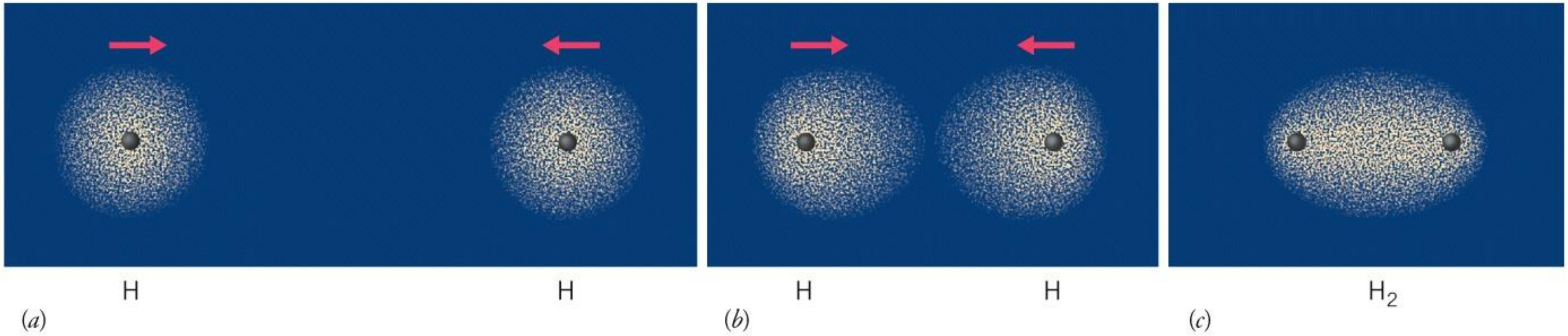
- Form individual separate molecules
  - Atoms bound by sharing electrons
- Do not conduct electricity
- Often low melting point

Covalent Bonds

- Shared pairs of electrons between two atoms
- Two H atoms come together, why?

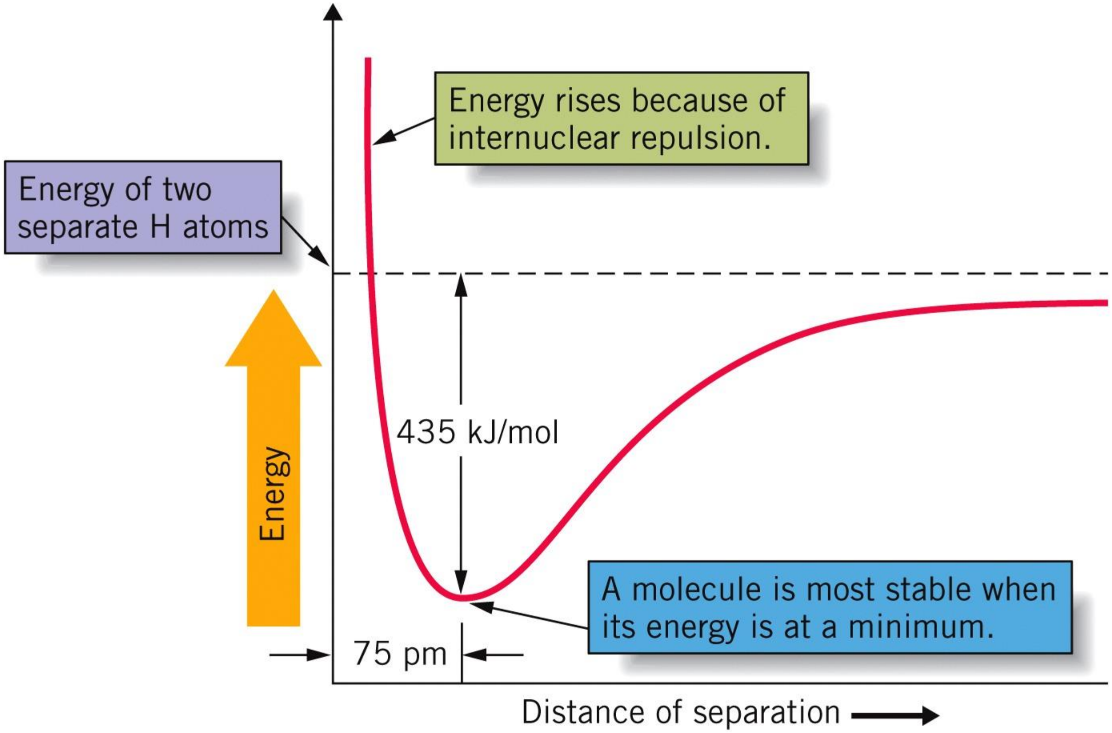
Covalent Bond

- Attraction of valence electrons of one atom by nucleus of other atom
- Shifting of electron density
- As distance between nuclei decreases, probability of finding either electron near either nucleus increases
- Pulls nuclei closer together



Covalent Bond

- As nuclei get close
  - Begin to repel each other
  - Both have high positive charge



- Final internuclear distance between two atoms in bond
  - Balance of attractive and repulsive forces
  - Bond forms since there is a net attraction

Covalent Bond

- **Two quantities characterize this bond**

Bond Length (bond distance)

- Distance between 2 nuclei = $r_A + r_B$

Bond Energy

- Also ***bond strength***
- Amount of energy released when bond formed (decreasing PE) or
- Amount of energy must put in to “break” bond

Your Turn!

Which species is most likely covalently bonded?

A. CsCl

B. NaF

C. CaF_2

D. CO

E. $MgBr_2$

Your Turn!

What is the primary driving force behind the formation of covalent bonds?

A. The energy released when two electrons attract each other

B. The energy gained when two electrons attract each other

C. The energy released when nuclei attract electrons

D. The energy released by two nuclei attracting each other

E. The energy gained by the repulsion between nuclei

Your Turn!

What force(s) limit(s) the distance between nuclei in a covalent bond?

A. The repulsive forces between nuclei
B. The attractive forces between nuclei
C. The attractive forces between electrons
D. The attractive forces between nuclei and electrons
E. The octet rule

Lewis Structures

- Molecular formula drawn with Lewis Symbols
- Method for diagramming electronic structure of covalent bonds
- Uses dots to represent electrons
- Covalent bond
  - Shared pair of electrons
  - Each atom shares electrons so has complete octet ns^2np^6
    - Noble gas electron configuration
    - Except H which has complete shell with 2 electrons

Octet rule and covalent bonding

When atoms form covalent bonds, they tend to share sufficient electrons so as to achieve outer shell having eight electrons

- Indicates how all atoms in molecule are attached to one another
- Accounts for ALL valence electrons in ALL atoms in molecule

Let's look at some examples

Noble Gases: eight valence electrons

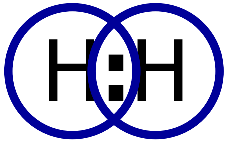
- Full octet ns^2np^6
- Stable monatomic gases
- Don't form compounds

Lewis Structures

Diatomic Gases:

- H and Halogens

H_2



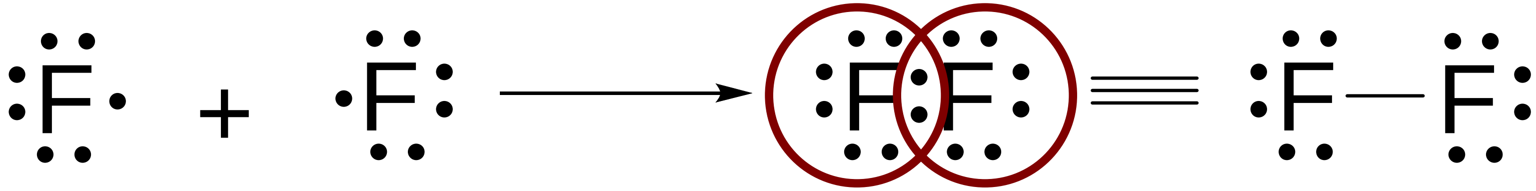
- H· + ·H → H:H or H—H
- Each H has two electrons through sharing
- Can write shared pair of electrons as a line (—)

  : or — signify a covalent bond

Lewis Structures

Diatomic Gases:

F_2

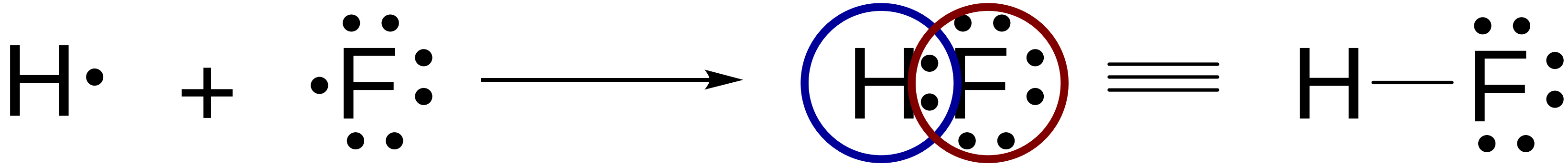


- Each F has complete octet
- Only need to form one bond to complete octet
- Pairs of electrons not included in covalent bond are called lone pairs
- Same for rest of halogens: Cl_2, Br_2, I_2

Lewis Structures

Diatomic Gases:

HF



- Same for HCl, HBr, HI
- Molecules are diatomics of atoms that need only one electron to complete octet
- Separate molecules
    - Gas in most cases because very weak intermolecular forces

Your Turn!

How many electrons are required to complete the octet around nitrogen?

A. 2

B. 3

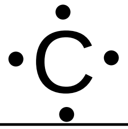
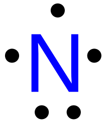
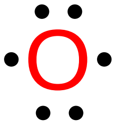
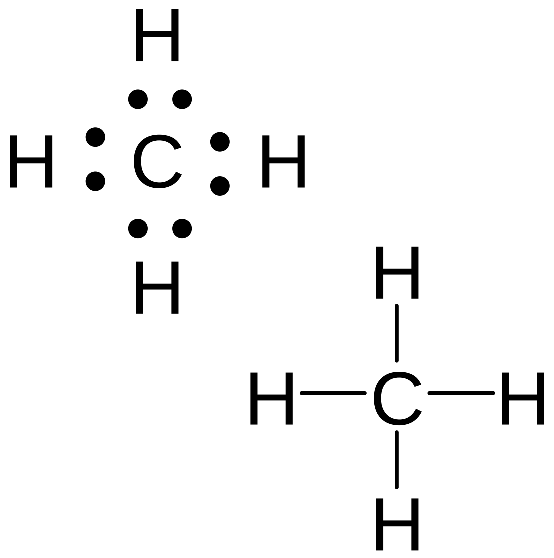
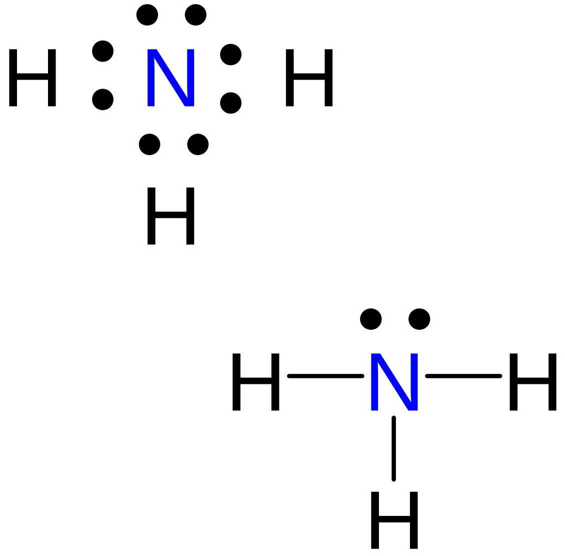
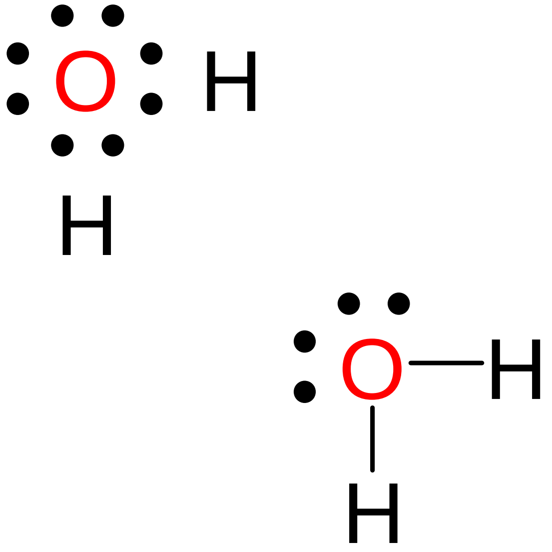
C. 1

D. 4

E. 6

Lewis Structures

Many nonmetals form more than one covalent bond

		
Needs 4 electrons Forms 4 bonds	Needs 3 electrons Forms 3 bonds	Needs 2 electrons Forms 2 bonds
		
methane	**ammonia**	**water**

Multiple Bonds

Single Bond

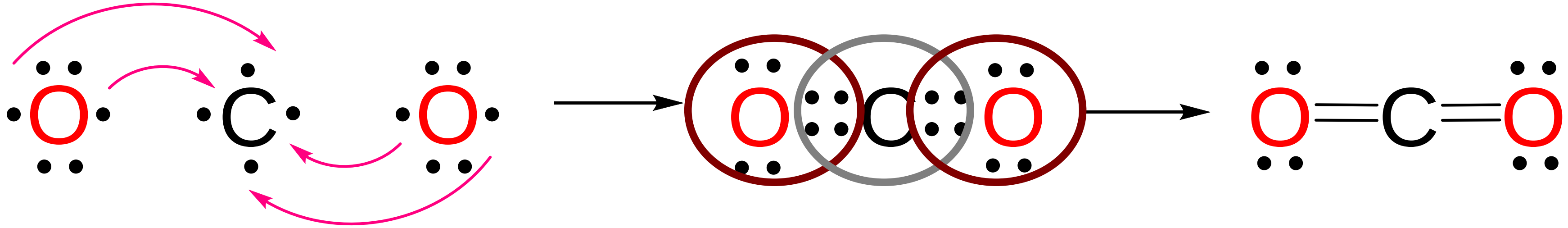
- Bond produced by sharing ***one pair*** of electrons between two atoms

- Many molecules share ***more than one pair*** of electrons between two atoms
  - **Multiple** bonds

Double Bonds

- Two atoms share two pairs of electrons

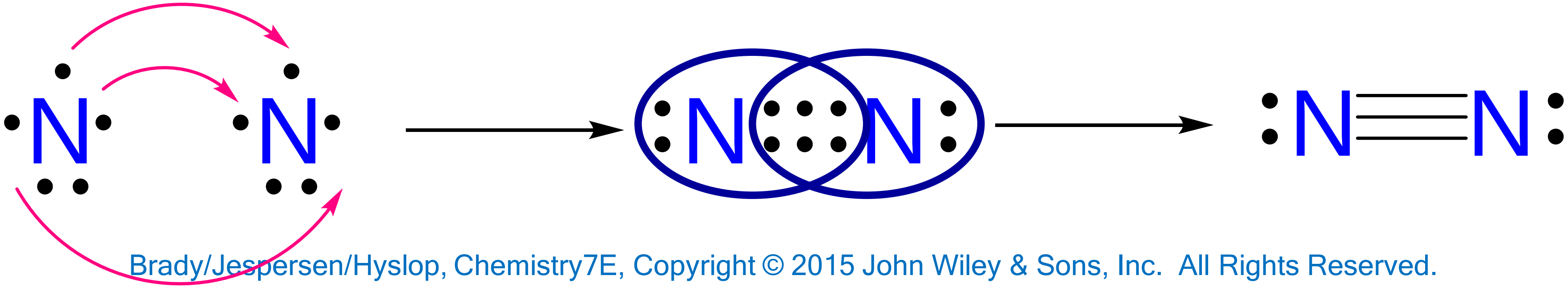
e.g., CO_2



Triple bond

- Three pairs of electrons shared between two atoms

e.g., N_2



Your Turn!

Which species is most likely to have multiple bonds?

A. CO

B. H_2O

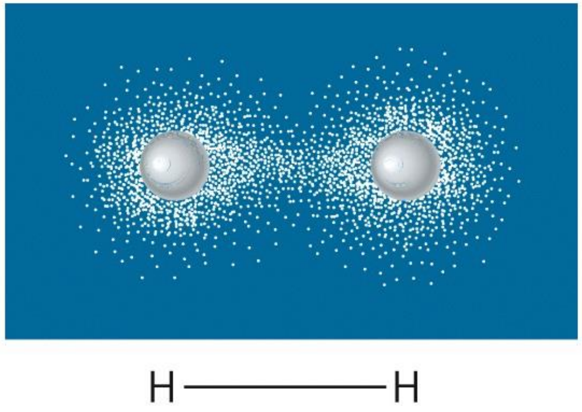
C. PH_3

D. BF_3

E. CH_4

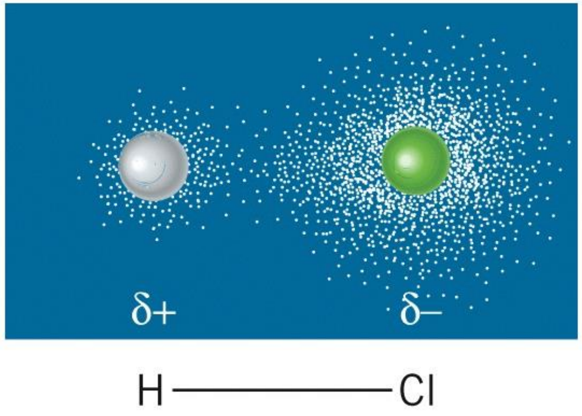
Electronegativity and Bond Polarity

- Two atoms of same element form bond
    - **Equal** sharing of electrons



(*a*)

- Two atoms of different elements form bond
    - **Unequal** sharing of electrons



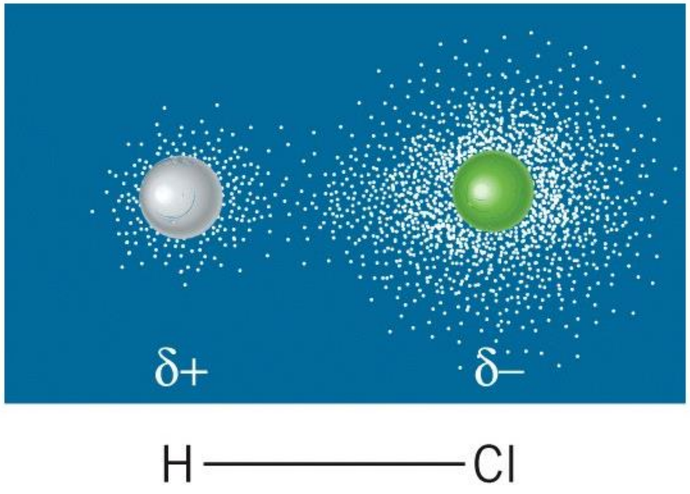
(*b*)

Why?

- One atom usually attracts electrons more strongly than the other

Result

- Unbalanced distribution of electron density within bond
  - Electron cloud **tighter** around Cl in HCl
  - Slight positive charge around H
  - Slight negative charge around Cl
  - This is not a complete transfer of an electron



Electronegativity and Bond Polarity

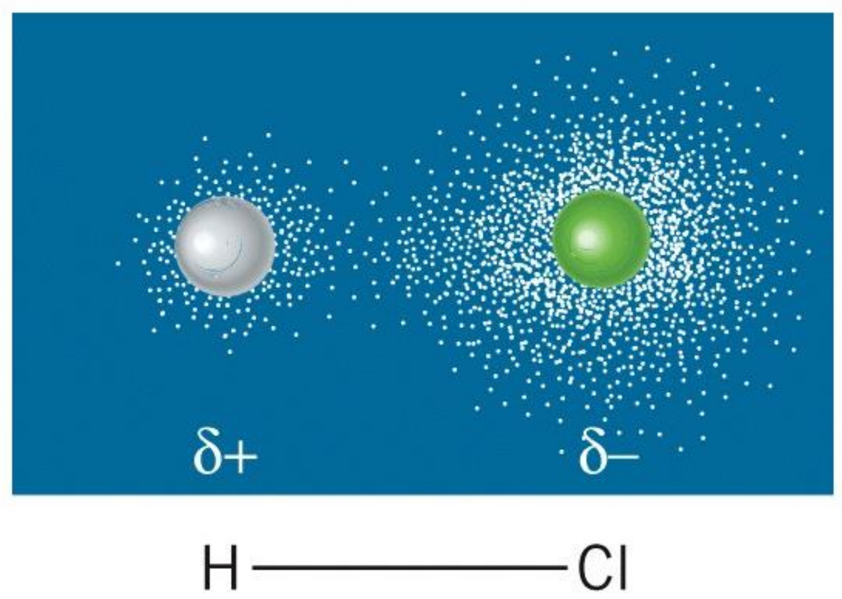
- Leads to concept of **partial charges**

δ^+ δ^-

H——Cl

δ^+ on H = +0.17

δ^- on Cl = –0.17



Polar Covalent Bond

- **Also known as a polar bond**
- Bond that carries partial + and – charges at opposite ends
- Bond is **dipole**
  - Two poles or two charges involved

Polar Molecule

- Molecule has partial positive and negative charges at opposite ends of a bond

Dipole Moment

- Quantitative measure of extent to which bond is polarized
- Dipole moment = Charge on either end × distance between them
- $\boldsymbol{\mu} = \mathbf{q} \times \mathbf{r}$
  - Units = debye (D)
  - 1 D = 3.34×10^{-30} C m (Coulomb meter)
- The size of the dipole moment or the degree of polarity in the bond depends on the differences in abilities of bonded atoms to attract electrons to themselves

Your Turn!

Which situation below results in the largest dipole moment?

A. +1 and -1 charges separated by 6 Å

B. +1 and -1 charges separated by 8 Å

C. +2 and -2 charges separated by 4 Å

D. +2 and -2 charges separated by 6 Å

E. +2 and -2 charges separated by 8 Å

$\mu = q \times r$ dipole moment increases as both q and r increase.

Dipole Moments and Bond Lengths for Some Diatomic Molecules

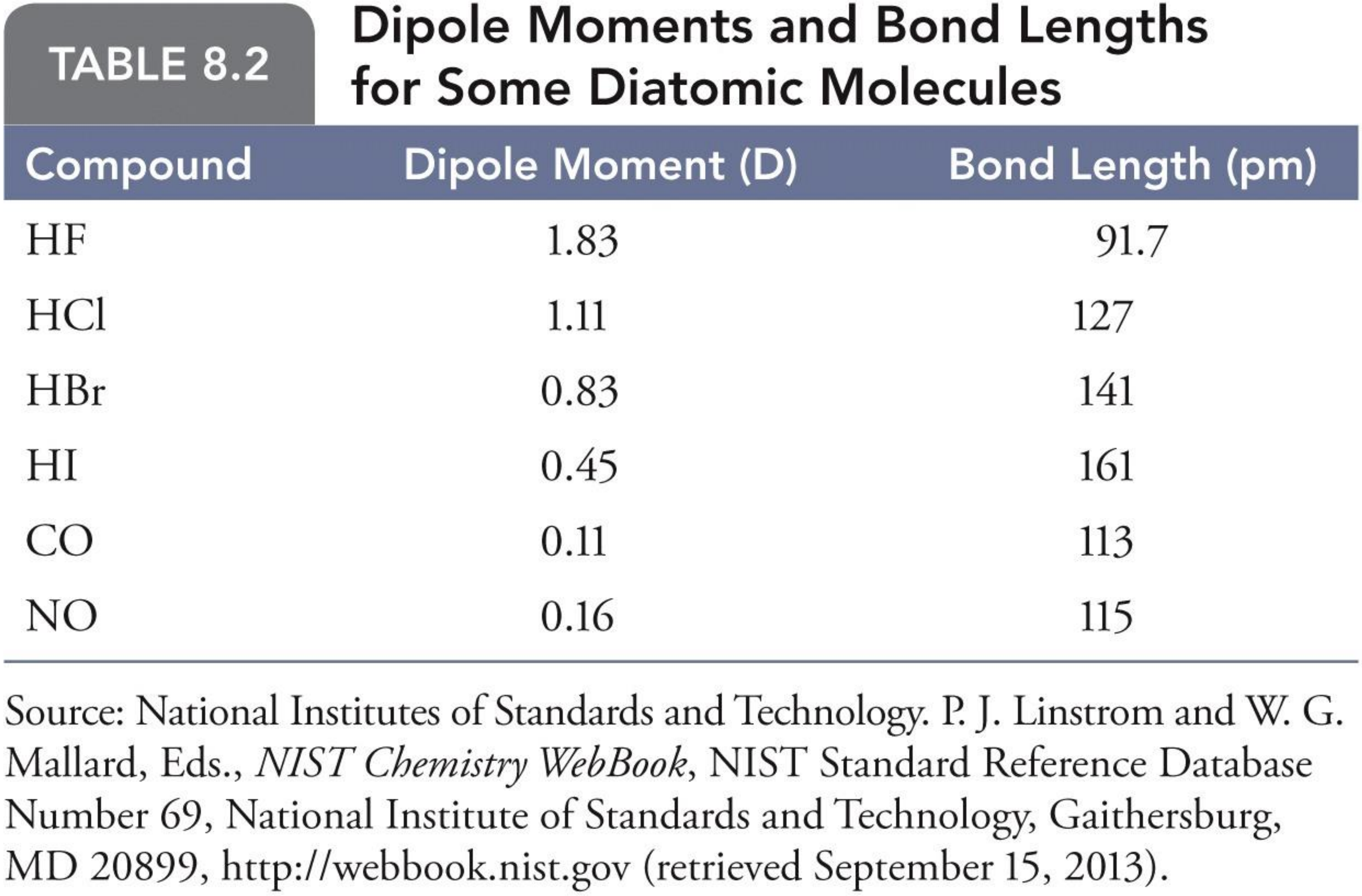


TABLE 8.2 Dipole Moments and Bond Lengths for Some Diatomic Molecules

Compound	Dipole Moment (D)	Bond Length (pm)
HF	1.83	91.7
HCl	1.11	127
HBr	0.83	141
HI	0.45	161
CO	0.11	113
NO	0.16	115

Source: National Institutes of Standards and Technology. P. J. Linstrom and W. G. Mallard, Eds., *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg, MD 20899, http://webbook.nist.gov (retrieved September 15, 2013).

Electronegativity (EN)

- Relative attraction of atom for electrons in bond
- Quantitative basis
  - Table of electronegativities – Fig. 8.9
- Difference in electronegativity

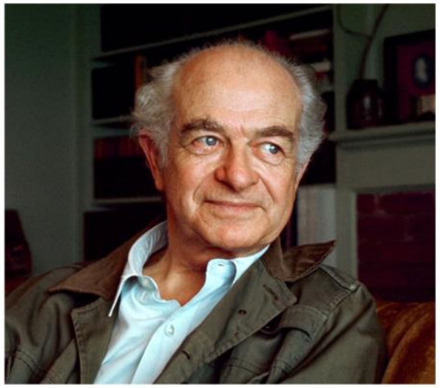
  = estimate of bond polarity

  $\Delta \mathbf{EN} = |\mathbf{EN}_1 - \mathbf{EN}_2|$

e.g., N—H Si—F

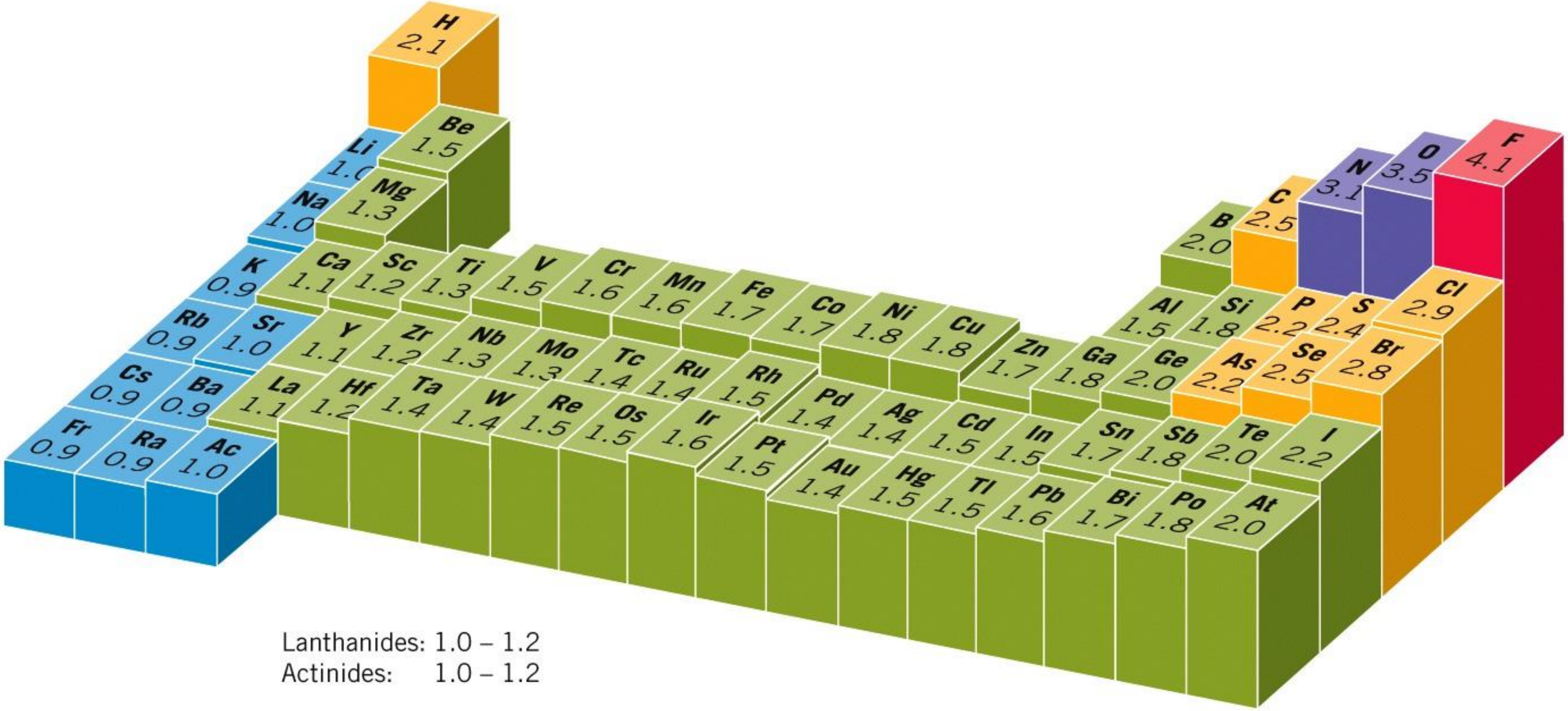
δ^- δ^+ δ^+ δ^-

Electronegativity Table



Ted Streshinsky/©Corbis

Linus Pauling



Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

Trends in Electronegativity

- EN increases from left to right across period as Z_{eff} increases
- EN decreases from top to bottom down group as n increases

Ionic and Covalent Bonding

- Are the two extremes of bonding
- Actual is usually somewhere in between.

Your Turn!

Which of the following species has the least polar bond?

A. HCl

B. HF

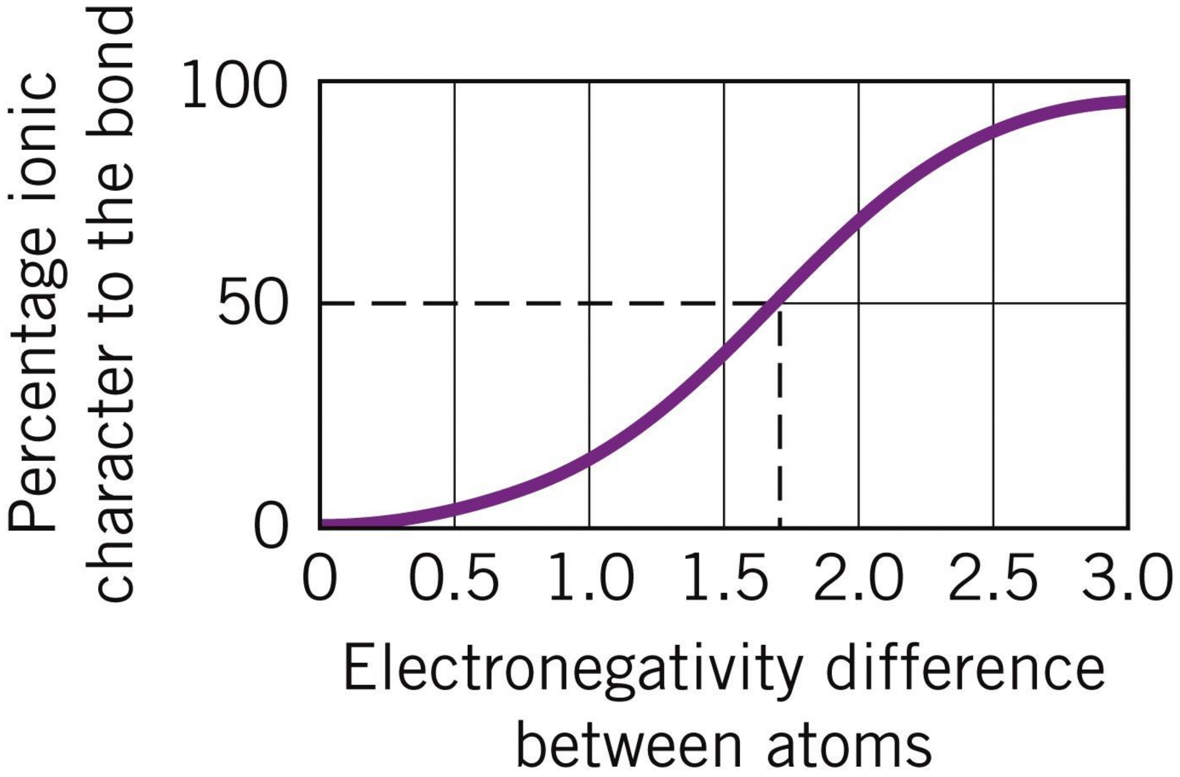
C. HI

D. HBr

Using Electronegativities

$$\Delta EN = |EN_A - EN_B|$$

- **Difference** in electronegativity
- Measure of ionic character of bond



Using Electronegativities

- **Nonpolar Covalent Bond**
  - No difference in electronegativity
- **Ionic Character of bond**
  - Degree to which bond is polar
  - ΔEN > 1.7 means mostly ionic
    - > 50% ionic
    - More electronegative element almost completely controls electron
  - ΔEN < 0.5
    - Means almost purely covalent
    - Nonpolar: < 5% ionic
  - 0.5 < ΔEN < 1.7 polar covalent

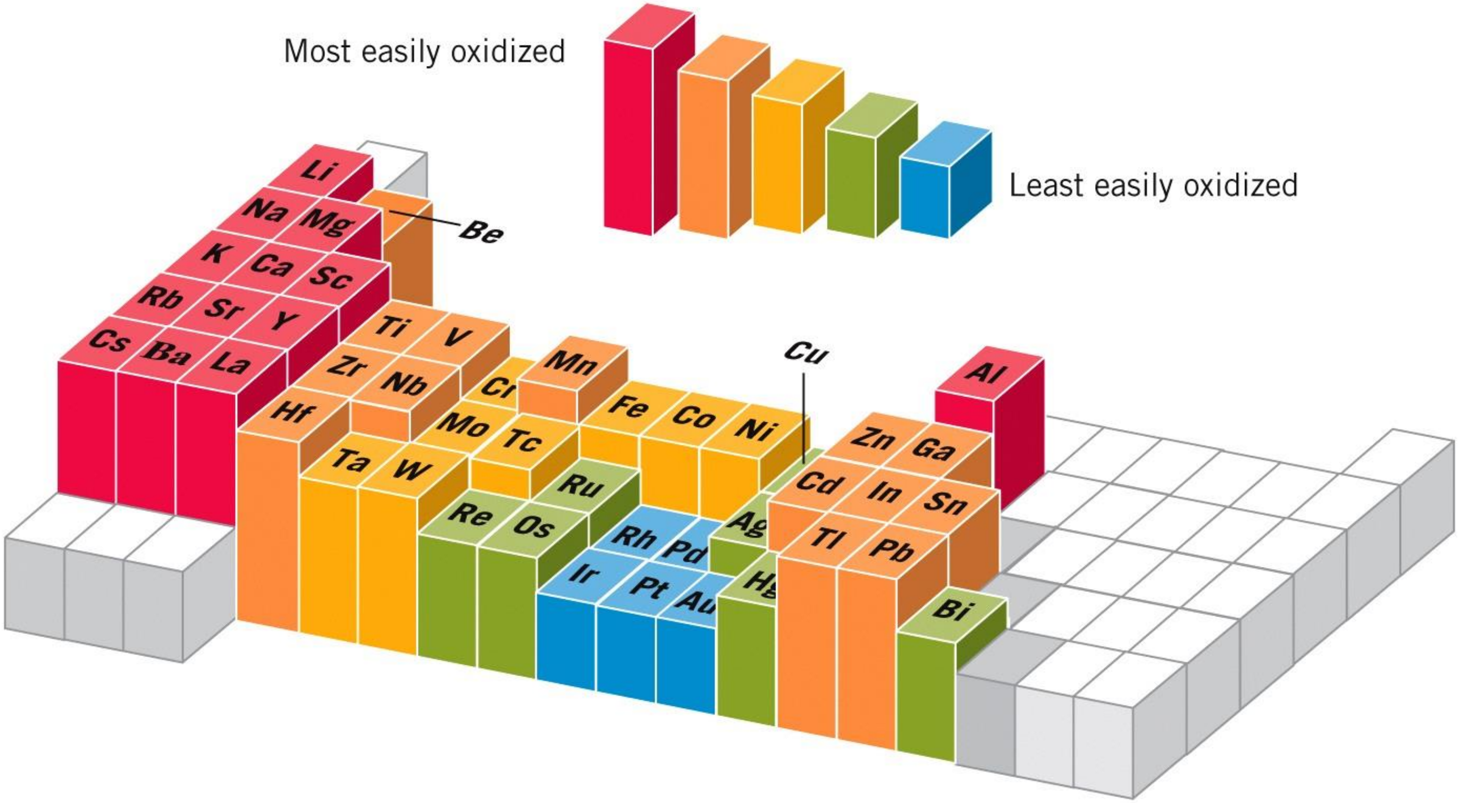
Result

- Elements in ***same*** region of periodic table
  - i.e., two nonmetals
  - Have similar electronegativities
  - Bonding more **covalent**

- Elements in ***different*** regions of periodic table
  - i.e., metal and nonmetal
  - Have different electronegativities
  - Bonding predominantly **ionic**

Reactivities of Elements Related to Electronegativities

- Parallels between EN and its **reactivity**
  - Tendency to undergo redox reactions



Reactivities of Elements Related to Electronegativities

Metals

- Low EN: easy to oxidize (Groups 1A and 2A)
- High EN: hard to oxidize (Pt, Ir, Rh, Au, Pd)
- Reactivity decreases across row as electronegativity increases

Nonmetals

- Oxidizing power increases across row as EN increases
- Oxidizing power decreases down a column as electronegativity decreases

Your Turn!

Predict the type of bonding (covalent or ionic) in the following: magnesium chloride, carbon tetrachloride, iron(III) oxide, sulfur dioxide, carbon disulfide

A. ionic, ionic, ionic, covalent, covalent

B. covalent, ionic, covalent, ionic, ionic

C. ionic, covalent, covalent, covalent, ionic

D. ionic, covalent, ionic, covalent, covalent

Drawing Lewis Structures

- Very useful
- Way of diagramming structure
- Used to describe structure of molecules
- Can be used to make reasonably accurate predictions of shapes of molecules

Drawing Lewis Structures

- Not all molecules obey the octet rule
  - Holds rigorously for second row elements like C, N, O, and F
  - B and Be sometimes have less than octet $BeCl_2$, BCl_3
  - 2nd row can **never** have **more** than eight electrons
  - 3rd row and below, atoms often **exceed** octet
- **Why?**
  - ***n*** = 3 shell can have up to 18 electrons as now have ***d*** orbitals in valence shell

Method for Drawing Lewis Structure

1. Decide how atoms are bonded
    - **Skeletal structure** = arrangement of atoms
    - **Central atom**
        - Usually given first
        - Usually least electronegative
2. Count all **valence** electrons (all atoms)
3. Place two electrons between each pair of atoms
    - Draw in single bonds

Method for Drawing Lewis Structure

4. Complete octets of **terminal atoms** (atoms attached to central atom) by adding electrons in pairs
5. Place any remaining electrons on central atom in pairs
6. If central atom does not have octet
   - Form double bonds
   - If necessary, form triple bonds

Example: SiF_4

$1\ \text{Si} = 1 \times 4e^- = 4\ e^-$

$4\ \text{F} = 4 \times 7e^- = 28\ e^-$

$\text{Total} = 32\ e^-$

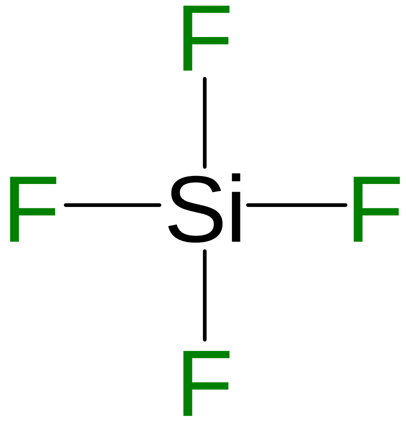
single bonds $-\ 8\ e^-$

$24\ e^-$

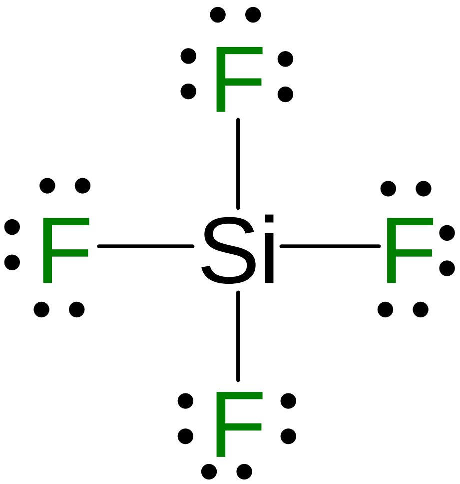
F lone pairs $-\ 24\ e^-$

$0\ e^-$

Skeletal Structure



Complete terminal atom octets



Example: H_2CO_3

- CO_3^{2-} oxoanion, so C central, and O s around, H^+ attached to two O s

1 C = 1 × 4e^- = 4 e^-

3 O = 3 × 6e^- = 18 e^-

2 H = 2 × 1e^- = 2 e^-

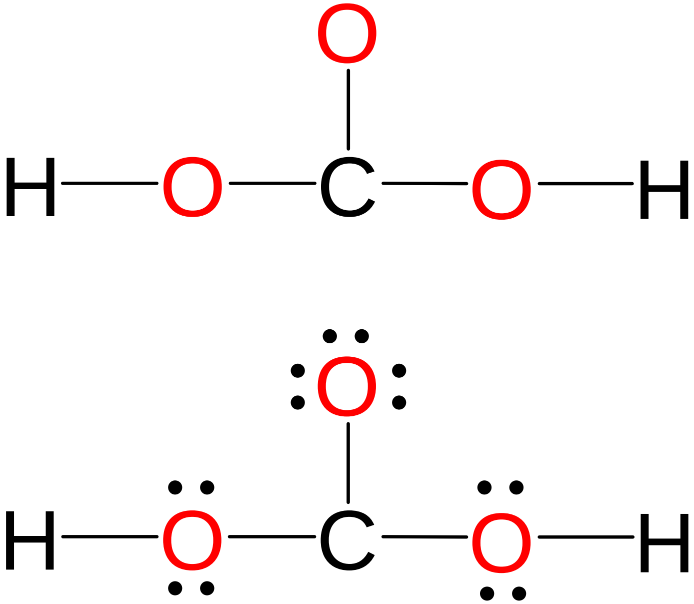
Total = 24 e^-

single bonds – 10 e^-

14 e^-

O lone pairs – 14 e^-

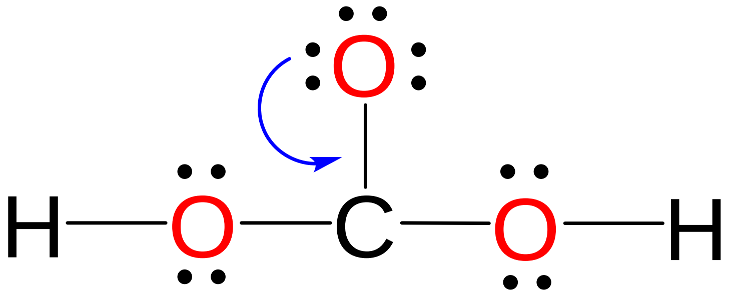
0 e^-

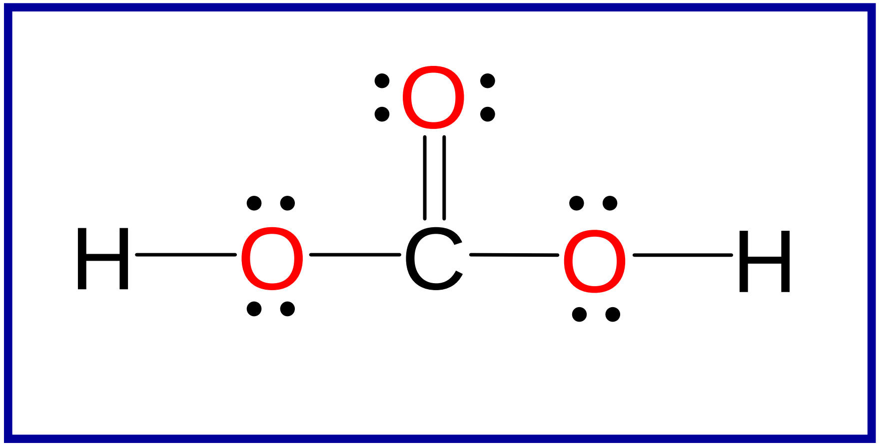


- But C only has 6 e^-

Example: H_2CO_3 (cont.)

- Too few electrons
- Must convert one of lone pairs on O to second bond to C
- Form double bond between C and O





Example: N_2F_2

$2\ N = 2 \times 5e^- = 10\ e^-$

$2F = 2 \times 7e^- = 14\ e^-$

Total $= 24\ e^-$

single bonds $-\ 6\ e^-$

$18\ e^-$

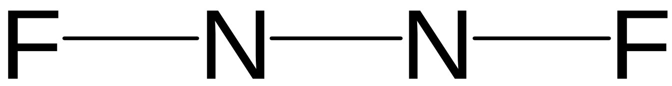
F lone pairs $-\ 12\ e^-$

$6\ e^-$

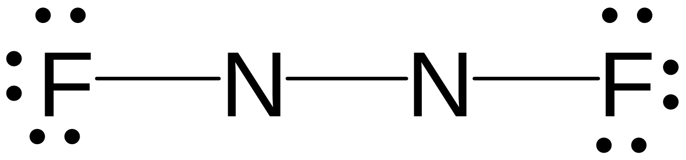
N electrons $-\ 6\ e^-$

$0\ e^-$

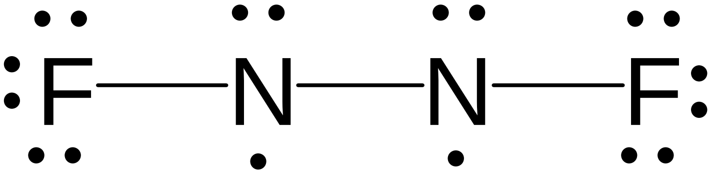
Skeletal Structure



Complete terminal atom octets

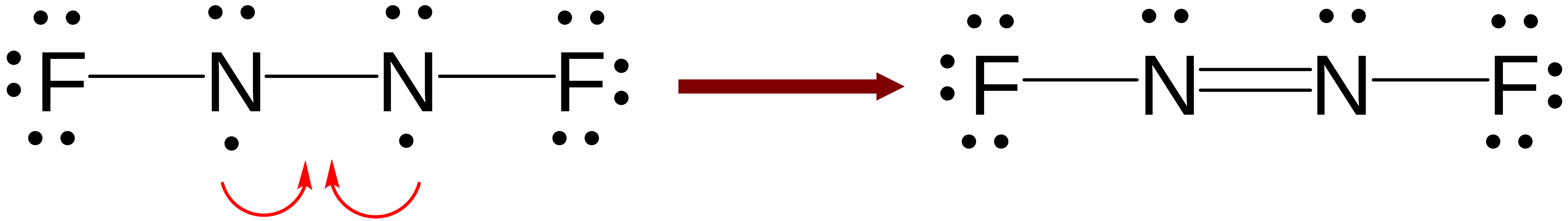


Put remaining electrons on central atom



Example: N_2F_2 (cont.)

- Not enough electrons to complete octets on nitrogen
- Must form double bond between nitrogen atoms to satisfy both octets



Expanded Octets

Elements after Period 2 in the Periodic Table

- Are larger atoms
- Have *d* orbitals
- Can accept 18 electrons
- For Lewis structures
  - Follow same process as before but add extra electrons to the central atom

Example: PCl_5

1 P = 1 × 5 e^- = 5 e^-

5 Cl = 5 × 7e^- = 35 e^-

Total = 40 e^-

single bonds − 10 e^-

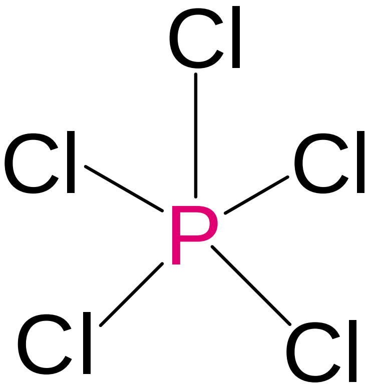
---

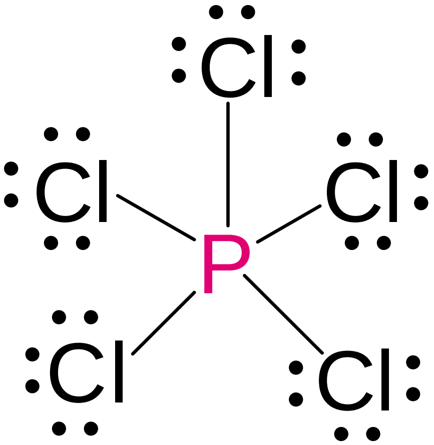
30 e^-

Cl lone pairs − 30 e^-

---

0 e^-





- P has 10 electrons
- Third period element
- Can expand its shell

Electron Deficient Structures

- Boron often has six electrons around it
  - Three pairs
- Beryllium often has four electrons around it
  - Two pairs

Example: BBr_3

1 B = 1 × 3 e^- = 3 e^-

3 Br = 3 × 7e^- = 21 e^-

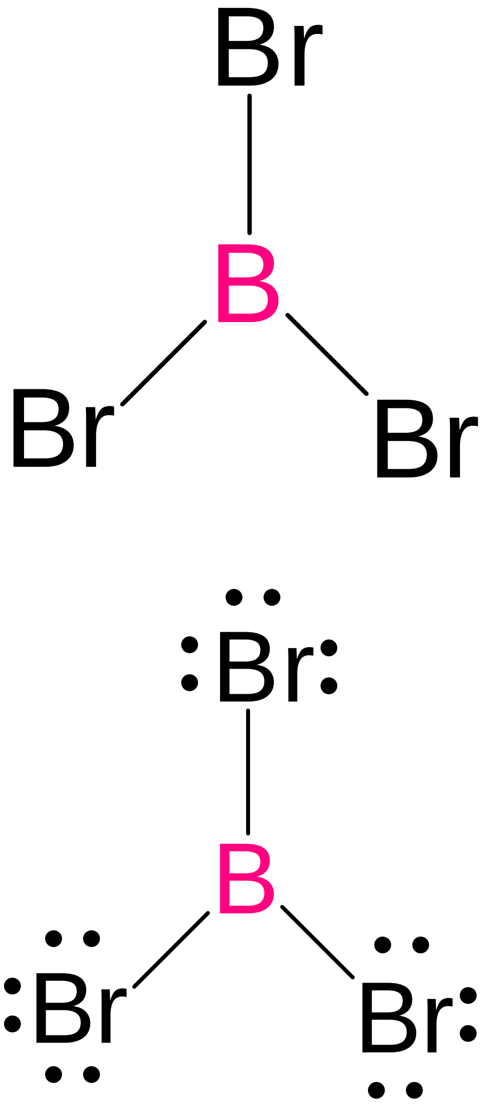
Total = 24 e^-

single bonds – 6 e^-

18 e^-

Br lone pairs – 18 e^-

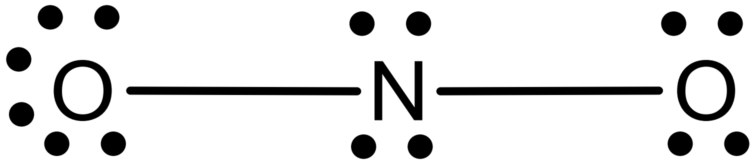
0 e^-



- B has only six electrons
- Does *not* form double bond
- Has *incomplete* octet

Your Turn!

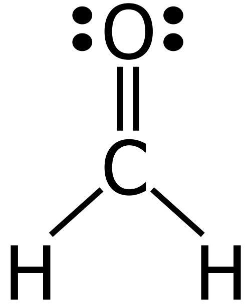
How many electrons does NO_2 have and how many are in the structure below?



A. 16, 18
B. 17, 18
C. 18, 18
D. 16, 16
E. 15, 16

Your Turn!

What type of bond exists between the C and O atoms in CH_2O (i.e., single, double, etc.)?



A. single bond

B. double bond

C. triple bond

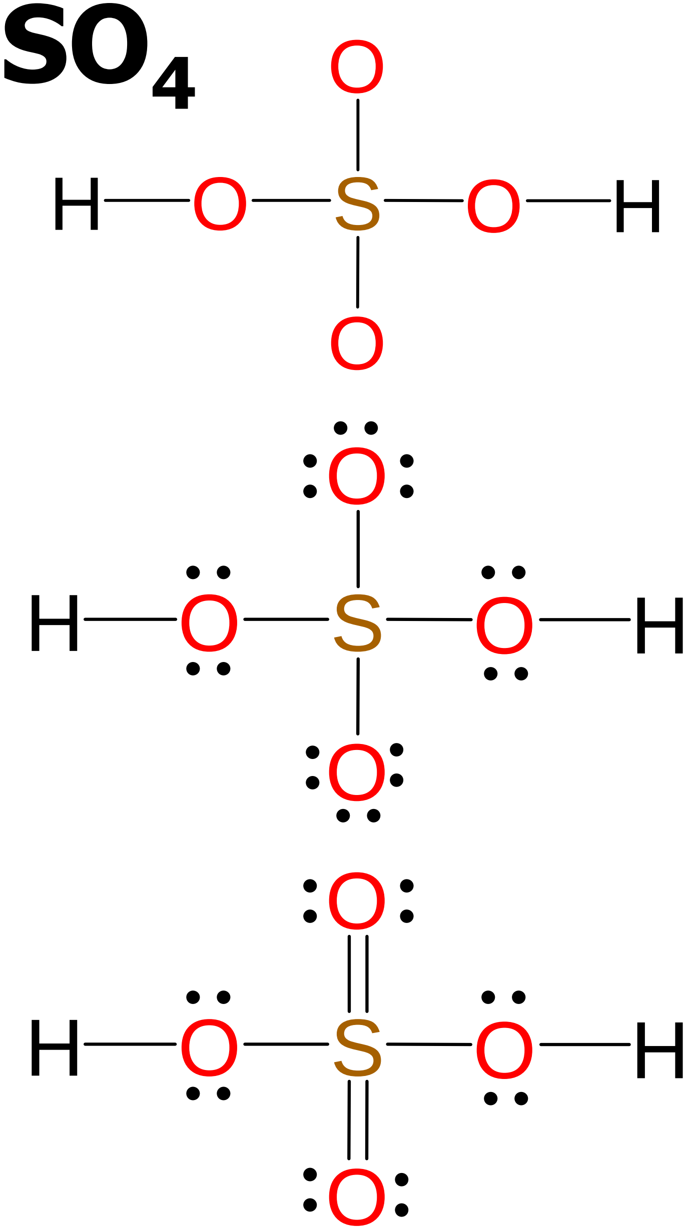
D. There is no bond between the C and the O because the oxygen is bonded to a H:

C-H-H-O

If more than one Lewis structure can be drawn, which is correct?

- Experiment *always* decides
- Concepts such as formal charge and resonance help to make predictions

Example: H_2SO_4



1 S = 1 × 6e^- = 6 e^-

4 O = 4 × 6e^- = 24 e^-

2 H = 2 × 1e^- = 2 e^-

Total = 32 e^-

single bonds – 12 e^-

---

20 e^-

O lone pairs – 20 e^-

---

0 e^-

- *n* = 3, has empty *d* orbitals
- Could *expand* its octet
- Could write structure with double bonds.

How Do We Know Which is Accurate?

Experimental evidence

- In this case bond lengths from X-ray data
- S—O bonds (no H attached) are shorter 142 pm
- S—O—H, S—O longer 157 pm
- Indicates that two bonds are shorter than the other two
- Structure with S=O for two O's without H's is more accurate
- Preferred Lewis structure
  - Even though it seems to violate octet rule unnecessarily

Formal Charge (FC)

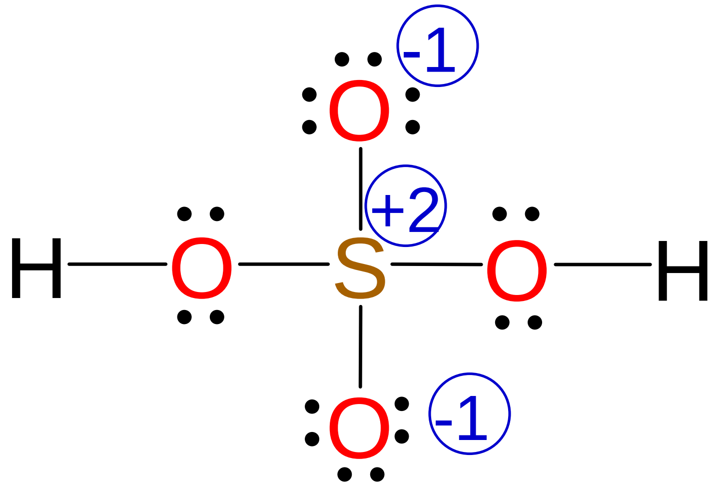
- Apparent charge on atom
- Bookkeeping method
- Does not represent real charges

FC = # valence e^-
– [# unshared e^- + ½ (# bonding e^-)]

FC = # valence e^-
– [# bonds to atom + # unshared e^-]

- Indicate formal charges by placing them in circles around atoms
- Sum of FC on all atoms must equal the overall charge on ion or molecule

FC = #valence e^- – [#bonds to atom + # unshared e^-]



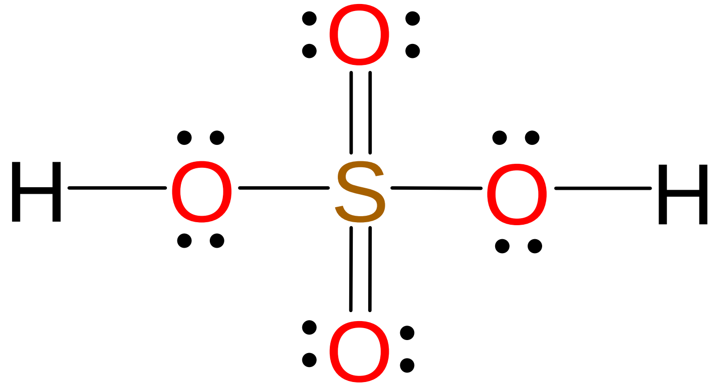
Structure 1

$FC_S = 6 - (4 + 0) = 2$

$FC_H = 1 - (1 + 0) = 0$

$FC_{O(s)} = 6 - (1 + 6) = -1$

$FC_{O(d)} = 6 - (2 + 4) = 0$



Structure 2

$FC_S = 6 - (6 + 0) = 0$

$FC_H = 1 - (1 + 0) = 0$

$FC_{O(s)} = 6 - (2 + 4) = 0$

$FC_{O(d)} = 6 - (2 + 4) = 0$

H_2SO_4

- No formal charges on any atom in structure 2

Conclusion:

- When several Lewis structures are possible
- Those with **smallest** formal charges
  - Most stable
  - Preferred

Most Stable Lewis Structure

1. Lowest possible formal charges are best
2. All FC $\leq |1|$
3. Any negative FC on most electronegative element

Example: CO_2

$1\ C = 1 \times 4e^- = 4\ e^-$

$2\ O = 2 \times 6e^- = 12\ e^-$

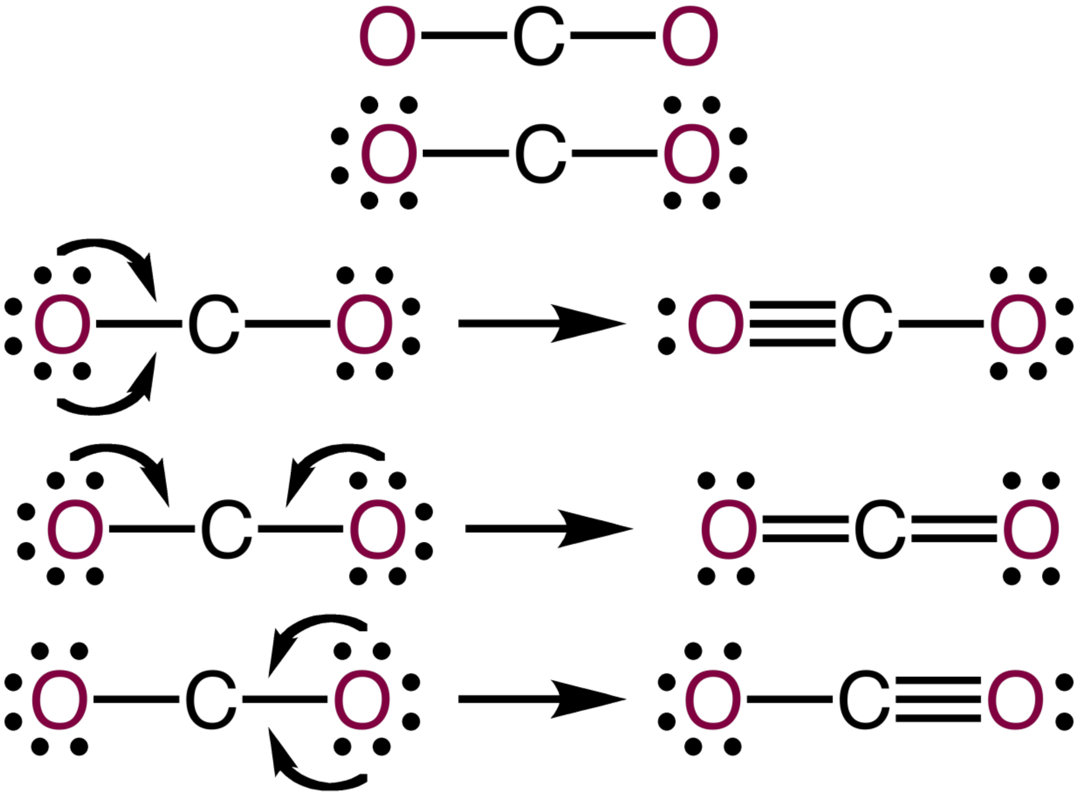
Total = $16\ e^-$

single bonds $-4\ e^-$

$12\ e^-$

O lone pairs $-12\ e^-$

$0\ e^-$



- C only has four electrons
- Need two extra bonds to O to complete octet
- 3 ways you can do this

- Which of these is correct?
- Need another criteria
- Come back to this

CO_2 Which Structure is Best

- Use formal charge to determine which structure is best

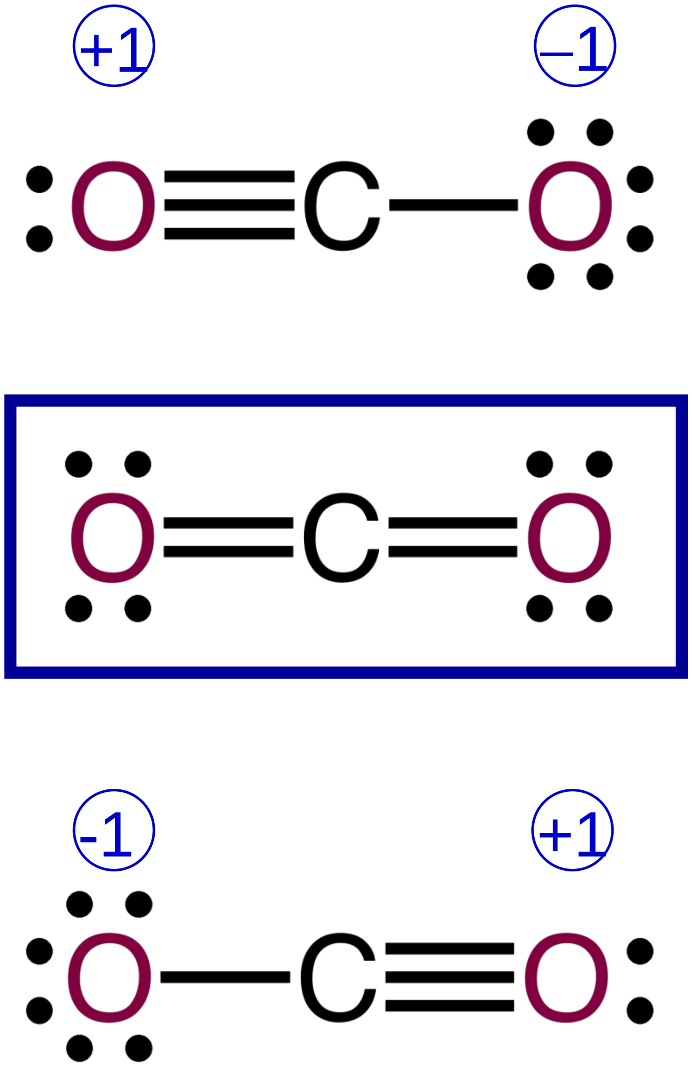
$FC_C = 4 - (4 + 0) = 0$

$FC_{O(single)} = 6 - (1 + 6) = -1$

$FC_{O(double)} = 6 - (2 + 4) = 0$

$FC_{O(triple)} = 6 - (3 + 2) = +1$

- Central structure best
- All FC’s = 0

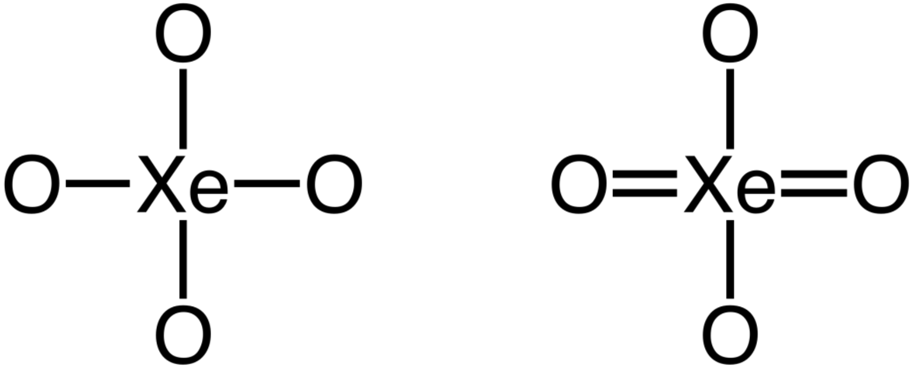


Can Use Formal Charges to Explain Boron Chemistry

- BCl_3
- Why doesn't a double bond form here?
- $FC_B = 3 - 0 - 3 = 0$
- $FC_{Cl} = 7 - 6 - 1 = 0$
- All FCs = 0 so the molecule has the best possible structure
- It doesn't need to form double bond

Your Turn!

What is the formal charge on Xe for the following?



A. +2, +4

B. +2, +3

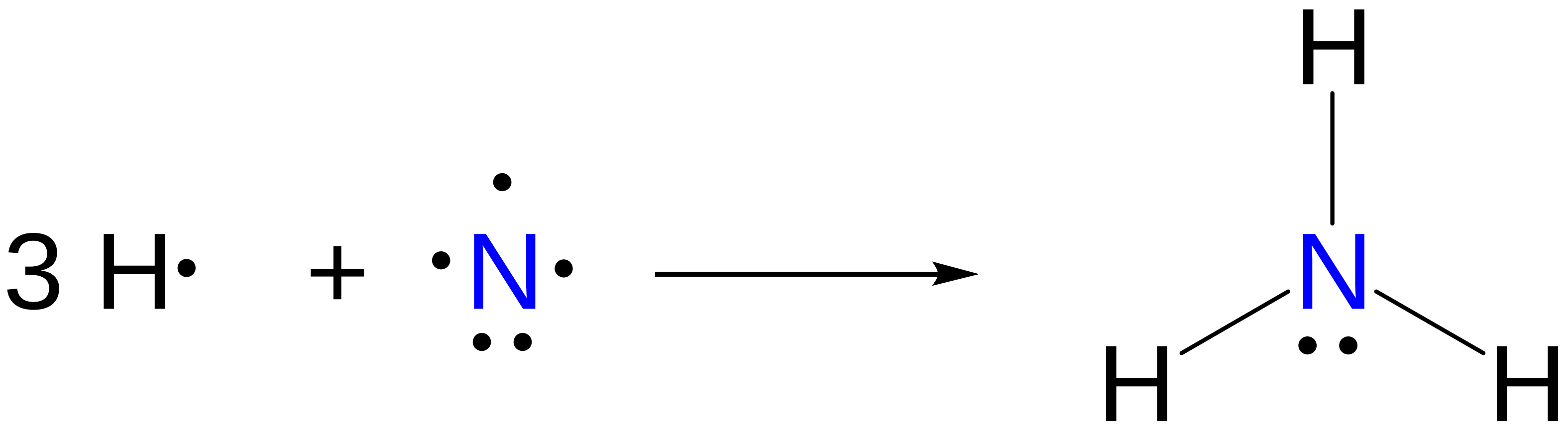
C. +4, 0

D. +4, +2

Coordinate Covalent Bonds

Ammonia

- Normal covalent bonds
- One electron from each atom shared between the two



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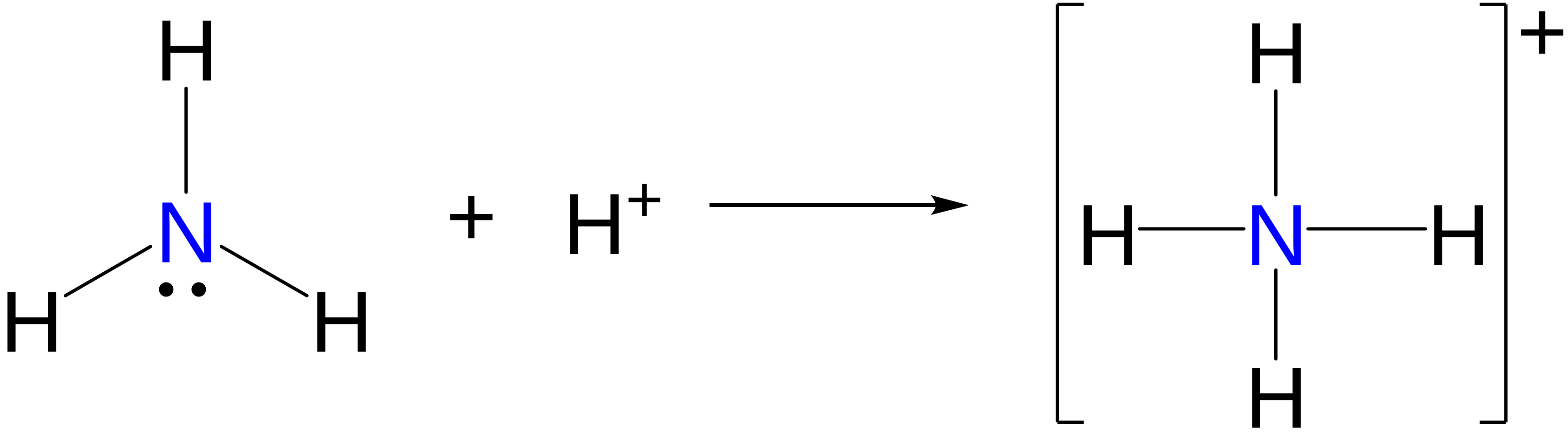
Coordinate Covalent Bond

Ammonium Ion

- H^+ has no electrons
- N has lone pair
- Can still get 2 electrons shared between them

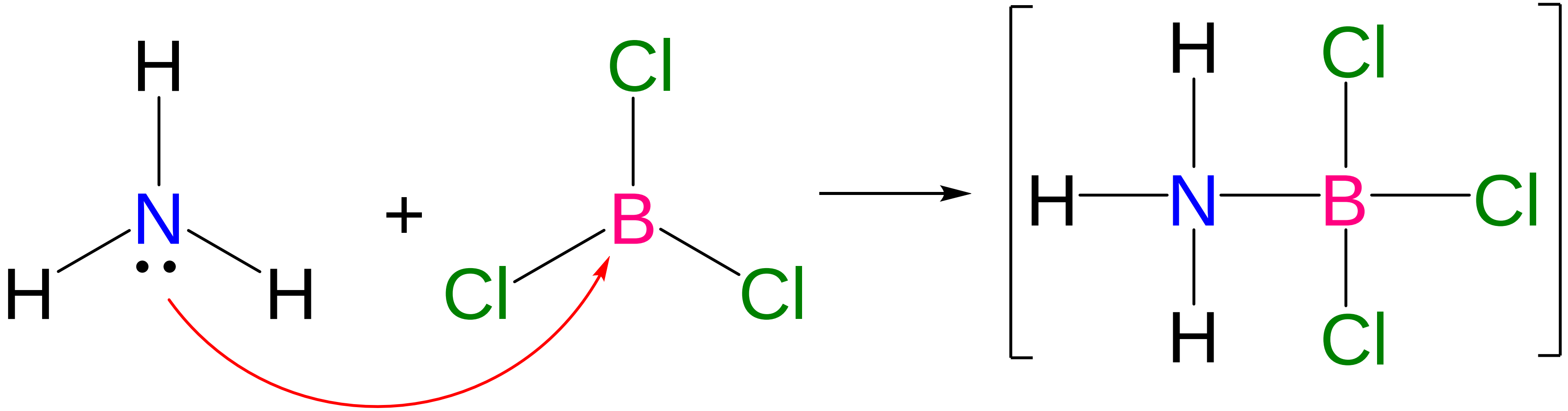


Coordinate Covalent Bond

- Both electrons of shared pair come from just one of two atoms
- Once bond formed, acts like any other covalent bond
- Can't tell where electrons came from after bond is formed
- Useful in understanding chemical reactions

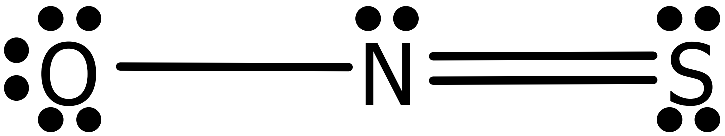
Coordinate Covalent Bond

- Especially **boron** (electron deficient molecule) reacts with nitrogen compounds that contain lone pair of electrons



Your Turn!

What is the formal charge on each atom in the structure below?



A. O: -2 N: 0 S: -2

B. O: 0 N: 0 S: 0

C. O: -1 N: 0 S: -1

D. O: -2 N: +1 S: +2

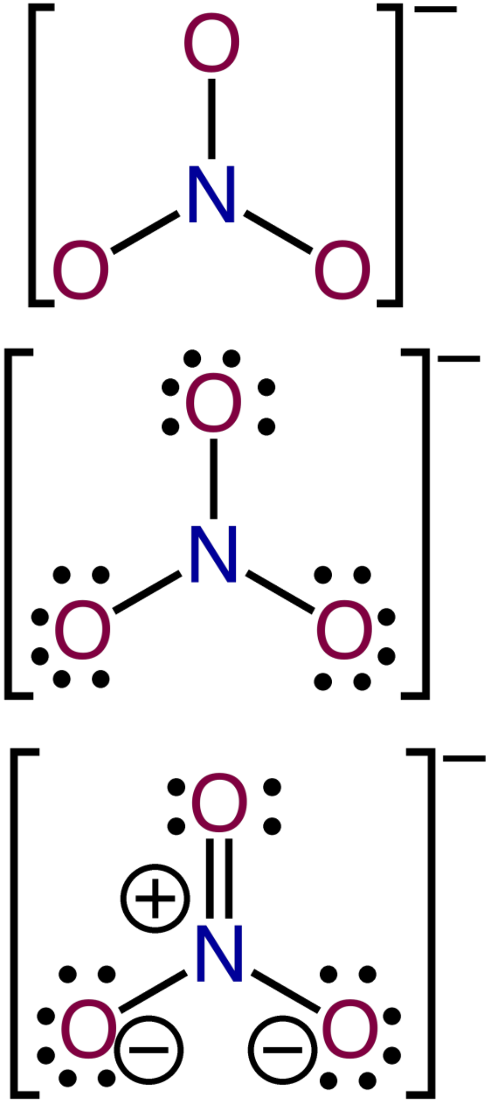
E. O: -1 N: 0 S: 0

Resonance: Explaining Multiple Equivalent Lewis Structures

- Can use formal charge to decide between two different Lewis structures
- Need an explanation of equivalent structures
- The resonance concept provides the way to interpret equivalent structures

Resonance: When a Single Lewis Structure Fails

Example: NO_3^-



$1\ \text{N} = 1 \times 5e^- = \quad 5\ e^-$

$3\ \text{O} = 3 \times 6e^- = \ 18\ e^-$

$-1\ \text{charge} \qquad = \quad 1\ e^-$

$\text{Total} = 24\ e^-$

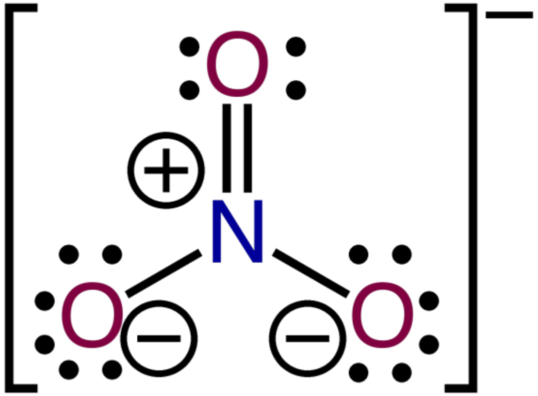
$\text{single bonds} \quad -6\ e^-$

$18\ e^-$

$\text{O lone pairs} \quad -18\ e^-$

$0\ e^-$

Example: NO_3^-



- Lewis structure predicts one bond shorter than other two

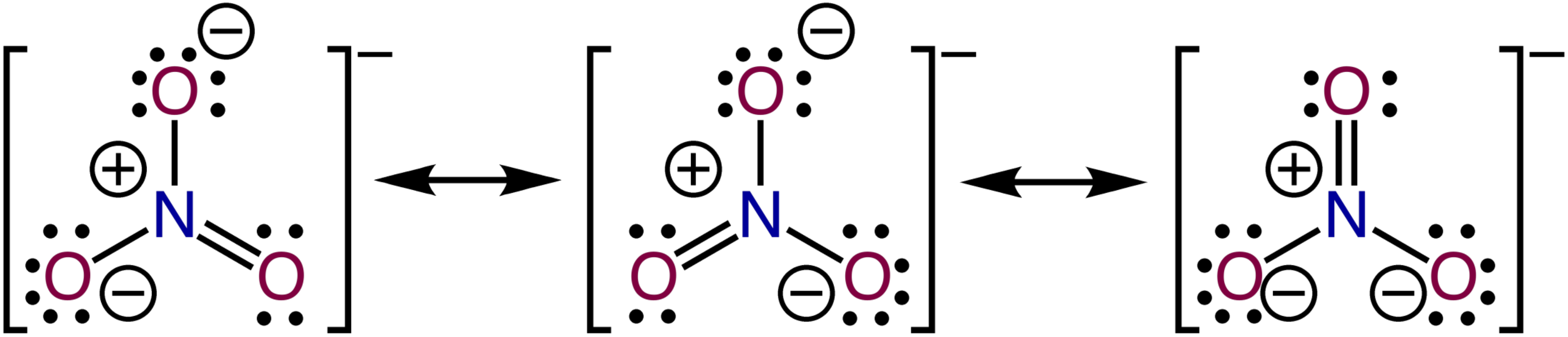
Experimental observation:

  - All three N—O bond lengths are same
  - All shorter than N—O single bonds

- Have to modify Lewis Structure
  - Electrons cannot distinguish O atoms
- Can write two or more possible structures simply by moving where electrons are
  - Changing placement of electrons

What are Resonance Structures?

- Multiple Lewis structures for single molecule
  - No single Lewis structure is correct
  - Structure not accurately represented by any one Lewis structure
  - Actual structure = “average” of all possible structures
  - Double headed arrow between resonance structures used to denote resonance

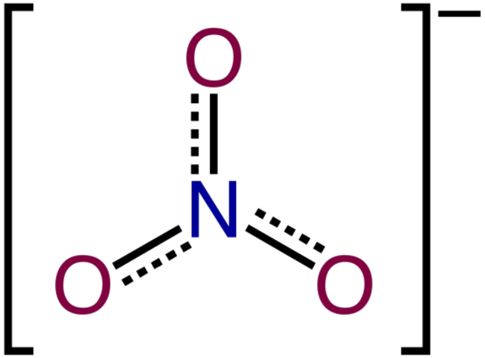


Resonance Structures

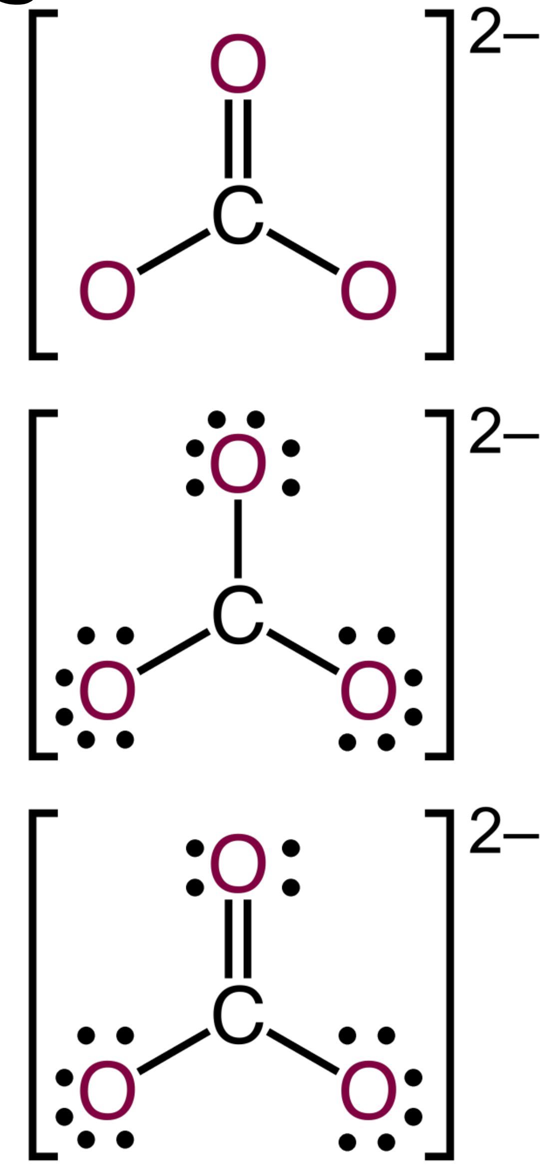
- Lewis structures assume electrons are localized between 2 atoms
- In resonance structures, electrons are **delocalized**
  - Smeared out over all atoms
  - Can move around entire molecule to give equivalent bond distances

Resonance Hybrid

- Way to depict resonance delocalization



Example: CO_3^{2-}



$1\ N = 1 \times 5e^- = 5\ e^-$

$3\ O = 3 \times 6e^- = 18\ e^-$

-1 charge $= 1\ e^-$

Total $= 24\ e^-$

single bonds $-\ 6\ e^-$

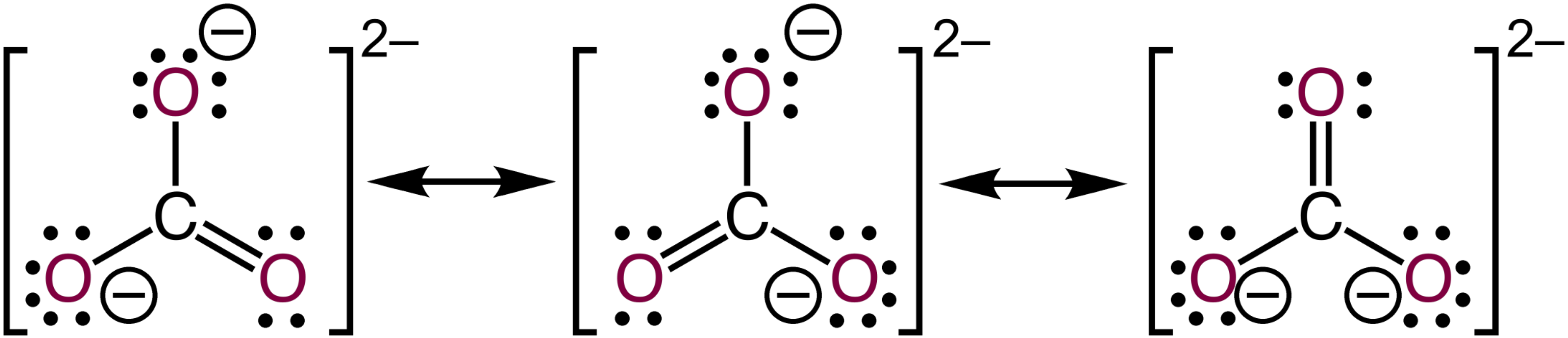
$18\ e^-$

O lone pairs $-18\ e^-$

$0\ e^-$

C only has 6 electrons so
a double bond is needed

Three Equivalent Resonance Structures



- All have same net formal charges on C and O' s
  - FC = –1 on singly bonded O's
  - FC = O on doubly bond O and C

Resonance Structures Not Always Equivalent

- Two or more Lewis Structures for **same** compound may or may not represent electron distributions of equal energy

How Do We Determine Which are Good Contributors?

1. All octets are satisfied

2. All atoms have as many bonds as possible

3a. FC $\leq |1|$

3b. Any negative charges are on the more electronegative atoms.

Drawing Good Resonance Structures

1. All must be valid Lewis Structures
2. Only electrons are shifted
   - Usually double or triple bond and lone pair
   - Nuclei can't be moved
   - Bond angles must remain the same
3. Number of unpaired electrons, if any, must remain the same
4. Major contributors are the ones with lowest potential energy (see above)
5. Resonance stabilization is most important when delocalizing charge onto two or more atoms

Example: NCO^-

1 C = 1 × 4e^- = 4 e^-

1 N = 1 × 5e^- = 5 e^-

1 O = 1 × 6e^- = 6 e^-

–1 charge = 1 e^-

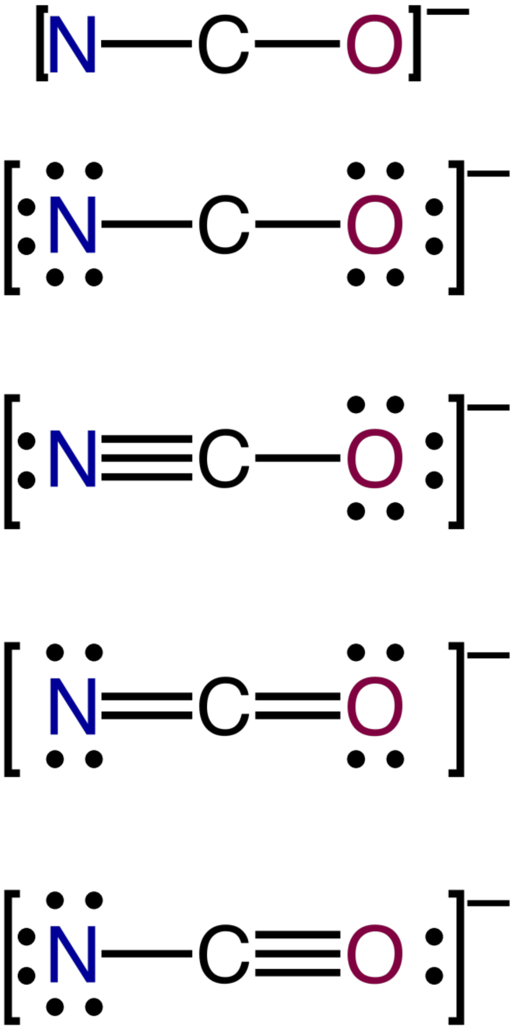
Total = 16 e^-

single bonds – 4 e^-

12 e^-

lone pairs –12 e^-

0 e^-

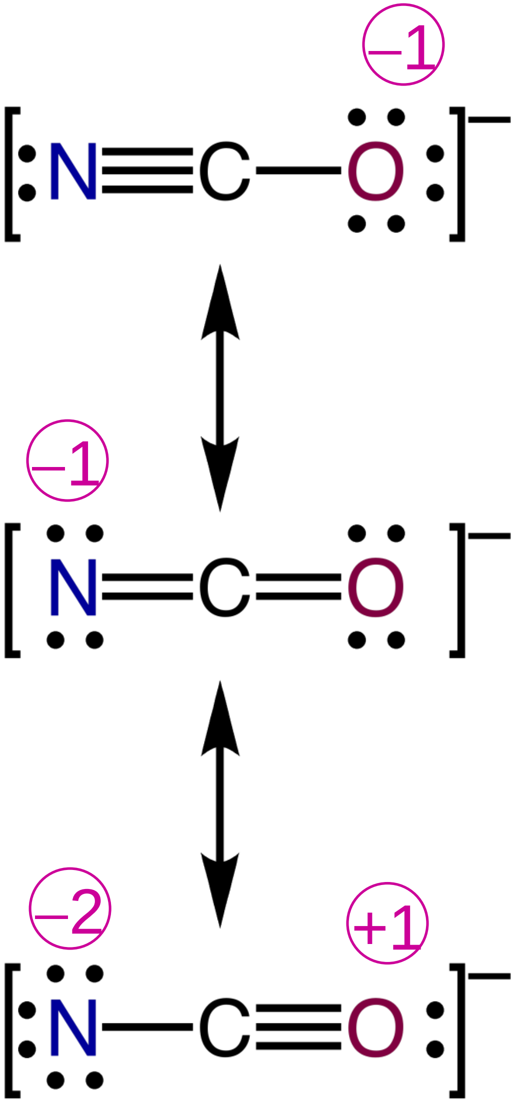


Example: NCO^-

$FC_N = 5 - 2 - 3 = 0$
$FC_C = 4 - 0 - 4 = 0$
$FC_O = 6 - 6 - 1 = -1$

$FC_N = 5 - 4 - 2 = -1$
$FC_C = 4 - 0 - 4 = 0$
$FC_O = 6 - 4 - 2 = 0$

$FC_N = 5 - 6 - 1 = -2$
$FC_C = 4 - 0 - 4 = 0$
$FC_O = 6 - 2 - 3 = +1$



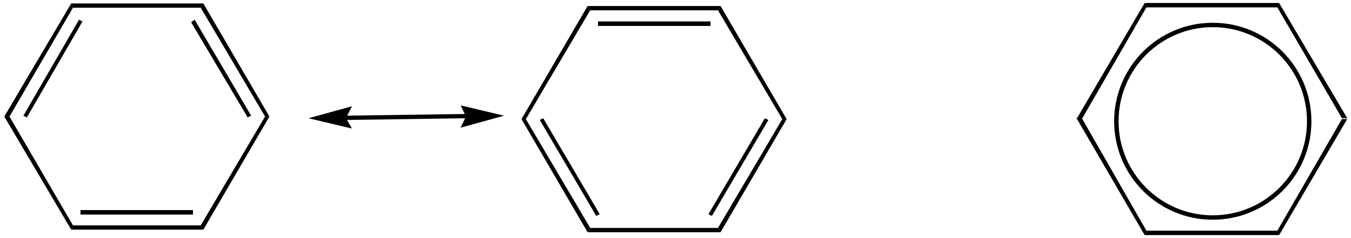
Best

OK

Not Acceptable

Resonance Stabilization

- Actual structure is more stable than either single resonance structure



- For benzene
- The extra stability is ~146 kJ/mol
- **Resonance energy**
  - Extra stabilization energy from resonance

Your Turn!

Which of the following is false?

A. Not all resonance structures for a given molecule are equivalent

B. Resonance structures indicate that the molecule rapidly switches between multiple electron distributions

C. Resonance structures are necessary when a single Lewis structure is not sufficient to depict the electron distribution in a molecule

D. Formal charges are calculated the same way in resonance structures as in other structures

Your Turn!

Which of the structures below exhibit resonance (hint: there is more than one)?

A. NO_2

B. H_2O

C. N_3^-

D. N_2O (nitrogen is central atom)

E. CH_3CH_2CH

Learning Check

Example: Draw the best Lewis structure for the following

$HClO_4$

XeF_4

I_3^-

BrF_5