Petrucci's

GENERAL CHEMISTRY

Principles and Modern Applications

TWELFTH EDITION

Petrucci | Herring | Madura | Bissonnette

Periodic Table of the Elements†

Period	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** 1.008																	2 **He** 4.0026
2	3 **Li** 6.94	4 **Be** 9.0122											5 **B** 10.81	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.180
3	11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.085	15 **P** 30.974	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.948
4	19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.867	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.933	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.630	33 **As** 74.922	34 **Se** 78.97	35 **Br** 79.904	36 **Kr** 83.798
5	37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.95	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
6	55 **Cs** 132.91	56 **Ba** 137.33	57–71 **La–Lu**	72 **Hf** 178.49	73 **Ta** 181.0	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89–103 **Ac–Lr**	104 **Rf** (267)	105 **Db** (268)	106 **Sg** (269)	107 **Bh** (270)	108 **Hs** (269)	109 **Mt** (277)	110 **Ds** (281)	111 **Rg** (282)	112 **Cn** (285)	113 **Nh** (286)	114 **Fl** (290)	115 **Mc** (290)	116 **Lv** (293)	117 **Ts** (294)	118 **Og** (294)

*Lanthanide series	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.01	71 **Lu** 174.97
†Actinide series	89 **Ac** (227)	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Atomic masses are relative to carbon-12. For certain radioactive elements, the numbers listed (in parentheses) are the mass numbers of the most stable isotopes. The scheme for numbering of groups is explained on page 80. The metals are 🟨 and the nonmetals are 🟦. Metalloids are indicated by 🟩. The noble gases are 🟥.

†Based on the version endorsed by the International Union of Pure and Applied Chemistry (IUPAC) on May 4, 2022.

Notes:

1. Atomic masses are from Pure Appl. Chem. Vol. 85, No. 5, pp. 1047–1078, 2013. They are given here with five significant figures where possible.
2. For H, Li, B, C, N, O, Mg, Si, S, Cl, Br, and Tl, the *conventional atomic mass*, a representative value from the *atomic mass interval*, is provided. (See page 77.)

$$\text{FC} = \text{number valence e}^- \text{ in free atom} - \text{number lone-pair e}^- - \frac{1}{2}\,\text{number bond-pair e}^- \qquad \textbf{(10.16)}$$

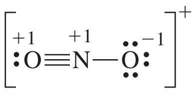
Now, let us assign formal charges to the atoms in structure (10.15), proceeding from left to right.

$:\!\text{O}\!\equiv$ FC $= 6$ valence e^- in O $-$ 2 lone-pair e^- $- \frac{1}{2}$ (8 bond-pair e^-) $= 6 - 2 - 3 = +1$

$\equiv\!\text{N}\!-$ FC $= 5$ valence e^- in N $-$ 0 lone-pair e^- $- \frac{1}{2}$ (8 bond-pair e^-) $= 5 - 0 - 4 = +1$

$-\ddot{\underset{..}{\text{O}}}\!:$ FC $= 6$ valence e^- in O $-$ 6 lone-pair e^- $- \frac{1}{2}$ (2 bond-pair e^-) $= 6 - 6 - 1 = -1$

Formal charges in a Lewis structure can be shown by using small numbers.



$$\left[\overset{+1}{:\!\text{O}}\!\equiv\!\overset{+1}{\text{N}}\!-\!\overset{-1}{\ddot{\underset{..}{\text{O}}}}\!:\right]^+$$

(10.17)

The following are general rules that can help to determine the plausibility of a Lewis structure based on its formal charges.

- The sum of the formal charges in a Lewis structure must equal *zero* for a neutral molecule and must equal the magnitude of the charge for a polyatomic ion. [Thus for structure (10.17), this sum is $+1 + 1 - 1 = +1$.]
- Where formal charges are required, they should be as small as possible.
- Negative formal charges usually appear on the most electronegative atoms; positive formal charges, on the least electronegative atoms.
- Structures having formal charges of the same sign on adjacent atoms are unlikely.

◀ We will see some exceptions to the idea that formal charges should be kept to a minimum in Section 10-6.

Lewis structure (10.17) conforms to the first two rules, but is not in good accordance with the third rule. Despite the fact that O is the most electronegative element in the structure, one of the O atoms has a positive formal charge. The greatest failing, though, is in the fourth rule. Both the O atom on the left and the N atom adjacent to it have positive formal charges. Structure (10.17) is not the most satisfactory Lewis structure. By contrast, the Lewis structure of $\text{NO}_2{}^+$ derived in Example 10-7 has only one formal charge, +1, on the central N atom. It conforms to the rules completely and is the most satisfactory Lewis structure.

EXAMPLE 10-8 Using Formal Charges in Writing Lewis Structures

Write the most plausible Lewis structure of nitrosyl chloride, NOCl, one of the oxidizing agents present in *aqua regia*, a mixture of concentrated nitric and hydrochloric acids capable of dissolving gold.

Analyze

Although the formula is written as NOCl, we can reject the skeletal structure N—O—Cl because it places the most electronegative atom as the central atom. (We are asked to consider N—O—Cl in Practice Example A.) Having ruled out N—O—Cl as a possible skeletal structure, we are left with the following as possibilities:

$$\text{O—Cl—N and O—N—Cl}$$

(continued)

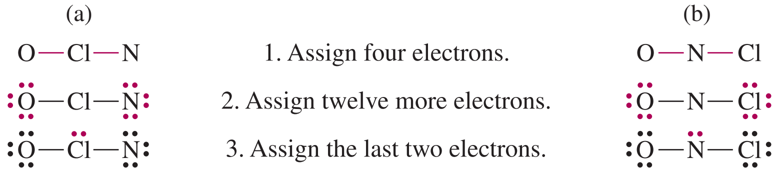
To determine the best structure, we must first complete the skeletal structures and then assign formal charges. The best structure will have the fewest and smallest formal charges.

Solve

Regardless of the skeletal structure chosen, the number of valence electrons (dots) and bonds that must appear in the final Lewis structure is

$$5 \text{ from N} + 6 \text{ from O} + 7 \text{ from Cl} = 18$$

When we apply the four steps listed below to the two possible skeletal structures, we obtain a total of four Lewis structures—two for each skeletal structure. This doubling occurs because in step 4, there are two ways to complete the octets of the central atoms. The final Lewis structures obtained are labeled (a_1), (a_2), (b_1), and (b_2).



1. Assign four electrons.
2. Assign twelve more electrons.
3. Assign the last two electrons.
4. Complete the octet on the central atom.

Evaluate formal charges by using equation (10.16). In structure (a_1),

for the N atom,

$$\text{FC} = 5 - 6 - \frac{1}{2}(2) = -2$$

for the O atom,

$$\text{FC} = 6 - 4 - \frac{1}{2}(4) = 0$$

for the Cl atom,

$$\text{FC} = 7 - 2 - \frac{1}{2}(6) = +2$$

Proceed in a similar manner for the other three structures. Summarize the formal charges for the four structures.

	(a_1)	**(a_2)**	**(b_1)**	**(b_2)**
N:	−2	−1	0	0
O:	0	−1	0	−1
Cl:	+2	+2	0	+1

Select the best Lewis structure in terms of the formal-charge rules. First, note that all four structures obey the requirement that formal charges of a neutral molecule add up to zero. In structure (a_1), the formal charges are large (+2 on Cl and −2 on N) and the negative formal charge is not on the most electronegative atom. Structure (a_2) has formal charges on all atoms, one of them large (+2 on Cl). Structure (b_1) is the ideal we seek—no formal charges. In structure (b_2), we again have formal charges. The best Lewis structure of nitrosyl chloride is

Assess

Based on structure (b_1), ONCl is a better way to write the formula of nitrosyl chloride.

PRACTICE EXAMPLE A: Write a Lewis structure for nitrosyl chloride based on the skeletal structure N—O—Cl, and show that this structure is not as plausible as the one obtained in Example 10-8.

PRACTICE EXAMPLE B: Write two Lewis structures for cyanamide, NH_2CN, an important chemical of the fertilizer and plastics industries. Use the formal charge concept to choose the more plausible structure.

10-5 Concept Assessment

For molecules, the most satisfactory Lewis structure may have no formal charges (FC = 0) in some cases and formal charges in others. For polyatomic ions, minimally the most satisfactory Lewis structure has a formal charge on at least one atom. Explain the basis of these observations.

10-1 ARE YOU WONDERING?

Do formal charges represent actual charges on the atoms?

Formal charges are not actual charges, which can be seen from a comparison of the electrostatic potential map of the HCN molecule and the formal charges derived from the Lewis structure.

Although the formal charges are all zero, the electrostatic potential map shows that the H atom in the HCN molecule is slightly positive (blue) and that the nitrogen atom is slightly negative (red). In molecules, the true charges on atoms are usually, but not always, between +1 and −1. For example, in the HCl molecule, the charge on H is about +0.17 and that on Cl is about −0.17. (See page 475.)

The method used for assigning formal charges is really just a form of "electron bookkeeping." In this text, we have now discussed two different concepts—oxidation states and formal charges—that are used for electron bookkeeping. Oxidation states and formal charges are both very useful. They are compared in the table below.

	Interpretation	Comments
Oxidation state	The charge an atom would have if the bonding electrons in each bond were *transferred* to the more electronegative atom.	• The oxidation state concept tends to exaggerate the ionic character of the bonding between atoms. • Oxidation states are used to predict and rationalize chemical properties of compounds.
Formal charge	The charge an atom would have if the bonding electrons in each bond were *divided equally* between the two atoms involved.	• The formal charge concept tends to exaggerate the covalent character of the bonding between atoms. • Formal charges are used to assess which Lewis structure is the most satisfactory representation of the true structure.

For many molecules, the bonding is closer to being "pure covalent" than it is to being "pure ionic" and so the formal charge on an atom is often—but not always—numerically closer to the true charge. That's why we focus on formal charges when assessing the relative importance of different Lewis structures. That being said, it is important to emphasize that chemists still question and debate whether it is true that the best structure is the one having the fewest and smallest formal charges.

10-5 Resonance

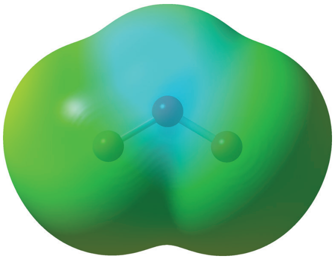
The ideas presented in the previous section allow us to write many Lewis structures, but some structures still present problems. We describe these problems in the next two sections.

Although we usually think of the formula of oxygen as O_2, there are actually two different oxygen molecules. Familiar oxygen is *dioxygen*, O_2; the other molecule is *trioxygen*—ozone, O_3. The term used to describe the existence of two or more forms of an element that differ in their bonding and molecular structure is *allotropy*—O_2 and O_3 are allotropes of oxygen. Ozone is found naturally in the stratosphere and is also produced in the lower atmosphere as a constituent of smog.

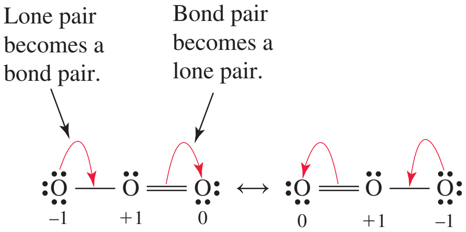
When we apply the usual rules for Lewis structures for ozone, we come up with these *two* possibilities.

▶ Bond lengths are discussed more fully in Section 10-8.

Each structure suggests that one oxygen-to-oxygen bond is single and the other is double. Yet experimental evidence indicates that the two oxygen-to-oxygen bonds are the same; each has a length of 127.8 pm. This bond length is shorter than the O—O single-bond length of 147.5 pm in hydrogen peroxide, H—Ö—Ö—H, but it is longer than the double-bond length of 120.74 pm in diatomic oxygen, :Ö=Ö:. The bonds in ozone are intermediate between a single and a double bond. The difficulty is resolved if we say that the true Lewis structure of O_3 is *neither* of the previously proposed structures but a composite, or *hybrid*, of the two, a fact that we can represent as



▲ **Electrostatic potential map of ozone**
All the atoms in an ozone molecule have the same electronegativity and yet the distribution of electron density is nonuniform. The reason will become apparent when we describe in a more sophisticated way the bonding in this molecule.



(10.18)

The situation in which two or more plausible Lewis structures contribute to the "correct" structure is called **resonance**. The true structure is a *resonance hybrid* of plausible contributing structures. Acceptable contributing structures to a resonance hybrid must all have the same skeletal structure (the atomic positions cannot change); they can differ only in how electrons are distributed within the structure. In expression (10.18), the two contributing structures are joined by a double-headed arrow. The arrow does *not* mean that the molecule has one structure part of the time and the other structure the rest of the time. *It has the same structure all the time*. By averaging the single bond in one structure with the double bond in the other, we might say that the oxygen-to-oxygen bonds in ozone are halfway between a single and double bond, that is, 1.5 bonds. The fact that the electrons in ozone are distributed over the whole molecule so as to produce two equivalent bonds is readily seen in the electrostatic potential map of ozone, shown in the margin.

The two resonance structures in expression (10.18) are equivalent; that is, they contribute equally to the structure of the resonance hybrid. In many cases, several contributing resonance structures do not contribute equally. For example, consider the azide anion, N_3^-, for which three resonance structures are given below.

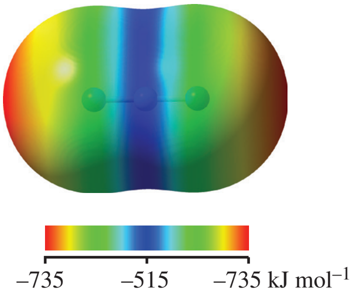
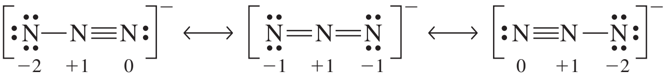


Figure 10-9 **Electrostatic potential map of the azide ion**

The electrostatic potential near the terminal N atoms is more negative than it is for the central N atom. This observation indicates that the central structure (at the bottom of this page) is the most important resonance structure for the N_3^- ion.



We can decide which resonance structure likely contributes most to the hybrid by applying the general rules for formal charges (page 457). The central resonance structure avoids the unlikely large formal charge of −2 found on an N atom in the other two structures. Consequently, we expect that the structure $^{-}\underset{..}{\overset{..}{N}}{=}\overset{+}{N}{=}\underset{..}{\overset{..}{N}}^{-}$ contributes most to the resonance hybrid of the azide anion. This choice is supported by the electrostatic potential map shown in Figure 10-9.

EXAMPLE 10-9 Representing the Lewis Structure of a Resonance Hybrid

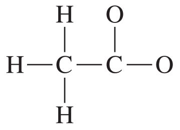
Write the Lewis structure of the acetate ion, CH_3COO^-.

Analyze

A key concept is that resonance structures differ only in how electrons are distributed within the structure. We cannot change the positions of the atoms. First, we draw a skeletal structure (see the electrostatic potential map below), and then we complete it by using the strategy we've used previously. Finally, we generate additional structures (resonance structures) by moving electron pairs.

Solve

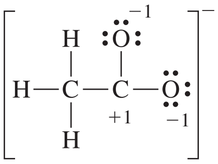
The skeletal structure has the three H atoms as terminal atoms bonded to a C atom as a central atom. The second C atom is also a central atom bonded to the first. The two O atoms are terminal atoms bonded to the second C atom.



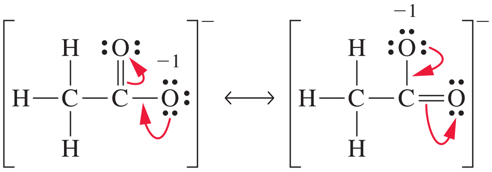
The number of valence electrons (dots) that must appear in the Lewis structure is

$$\underset{\text{From H}}{(3\times 1)} + \underset{\text{From C}}{(2\times 4)} + \underset{\text{From O}}{(2\times 6)} + \underset{\substack{\uparrow \\ \text{To establish charge of } 1-}}{1} = 3 + 8 + 12 + 1 = 24$$

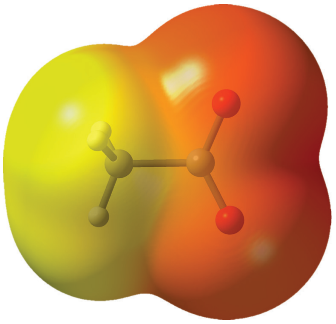
Twelve of the valence electrons are used in the bonds in the skeletal structure, and the remaining twelve are distributed as lone-pair electrons on the two O atoms.



In completing the octet of the C atom on the right, we discover that we can write two completely equivalent Lewis structures, depending on which of the two O atoms furnishes the lone pair of electrons to form a carbon-to-oxygen double bond. The true Lewis structure is a resonance hybrid of the following two contributing structures.



(10.19)



▲ **Acetate anion**

Assess

Even though the formal process of converting one resonance structure to another moves electrons, resonance is not meant to indicate the motion of electrons. The acetate anion has a structure that is a composite of the two resonance forms that we have constructed.

PRACTICE EXAMPLE A: Draw Lewis structures to represent the resonance hybrid for the SO_2 molecule.

PRACTICE EXAMPLE B: Draw Lewis structures to represent the resonance hybrid for the nitrate ion.

10-6 Concept Assessment

Is resonance possible in the acetic acid (CH_3CO_2H) molecule? Explain.

10-6 Exceptions to the Octet Rule

The octet rule has been our mainstay in writing Lewis structures, and it will continue to be one. Yet at times, we must depart from the octet rule, as we will see in this section.

Odd-Electron Species

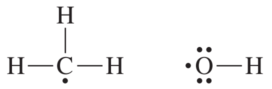
The molecule NO has 11 valence electrons, an odd number. If the number of valence electrons in a Lewis structure is odd, there must be an unpaired electron somewhere in the structure. Lewis theory deals with electron pairs and does not tell us where to put the unpaired electron; it could be on either the N or the O atom. To obtain a structure free of formal charges, however, we will put the unpaired electron on the N atom.

$$\cdot\ddot{\mathrm{N}}{=}\ddot{\mathrm{O}}\colon$$

The presence of unpaired electrons causes odd-electron species to be paramagnetic. NO is paramagnetic. Molecules with an even number of electrons are expected to have all electrons paired and to be diamagnetic. An important exception is seen in the case of O_2, which is paramagnetic despite having 12 valence electrons. Lewis theory does not provide a good electronic structure for O_2, but the molecular orbital theory that we will consider in the next chapter is much more successful.

▶ Experimental evidence for the paramagnetism of O_2 is shown in Figure 10-3.

The number of stable odd-electron molecules is quite limited. More common are **free radicals**, or simply *radicals*, highly reactive molecular fragments with one or more unpaired electrons. The formulas of free radicals are usually written with a dot to emphasize the presence of an unpaired electron, such as in the *methyl* radical, $\cdot CH_3$, and the *hydroxyl* radical, $\cdot OH$. The Lewis structures of these two free radicals are



$$\mathrm{H}{-}\underset{\cdot}{\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}{-}\mathrm{H} \qquad \cdot\underset{\cdot\cdot}{\ddot{\mathrm{O}}}{-}\mathrm{H}$$

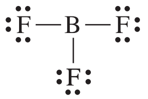
Both of these free radicals are commonly encountered as transitory species in flames. In addition, $\cdot OH$ is formed in the atmosphere in trace amounts as a result of photochemical reactions.

$$\cdot OH + CO \longrightarrow CO_2 + \cdot H$$

Many important atmospheric reactions involve free radicals as reactants, such as in the above oxidation of CO to CO_2. Free radicals, because of their unpaired electron, are highly reactive species. The hydroxyl radical, for example, is implicated in DNA damage that can lead to cancer.

Incomplete Octets

Our initial attempt to write the Lewis structure of boron trifluoride leads to a structure in which the B atom has only *six* electrons in its valence shell—an *incomplete octet*.



$$\colon\underset{\cdot\cdot}{\ddot{\mathrm{F}}}{-}\underset{\underset{\colon\underset{\cdot\cdot}{\mathrm{F}}\colon}{|}}{\mathrm{B}}{-}\underset{\cdot\cdot}{\ddot{\mathrm{F}}}\colon \tag{10.20}$$