Chapter 7 Part 2

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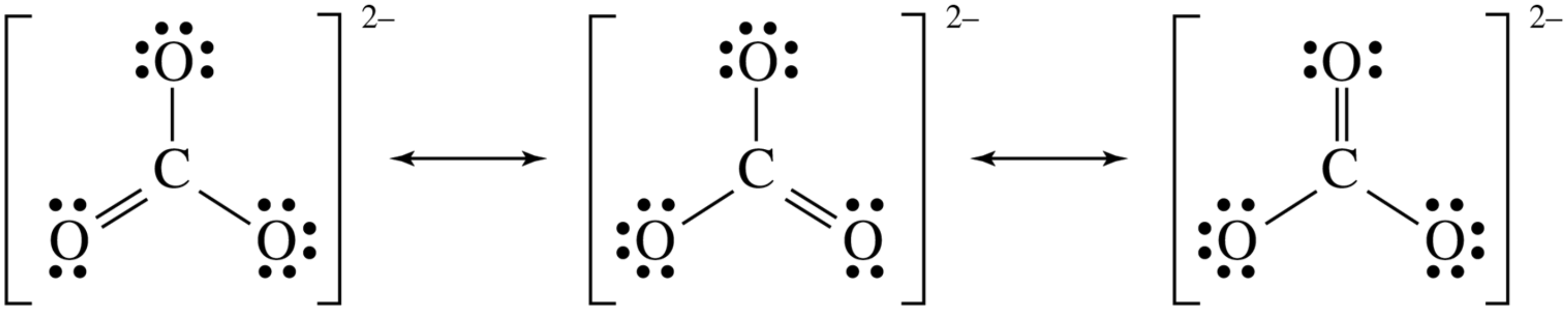
Resonance

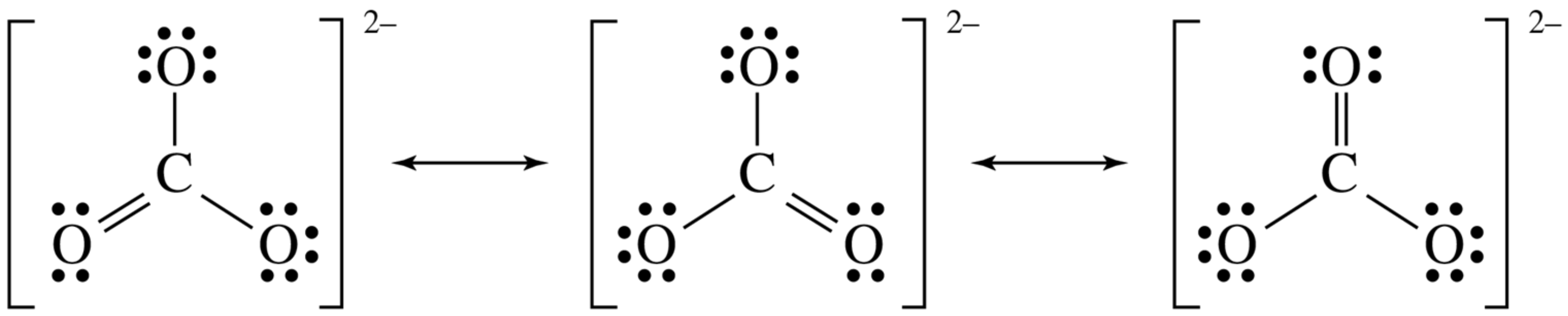
- While Lewis structures help visualize the bonding in molecules, they have limitations.
- In some cases, a molecule cannot be represented accurately by a single Lewis structure but requires multiple structures.
- These structures differ only in the placement of multiple bonds and lone pairs.
- Molecules/ions that have such structures are said to exhibit resonance and the structures are referred to as resonance structures.

Resonance Structures of the Carbonate Ion

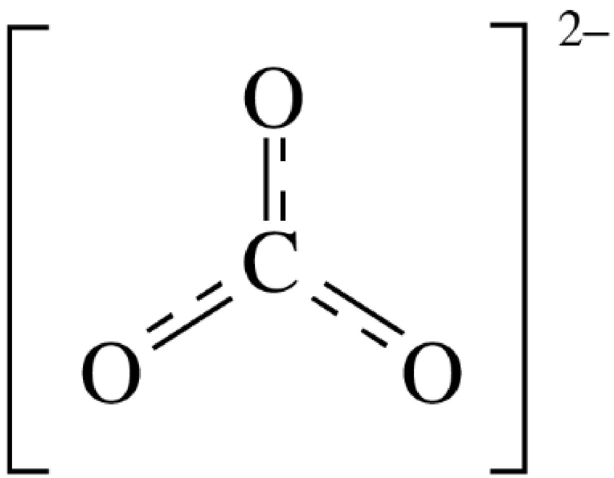


Interpreting Resonance Structures

- It is equally likely that the double bond is located between C and any one of the O atoms.
- In fact, the pair of electrons shown as the double bond is shared (spread out) among all three locations.
- This is a delocalized bond and is designated as such by the double-headed arrows between the structures, or as a resonance hybrid.
- All three C–O bonds in the carbonate ion are equivalent and have properties in between a single and double bond.



Resonance Hybrid: Delocalized View of the Carbonate Ion



- This resonance hybrid structure is an alternative way of showing the delocalized bond.
- All three C–O bonds in the carbonate ion are equivalent and have properties in between those of a single and double bond.

Draw resonance structures for the nitrite ion, NO_2^-.

Formal Charge

- Sometimes it is possible to draw multiple valid Lewis structures that are not equivalent.
- Use formal charge to decide which structure (or structures) is the better representation of the real molecule.
- Formal charge is a type of electron bookkeeping in which you assign a fictitious charge to each atom in a molecule by comparing the number of valence electrons the atom appears to have in the structure to the number of valence electrons it brought to the molecule.

$$\text{Formal charge} = \begin{pmatrix} \text{\# of} \\ \text{valence e}^- \end{pmatrix} - \begin{pmatrix} \text{\# of} \\ \text{nonbonding e}^- \end{pmatrix} - \begin{pmatrix} \text{\# of bonds} \\ \text{to that atom} \end{pmatrix}$$

Formal Charge

What is the formal charge on chlorine in the chlorite ion, ClO_2^-?

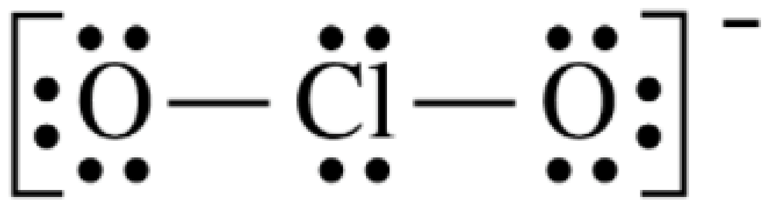
A. −7

B. −1

C. 0

D. +1

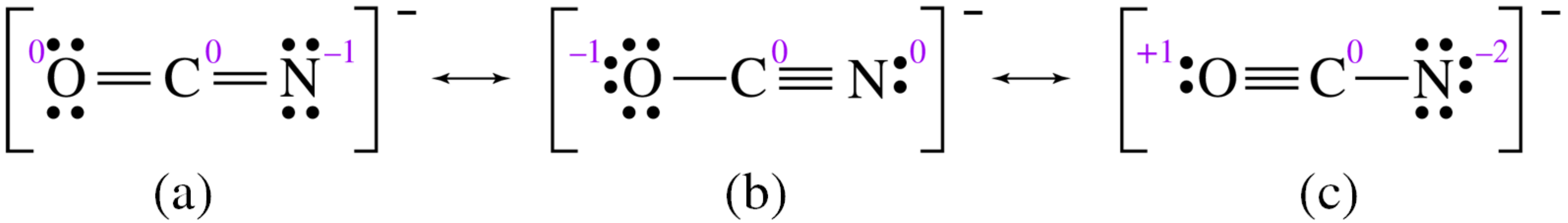
E. +7



Formal Charge and Lewis Structures

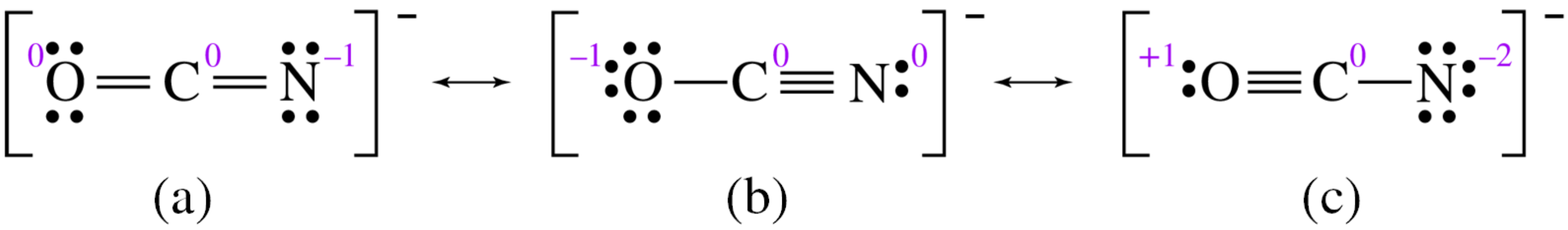
- The most likely Lewis structures
  - have small or zero formal charges, especially for the central atom;
  - have negative formal charges associated with elements of higher electronegativity; and
  - have positive formal charges associated with elements of lower electronegativity.
- Formal charge helps to determine which possible structure is more energetically favorable.

Calculating Formal Charge of Cyanate Ion Lewis Structures



Structure	(a)	(b)	(c)
O formal charge	$6 - 2 - 4 = 0$	$6 - 1 - 6 = -1$	$6 - 3 - 2 = +1$
N formal charge	$5 - 2 - 4 = -1$	$5 - 3 - 2 = 0$	$5 - 1 - 6 = -2$

Which Structure Best Represents Cyanate Ion?



- Structure (c) has higher formal charge and has negative formal charge on N rather than O. It is the least likely structure.
- Both structures (a) and (b) have low formal charge, but structure (b) places the negative formal charge on O, which is more electronegative than N.
- Therefore, structure (b) most closely resembles the true structure of cyanate ion.

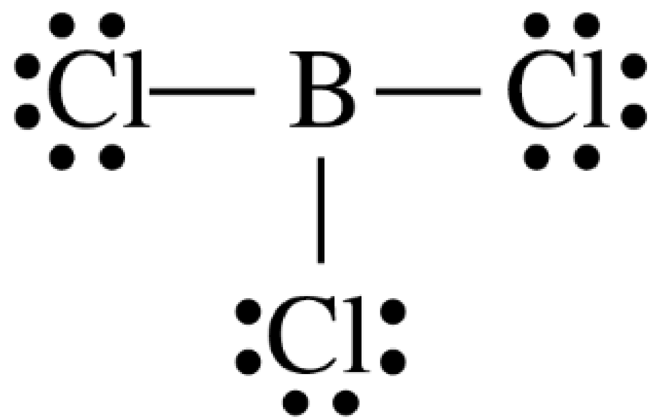
Formal Charge and Resonance

A. Draw the (3) resonance structures of dinitrogen monoxide, N_2O.
B. Then use formal charge to determine which structure is more likely to resemble the real molecule.

Octet Rule Exceptions: Less Than an Octet

- Hydrogen forms a duet, not an octet.
- Other very small atoms also have form molecules with less than an octet.
  - Beryllium forms molecules with four electrons in its valence shell.
  - Boron atoms, in molecules, generally have six electrons in their valence shells.

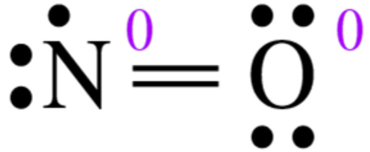
Beryllium and Boron with Less Than an Octet

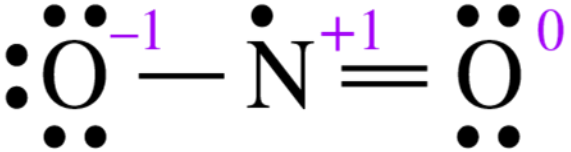


Octet Rule Exceptions: Radicals

- Molecules with an odd number of valence electrons typically have one atom with seven valence electrons.
- Molecules with unpaired electrons are referred to as radicals.
- Common examples are NO and NO_2.

Unpaired Electrons: Radicals

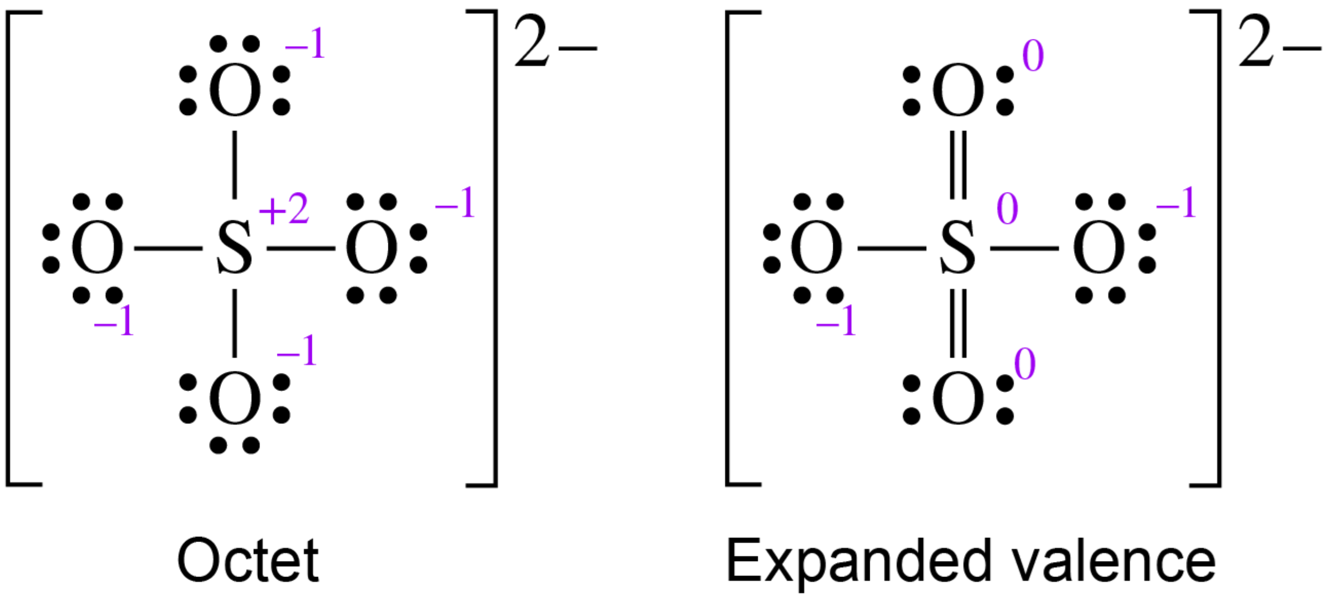




Octet Rule Exceptions: More Than an Octet

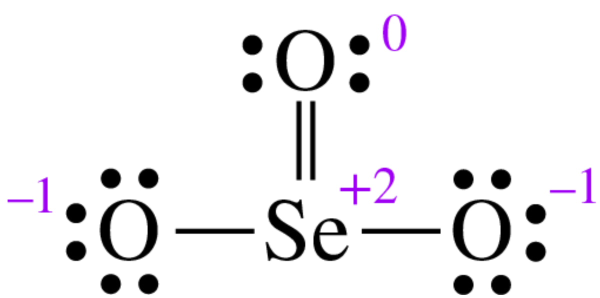
- If the central element in a molecule or polyatomic ion is in the third period or beyond, it can sometimes expand its valence shell beyond eight electrons.
- Central atoms with expanded valence shells, also known as expanded octets, can share more than four pairs of electrons.
- Expanded octets result in lower formal charges, in most cases.

Octet Rule Exceptions: More Than an Octet



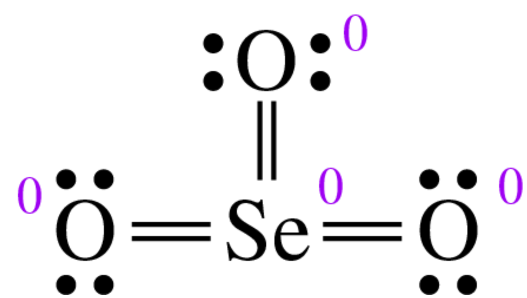
Octet Rule Exceptions: More Than an Octet

Octet rule



or

Expanded octets



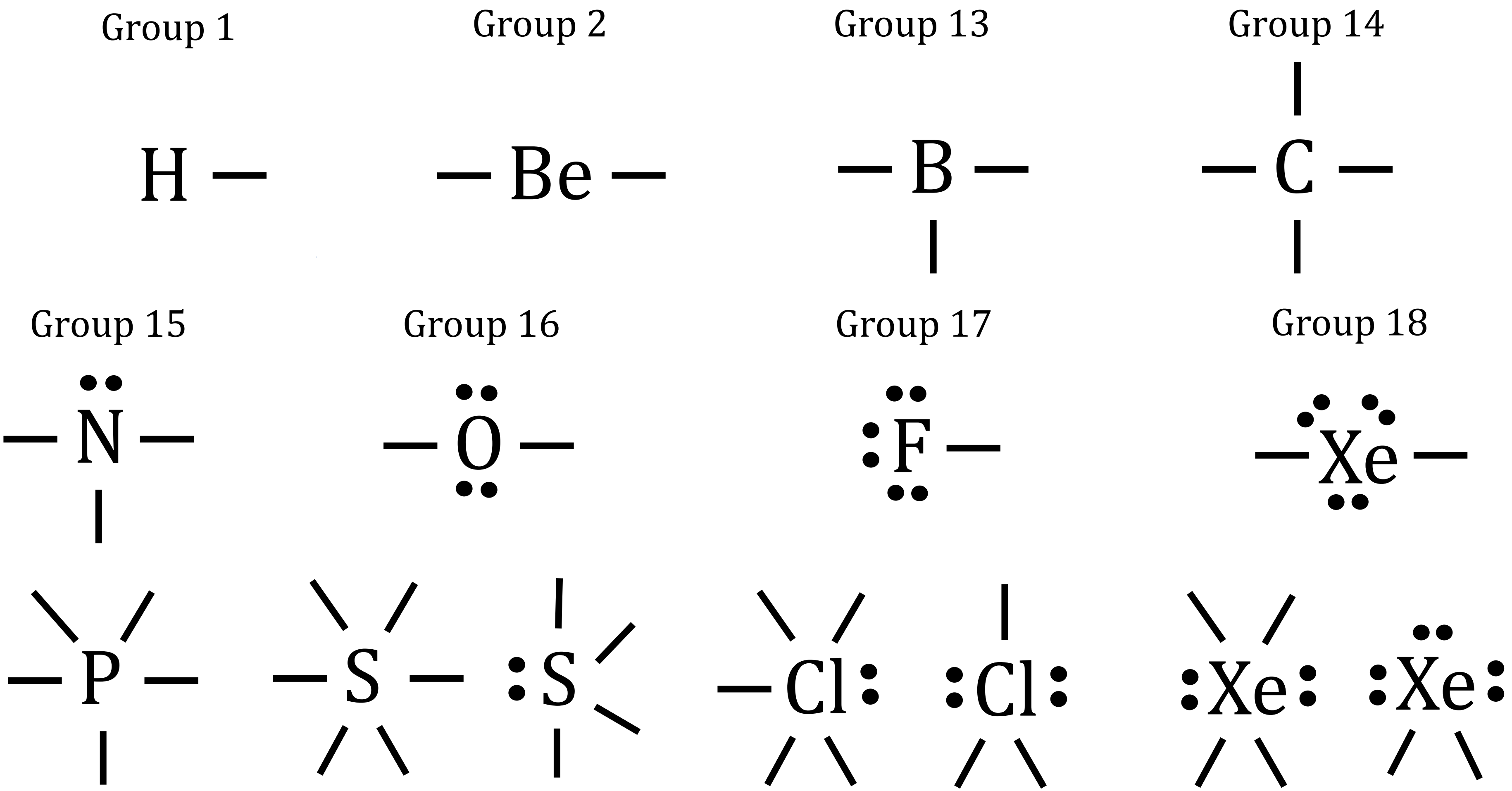
Drawing Lewis Structures (XeF_4)

1. Count the valence electrons
2. Arrange atoms by placing the least electronegative elements in the middle
3. Add single bonds
4. Add remaining electrons
5. Check octet and duet rules to determine whether multiple bonds are needed

Summary of Octet Rule and Its Exceptions

Criterion	Description	Examples
H, Be, or B	Do not obey the octet rule; H, Be, and B have two, four, and six electrons, respectively, in structures.	H_2, BeH_2, BH_3
C, N, O, or F (period 2 nonmetals)	Obey the octet rule; must have exactly eight electrons in structures (unless there is an odd number of valence electrons).	CO_2, NF_3, CN^-
Unpaired, single electron (radical)	Odd number of valence electrons; the least electronegative atom has seven electrons.	NO, NO_2
Period 3 elements and beyond as the central atom.	Must have at least eight electrons (with the exception of radicals) but can accommodate more than eight electrons.	PCl_5, I_3^- (central atom)
Period 3 elements and beyond as an outer atom.	Obey the octet rule; tend to have exactly eight electrons in structures (unless there is an odd number of valence electrons).	PCl_5, I_3^- (outer atoms)

Bonding Motifs Based on Formal Charge



Drawing Lewis Structures

Draw the most stable Lewis structures for the molecule given.

A. BF_3
B. SO_2
C. CH_2O
D. SiF_2Cl_2
E. NH_4^{+}
F. PO_4^{3-}

Lewis Structures

Which Lewis structure contains a radical?

A. CN^-
B. ClO_2
C. BH_3
D. NH_3

Lewis Structures

Which Lewis structure uses an expanded octet?

A. CN^{-}
B. BH_3
C. NH_3
D. SF_4