جامعة القاهرة

CHEMISTRY DEPARTMENT
قسم الكيمياء

General Chemistry I

NAC 1101

Lecture 8

Chemical Bonding

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Outline

- Formal Charge & Oxidation No.
- Resonance Structures
- Exceptions to the Octet Rule
- Strengths & Lengths of Covalent Bonds

Formal Charge, FC

The FC of any **atom** in a molecule is the charge the atom would have if each bonding electron pair in the molecule were shared equally between its two atoms.

- FC is used to favor one of multiple valid Lewis structures of a molecule or polyatomic ion.

How to calculate FC

1) All unshared (nonbonding) es are assigned to the atom on which they are found.
2) For any bond—single, double, or triple—half of the bonding electrons are assigned to each atom in the bond.
3) The FC of each atom is calculated by subtracting the number of es assigned to the atom from the number of Ves in the neutral atom:

$$FC = Ves - \left(\frac{\text{bonding } es}{2}\right) - \text{nonbonding } es$$

Exercise

○ Calculate FC for atoms in CN^- ion.

Solution

Lewis's structure is $\left[:C\equiv N:\right]^-$

- ○ The neutral C atom has 4 Ves.
- ○ There are 6 es in the cyanide triple bond and 2 nonbonding es on C.

$$FC_C = Ves - \left(\frac{\text{bonding } es}{2}\right) - \text{nonbonding } es$$

$$FC_C = 4 - \left(\frac{6}{2}\right) - 2 = -1$$

$$FC_N = 5 - \left(\frac{6}{2}\right) - 2 = 0$$

$$\left[:\overset{-1}{C}\equiv\overset{0}{N}:\right]^-$$

$$\sum FC = \text{ion's charge}$$

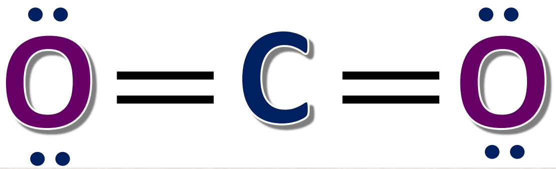
- FC There on a neutral molecule must add to zero, whereas those on an ion add to give the charge on the ion.
- If we can draw several Lewis structures for a molecule, the concept of formal charge can help us decide which is the most important, which we shall call the dominant Lewis structure.
- CO_2 has 2 valid Lewis structures: one with 2 double bonds and one with a single bond and a triple bond.

Ves	6	4	6	6	4	6
−es assigned to atoms	6	4	6	7	4	5
FC	0	0	0	−1	0	+1

Dominant Lewis's Structure

1) The dominant Lewis structure is generally the one in which the atoms bear formal charges closest to zero.
2) A Lewis structure in which any negative charges reside on the more electronegative atoms is generally more dominant than one that has negative charges on less electronegative atoms.

Accordingly,

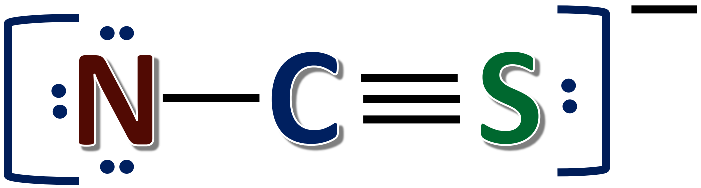


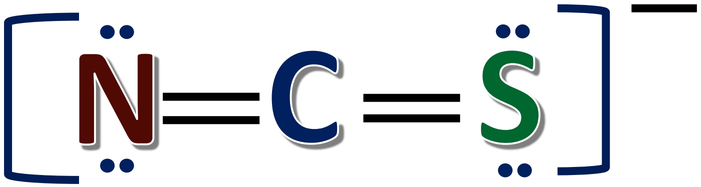
$$\underset{\cdot\cdot}{\ddot{O}}=C=\underset{\cdot\cdot}{\ddot{O}}$$

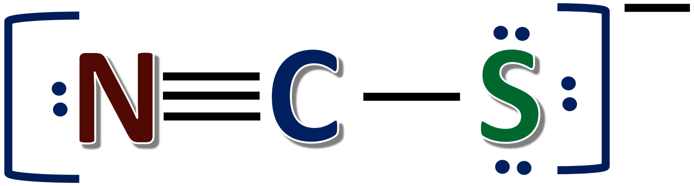
- ○ is dominant because the atoms carry no FC.
- ○ The other Lewis structure contribute to the actual structure to a much smaller extent.

Exercise

- Three possible Lewis structures for the thiocyanate ion, NCS^-, are below.
- Determine the formal charges in each structure.
- Based on the formal charges, which Lewis structure is the dominant one?

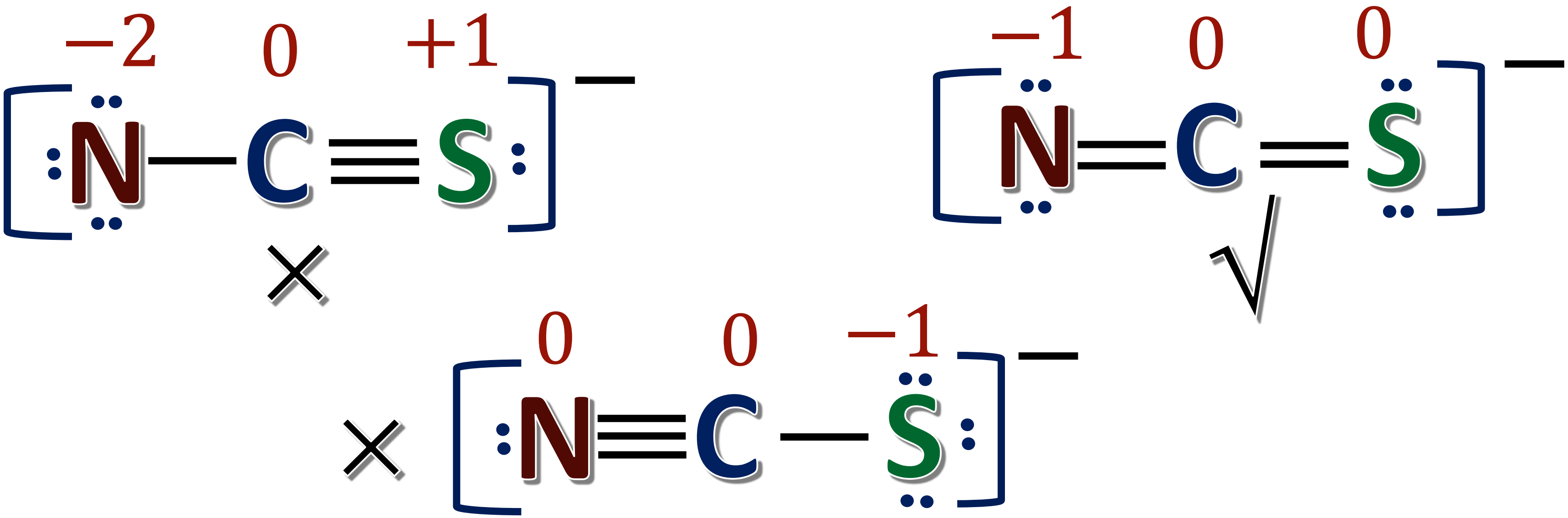






Solution

- Neutral N, C, and S atoms have five, four, and six Ves, respectively.



- The dominant Lewis structure generally produces FC of the smallest magnitude.
- N is more electronegative than C or S. Therefore, we expect any negative FC to reside on the N atom.
- Hence, the dominant Lewis structure is

Oxidation Number, ON

- [IUPAC] The charge that would be left on an atom if all es of each bond ending up at that atom were attributed to the most electronegative atom.
- The concept of electronegativity is the basis of these numbers. An atom's ON is the charge the atom would have if its bonds were completely ionic.
  - in determining ON, all shared es are counted with the more electronegative atom.
- A hypothetical charge acquired by the element due to its existence in a compound.

Rules of assigning ON

Simple binary ionic compound, NaCl

- is the number of e’s gained or lost by an atom upon the formation of this compound.
- It corresponds to the actual charge on the ion.

Molecular species

ON is assigned based on an arbitrary set of rules:

- Generally, the element farther to the right and higher up in PT is assigned a negative ON, and the element farther to the left and lower down in the periodic table is assigned a positive ON.

- Keep first in mind that:
  - ✓ ON are always assigned on a per atom basis ($K_2Cr_2O_7$).
  - ✓ Treat the rules in order of decreasing

Rules

1. The ON of the atoms in any free, uncombined element is zero. This includes polyatomic elements such as H_2, O_2, O_3, P_4, and S_8.

2. The ON of an element in a simple (**monatomic**) ion (e.g., Cl^-) is equal to the charge on the ion.

3. Sum of ONs of all atoms in a neutral compound is zero.

4. In a polyatomic ion, the sum of ONs of the constituent atoms is equal to the charge on the ion.

5. Fluorine has an ON of –1 in its compounds.

6. Hydrogen has an ON of 1 in compounds unless it is combined with metals, in which case it has an ON of –1. Examples of these exceptions are NaH and CaH_2.

7. Oxygen usually has an ON of –2 in its compounds. Exceptions:

a. Oxygen has an ON of –1 in hydrogen peroxide, H_2O_2, and in peroxides, which contain the O_2^{2-} ion; e.g., CaO_2 and Na_2O_2.

b. Oxygen has an ON of –1/2 in superoxides, which contain the O_2^{-} ion; examples are KO_2 and RbO_2.

c. When combined with fluorine in OF_2, oxygen has an ON of +2.

8. The position of the element in the periodic table helps to assign its oxidation number:

a. Group IA elements have ONs of +1 in all compounds.

b. Group IIA elements have ONs of +2 in all compounds.

c. Group IIIA elements have ONs of +3 in all compounds, with a few rare exceptions.

d. Group VA (N & P) elements have ONs of –3 in binary compounds with metals, with H, or with NH_4^+. Exceptions are compounds with a Group VA element combined with an element to its right in the periodic table; in this case, their ONs can be found by using rules 3 and 4.

e. Group VIA (S & Se) elements below oxygen have ONs of –2 in binary compounds with metals, with H, or with NH_4^+. When these elements are combined with oxygen or with a lighter halogen, their ONs can be found by using rules 3 and 4.

Element	Common ON	Examples	Other ONs
H	+1	H_2O, CH_4, NH_4Cl	–1 in metal hydrides, NaH
GIA	+1	KCl, NaH, $RbNO_3$, K_2SO_4	None
GIIA	+2	$CaCl_2$, $Ba(NO_3)_2$, $SrSO_4$	None
GIIIA	+3	$AlCl_3$, BF_3, GaI_3	None in common Cpds
GIVA	+2 +4	CO, PbO, $SnCl_2$, $Pb(NO_3)_2$ CCl_4, SiO_2, $SnCl_4$	Many others for C and Si
GVA	–3 in binary Cpds with metals –3 in NH4+, binary Cpds with H	Mg_3N_2, Na_3P NH_3, PH_3	+3, NO_2^-, PCl_3 +5, NO_3^-, PO_4^{3-}
O	–2	H_2O, P_4O_{10}, Fe_2O_3, CaO, ClO_3^-	+2 in OF_2 –1 in peroxides, H_2O_2 –1/2 in superoxides, KO_2, RbO_2
GVIA other than O	–2 in binary cpds with metals and H –2 in binary cpds with NH4+	H_2S, CaS, Fe_2S_3, Na_2Se $(NH_4)_2S$, $(NH_4)_2Se$	+4 with O and lighter halogens, SO_2, SO_3^{2-}, SF_4 +6 with O and lighter halogens, SO_3, SF_6
GVIIA	–1 in binary cpds with metals and H –1 in binary cpds with NH_4^+	MgF_2, KI, $ZnCl_2$ NH_4Cl	Cl, Br, or I with O or with a lighter halogen +1, BrF, ClO^- +3, ICl_3, ClO_2^- +5, BrF_5, ClO_3^- +7, IF_7, ClO_4^-

9. Group VIIA elements have ONs of –1 in binary compounds with metals, with H, with NH_4^+, or with a heavier halogen. When these elements except fluorine (i.e., Cl, Br, I) are combined with oxygen or with a lighter halogen, their oxidation numbers can be found by using rules 3 and 4.

Problem

- Determine the oxidation numbers of nitrogen in the following species: (a) N_2O_4, (b) NH_3, (c) HNO_3, (d) NO_3^-, (e) N_2.

Plan ⇨

- We first assign **ONs** to elements that exhibit a single common ON.
- **Recall** that **ONs** are represented per atom and that the sum of the **ONs** in a neutral compound is zero, and the sum of the **ONs** in an ion equals the charge on the ion.

Solution

a) The ON of O is –2. The sum of ONs for all atoms in a compound must be zero:

Total ONs in $N_2O_4 = 2x + 4(-2) = 0 \Rightarrow x = +4$

(b) The ON of H is 1:

Total ONs in NH_3= x + 3(+1)= 0, ⇒ x = – 3

(c) ON of H =1 and ON of O is 2.

Total ONs in HNO_3 = 1 + x + 3(–2)= 0, ⇒ x = +5

(d) The sum of ONs for all atoms in an ion equals the charge on the ion:

Total ONs in NO_3^-= x + 3(– 2) = – 1, ⇒ x = +5

(e) N_2 : The ON of any free element is zero.

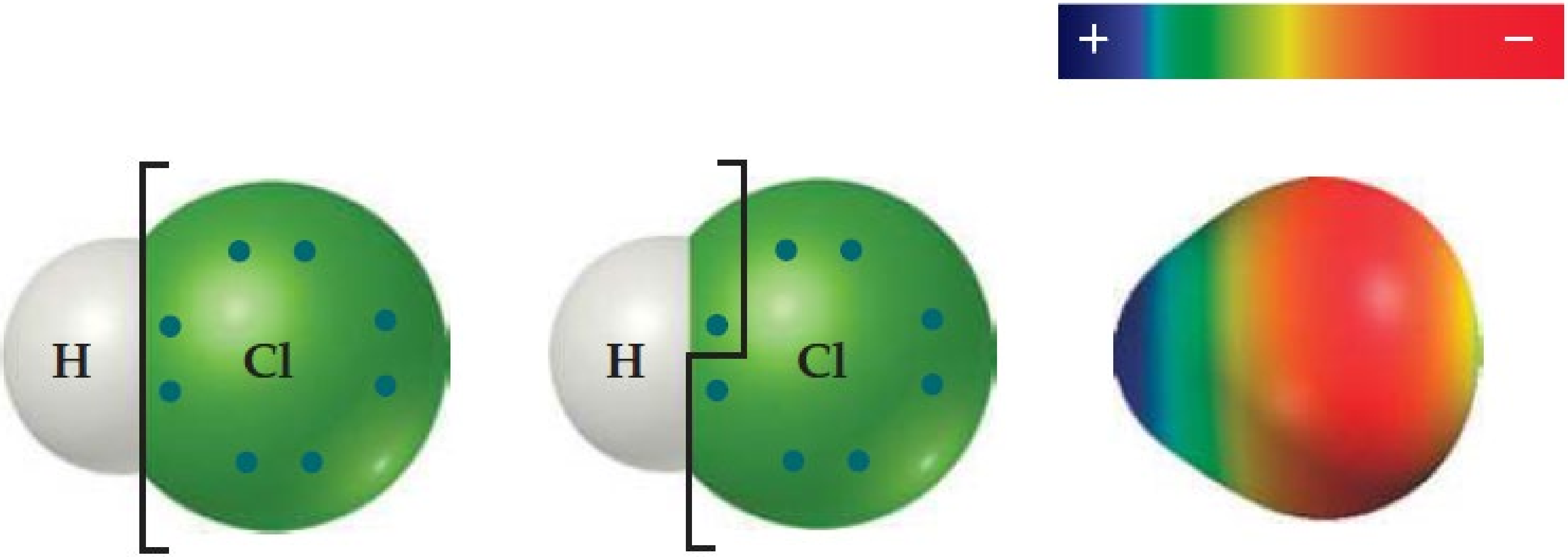
FC & ON

- FC calculations ignored the *EN* of elements, in contrast to ON.
- For HCl, ON assigned bonding es to Cl atom (most electronegative) to end up with 8 Ves on Cl atom (ON= −1) & 0 Ves on H atom (ON= +1).
- For HCl, FC assigned bonding es equally to the two bonded atoms; Cl atom has 7 Ves & H atom has 1 Ve (same as neutral atoms to end up with FCs of 0 on both atoms).
- Neither ON (*overstates the role of EN*) nor FC (*ignore the role of EN*) gives an accurate depiction of the actual charges on atoms .

Actual Charge's Share

- Cl has an *EN* of 3.0, while *EN* of H is 2.1.
- Cl atom might therefore be expected to have roughly $\frac{3.0}{3.0+2.1} = 0.59$ of electrical charge in the bonding pair, whereas the H atom would have 0.41 of the charge.
- Because the bond consists of 2 es, the Cl atom's share is 0.59 × 2e = 1.18e, or 0.18e more than the neutral Cl atom.
- This gives rise to a partial negative charge of 0.18– on Cl and a partial positive charge of 0.18+ on H. (agrees with dipole moment measurements 0.178+ on H & 0.178– on Cl)
- In contrast to ON and FC, signs + or – is written after number in actual charges)

HCl



(a) (b) (c)

ON

FC

electron-density distribution

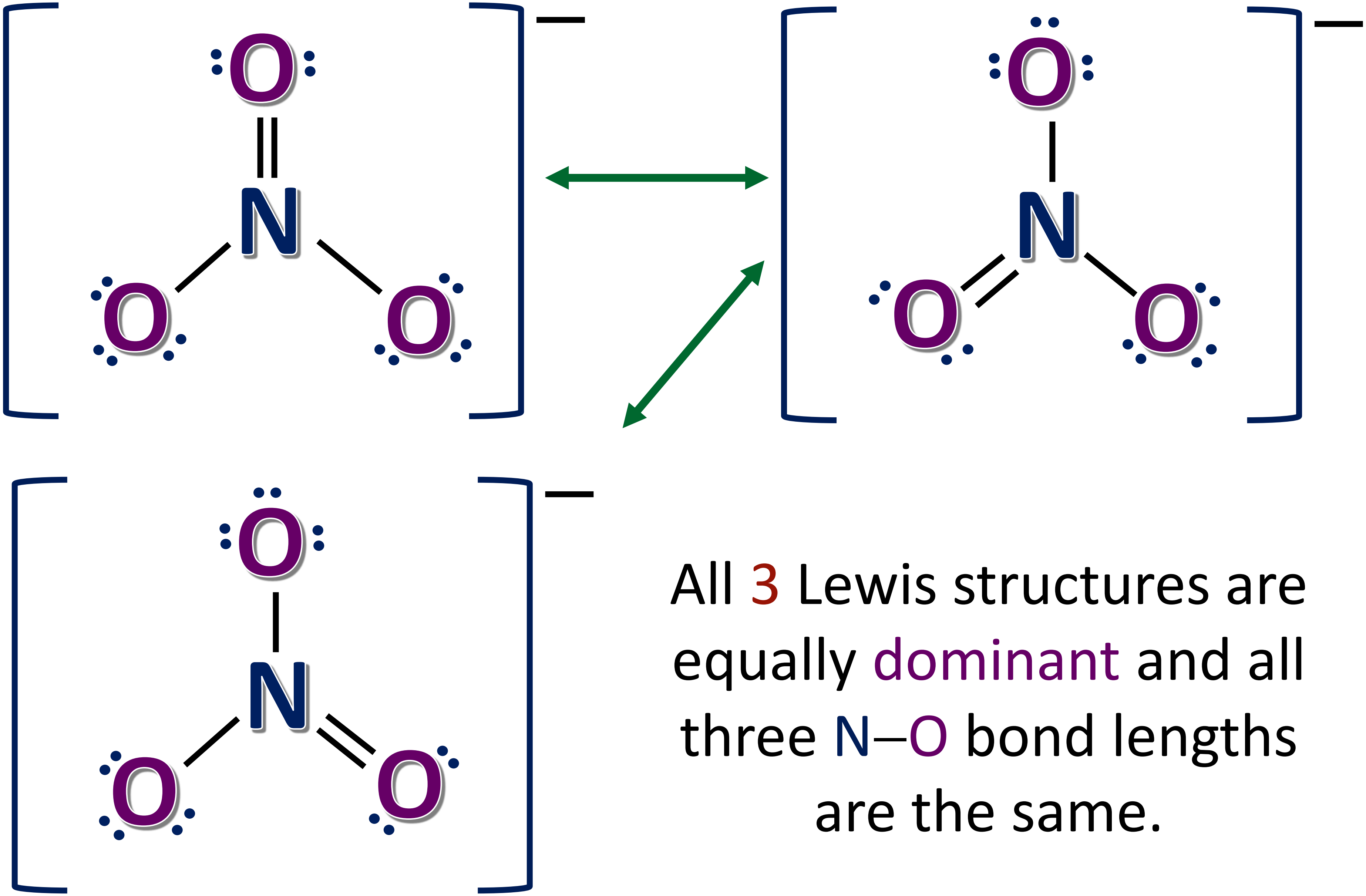
Resonance Structures

Completely equivalent Lewis structures having different placement of electrons.

Ozone

- ○ Ozone always has 2 equivalent O–O bonds whose lengths are intermediate between the lengths of an O–O single bond and an O=O double bond.

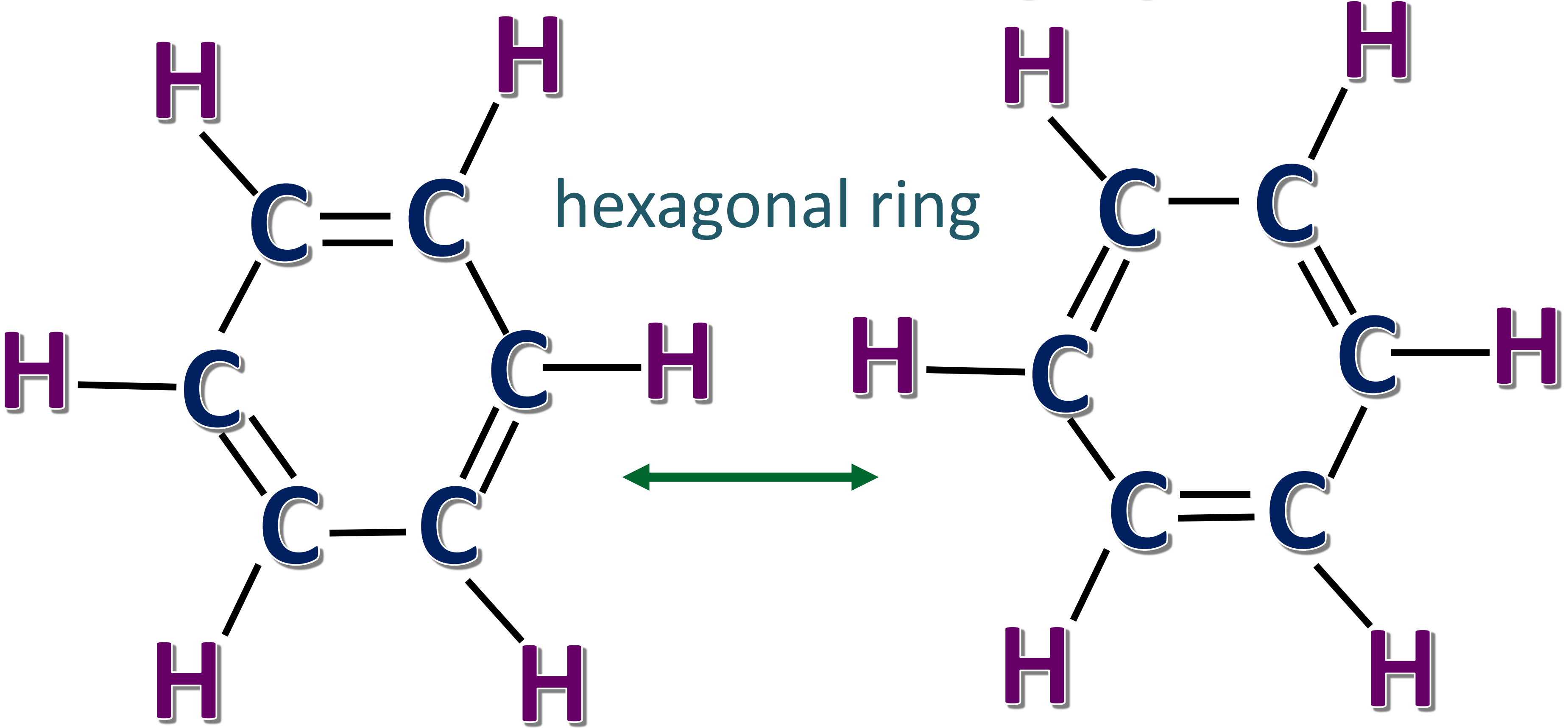
Nitrate, NO_3^-



All 3 Lewis structures are equally dominant and all three N–O bond lengths are the same.

○ For some molecules or ions, all possible Lewis structures may not be equivalent; where one or more resonance structures are more dominant than others.

Benzene, C_6H_6



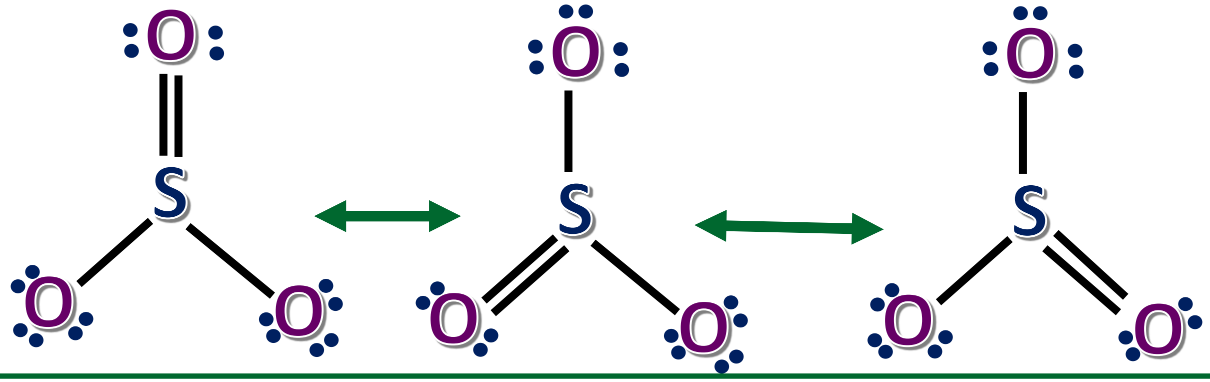
hexagonal ring

- Experimental data show that all six C–C bonds are of equal length, 140 pm, intermediate between the typical bond lengths for a C–C single bond (154 pm) and a C=C double bond (134 pm).
- Each of the C–C bonds in benzene can be thought of as a blend of a single bond and a double bond.
- The bonding arrangement in benzene confers special stability to the molecule. As a result, millions of organic compounds contain the six-membered ring characteristic of benzene.

Exercise

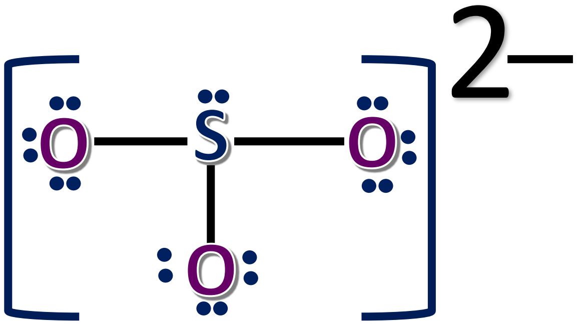
- Which is predicted to have the shorter sulfur–oxygen bonds, SO_3 or SO_3^{2-} ?

Solution



S–O bond length in SO_3 should be between length of a single bond and length of a double bond, i.e., should be shorter than single bonds but not as short as double bonds.

SO_3 should have the shorter S–O bonds and SO_3^{2-} the longer ones.



Exceptions to the Octet Rule

- The octet rule is so simple and useful in introducing the basic concepts of bonding that you might assume it is always obeyed.
  - It is limited in dealing with ionic compounds of the transition metals.
  - It fails in many situations involving covalent bonding.
- These exceptions to the octet rule are of three main types:

1) Molecules and polyatomic ions containing an odd number of electrons.
2) Molecules and polyatomic ions in which an atom has fewer than an octet of valence electrons.
3) Molecules and polyatomic ions in which an atom has more than an octet of valence electrons

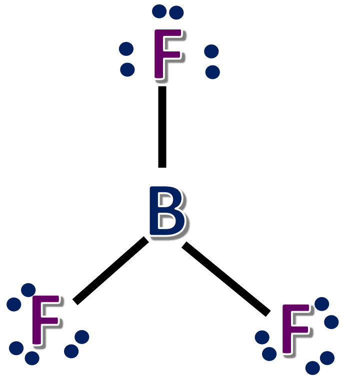
Odd Number of Ves

5+ 6 = 11 Ves

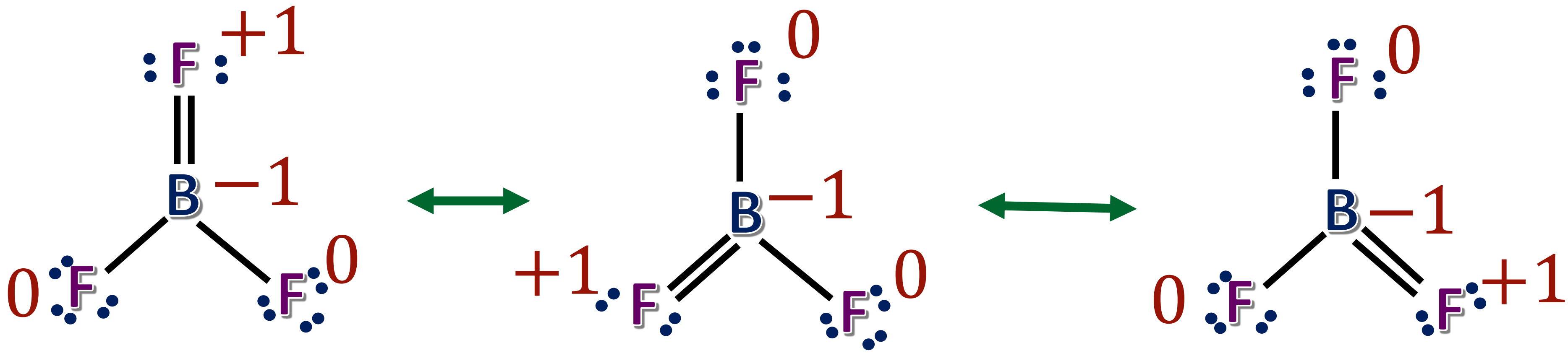
- In a few molecules and polyatomic ions, such as ClO_2, NO, NO_2, and O_2^-, the number of Ves is odd.
- Complete pairing of these es is impossible, and an octet around each atom cannot be achieved.

Less Than an Octet of Ves

- BF_3 has only 6 es around the boron atom. This gives the following structure with FC of 0 around B & F.

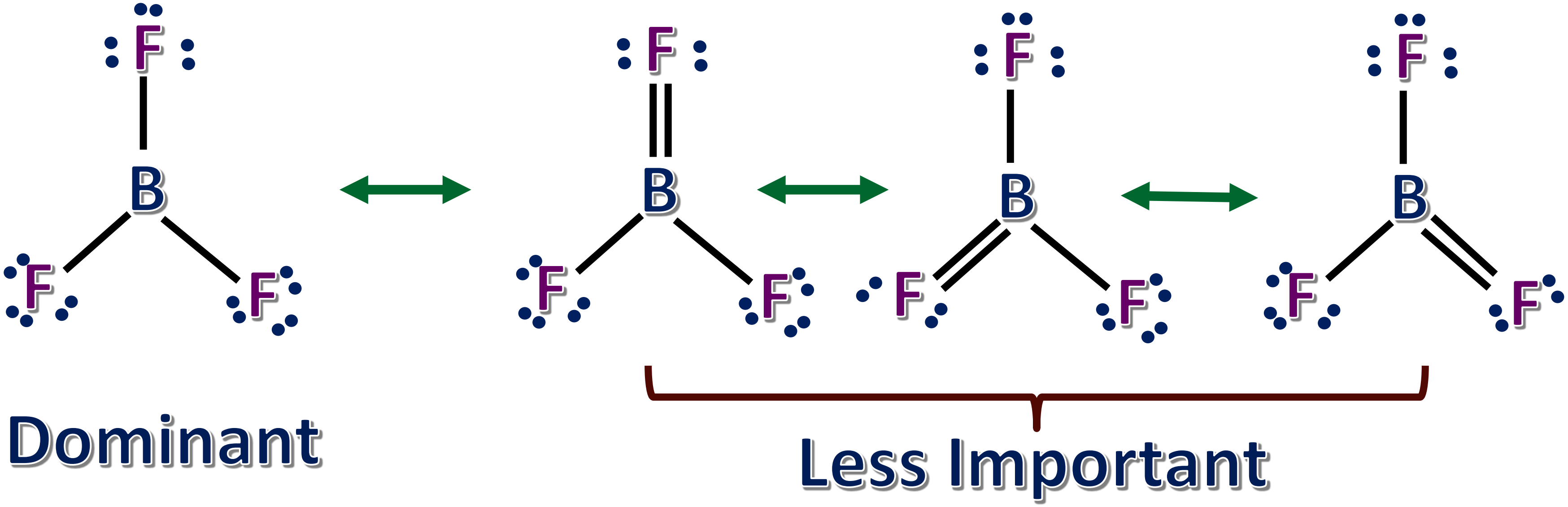


- One way to complete the octet around B:



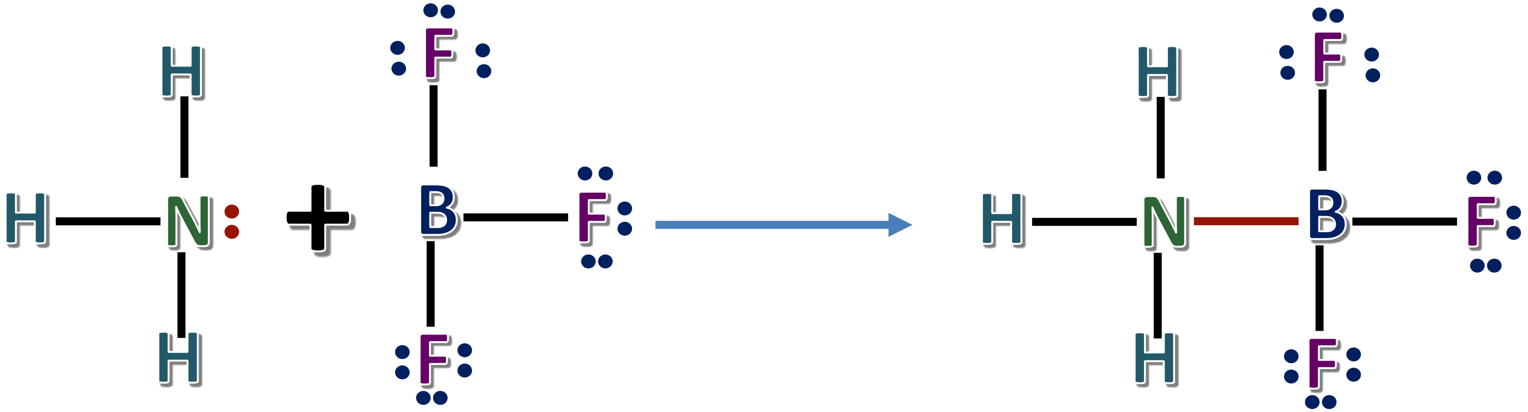
- Each of them forces a F atom to share additional es with B, which is inconsistent with the high EN of F.

- FCs tell us that this is an unfavorable situation. In each structure, the F atom involved in the B=F double bond has a formal charge of +1, while the less electronegative B atom has a formal charge of −1.



Reactivity of BF_3

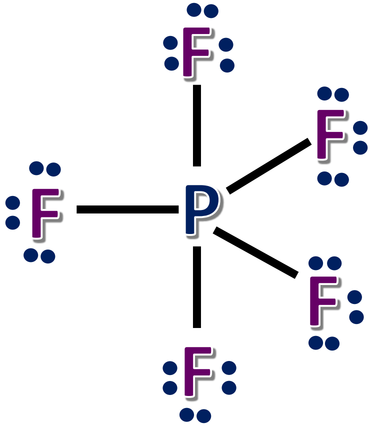
- Confirms its presence in the dominant structure.
- It reacts energetically with molecules having an unshared pair of electrons that can be used to form a bond with B,



In the stable compound NH_3BF_3, B has an octet of Ves

More Than an Octet of Ves (largest class)

- PF_5: we are forced to place 10 es around the central P atom:



- Molecules and ions with more than an octet of electrons around the central atom are often called hypervalent.

- Other examples of hypervalent species are SF_4, AsF_6^-, and ICl_4^-.

Hypervalent molecules

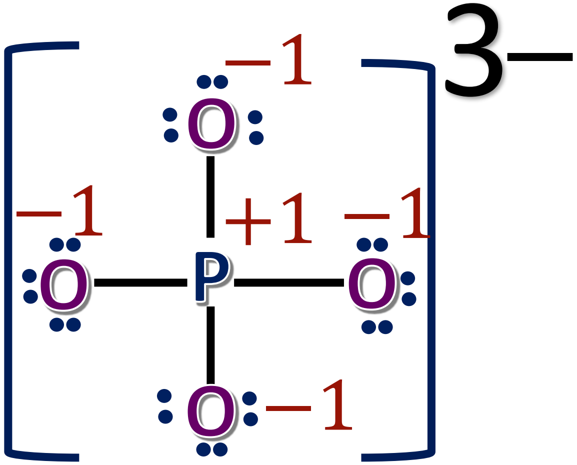
- are formed only for central atoms from Period 3 and below in the PT due to the relatively larger size of the central atom.
  - For example, a P atom is large enough that five F (or even five Cl) atoms can be bonded to it without being too crowded.
  - By contrast, an N atom is too small to accommodate five atoms bonded to it (NCl_5 and OF_4, do not exist.).
- Because size is a factor, hypervalent molecules occur most often when the central atom is bonded to the smallest and most electronegative atoms—F, Cl, and O.

Hypervalency

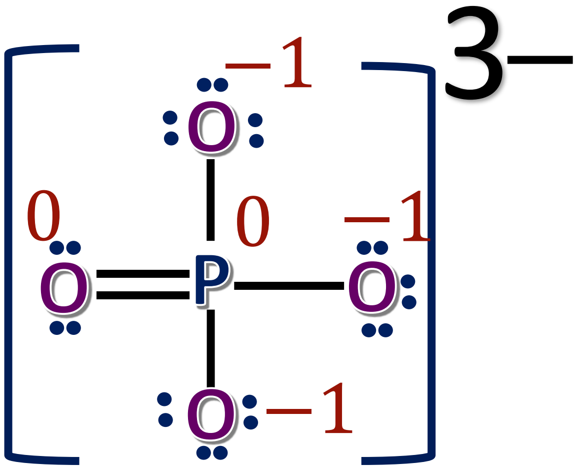
- Accommodation of a valence shell more than 8 es is also consistent with the presence of unfilled nd orbitals in atoms from Period 3 and below.
  - Elements of the second period have only the 2s and 2p valence orbitals for bonding.
- Theoretical work on the bonding in molecules such as PF_5 and SF_6 suggests that the presence of unfilled 3d orbitals in P and S has a relatively minor impact on the formation of hypervalent molecules.
- Most chemists now believe that the larger size of the atoms from Periods 3 through 6 is more important to explain hypervalency than is the presence of unfilled d orbitals.

Octet rule vs. FC

- If you have to choose between satisfying the octet rule and obtaining the most favorable formal charges by using more than an octet of es.



P atom obeys the octet rule



FC is minimum

multiple Lewis structures can contribute to the actual electron distribution in an atom or molecule

Strengths and Lengths of Covalent Bonds

The stability of a molecule is related to the strengths of its covalent bonds (assessed from their enthalpies)

- Multiple bonds are generally stronger than single bonds.

C—C	C=C	C≡C
154 pm	134 pm	120 pm
348 kJ/mol	614 kJ/mol	839 kJ/mol

TABLE 8.3 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O=O	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

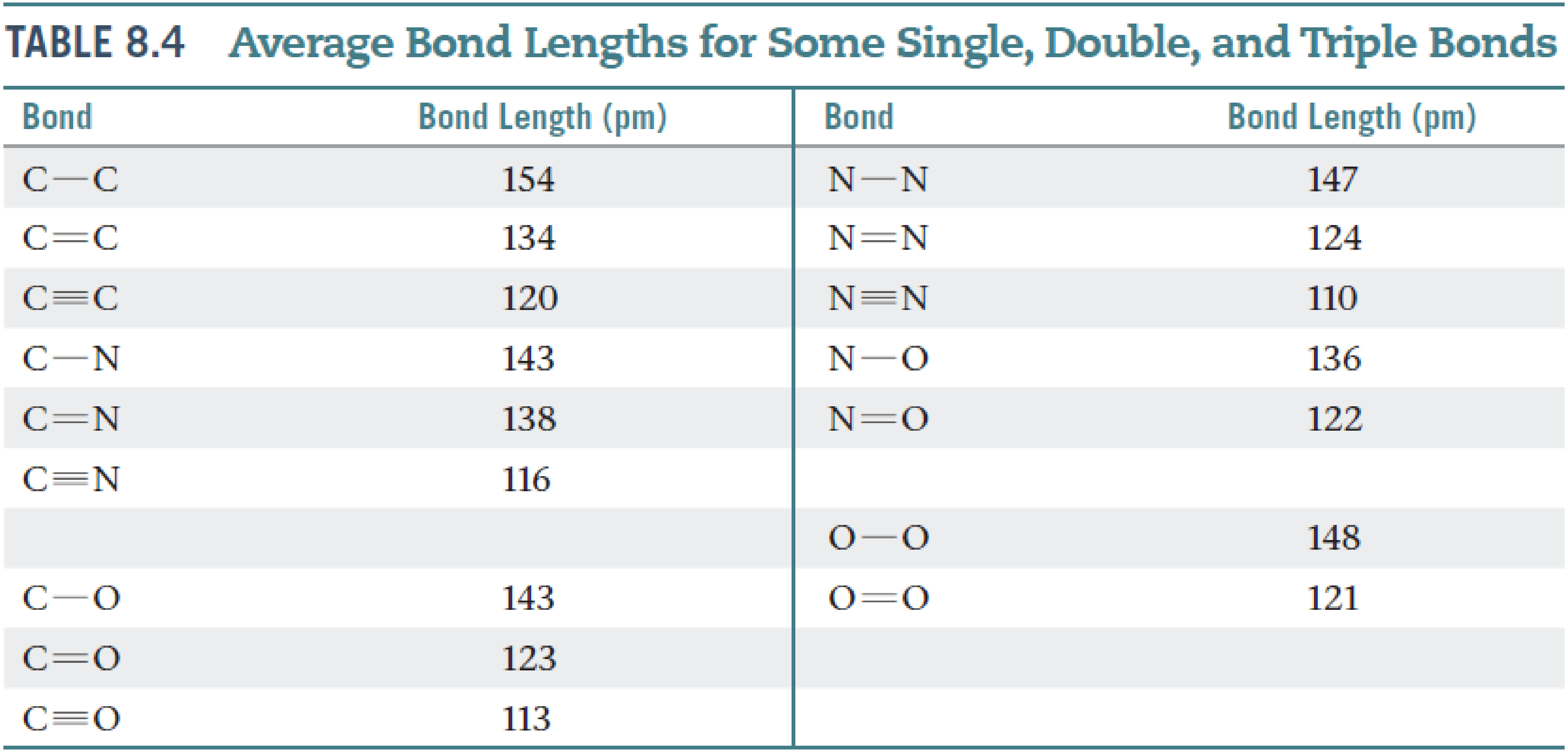
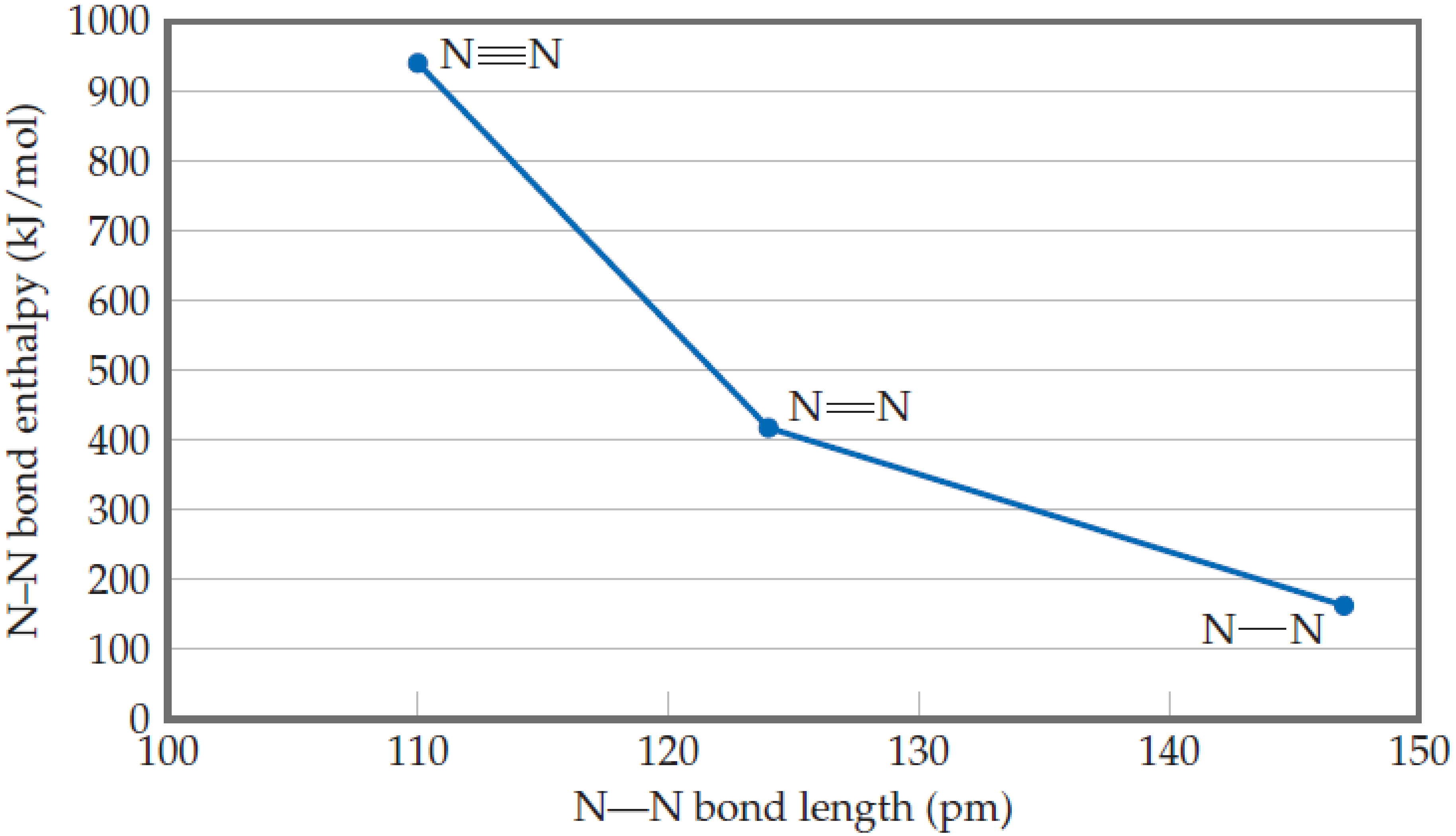


TABLE 8.4 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (pm)	Bond	Bond Length (pm)
C—C	154	N—N	147
C=C	134	N=N	124
C≡C	120	N≡N	110
C—N	143	N—O	136
C=N	138	N=O	122
C≡N	116		
		O—O	148
C—O	143	O=O	121
C=O	123		
C≡O	113		

- As the number of bonds between two atoms increases, the bond grows shorter and stronger.


N≡N
N═N
N—N
N–N bond enthalpy (kJ /mol)
1000
900
800
700
600
500
400
300
200
100
0
100
110
120
130
140
150
N—N bond length (pm)

Exercise

- Phosgene has the following elemental composition: 12.14% C, 16.17% O, and 71.69% Cl by mass. Its molar mass is 98.9 g/mol.
- Determine the molecular formula of this compound.
- Draw three Lewis structures for the molecule that satisfy the octet rule for each atom. (The Cl and O atoms bond to C)
- Using formal charges, determine which Lewis structure is the dominant one.
- Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from CO(g) and Cl_2(g).

Solution

Empirical formula

$$(12.14\ g\ C)\left(\frac{1\ mol\ C}{12.01\ g\ C}\right) = 1.011\ mol\ C$$

$$(16.17\ g\ O)\left(\frac{1\ mol\ O}{16.00\ g\ O}\right) = 1.011\ mol\ O$$

$$(71.69\ g\ Cl)\left(\frac{1\ mol\ Cl}{35.45\ g\ Cl}\right) = 2.022\ mol\ Cl$$

Empirical formula is $COCl_2$

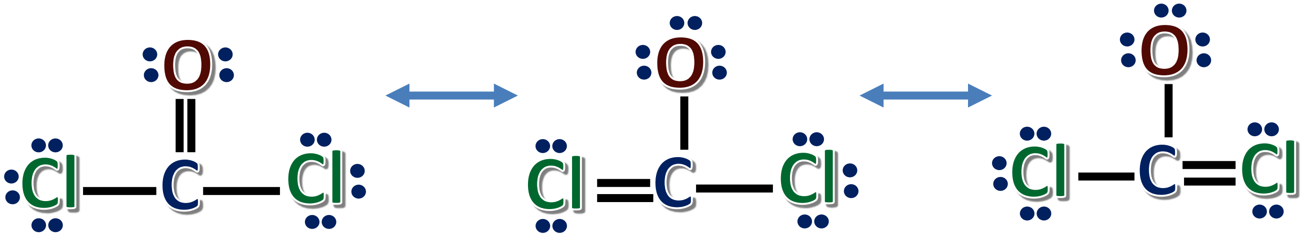
Molar mass of Empirical formula

=12.01 + 16.00 + 2(35.45) = 98.91 g/mol

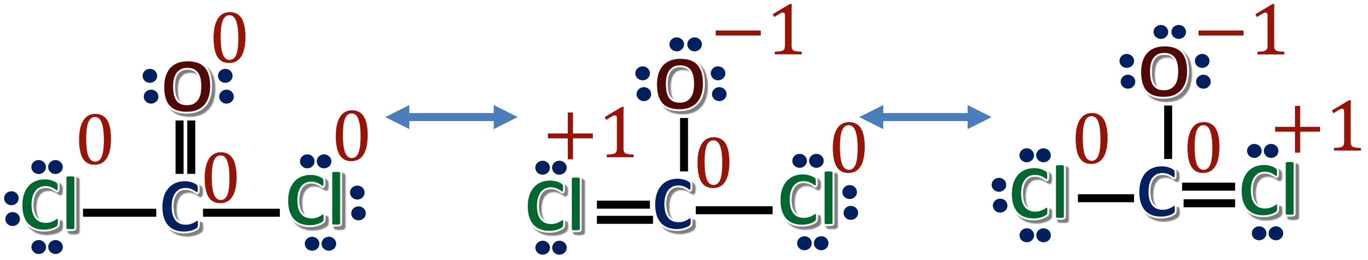
$COCl_2$ is the molecular formula

Lewis structures

Ves= 4 + 6 + 2(7) = 24



FC



Chemical equation

Rx involves breaking a C≡O bond (1072 kJ) and a Cl–Cl (242 kJ) bond and forming a C=O bond (799 kJ) and two C–Cl bonds (328 kJ each).

$$\Delta H = [1027 + 242] - [799 + 2(328)] = -141\,kJ$$

Exothermic

- ○ Nevertheless, energy is needed from sunlight or another source for the reaction to begin, as is the case for the combustion of H_2(g) and O_2(g) to form H_2O(g).

Thank You