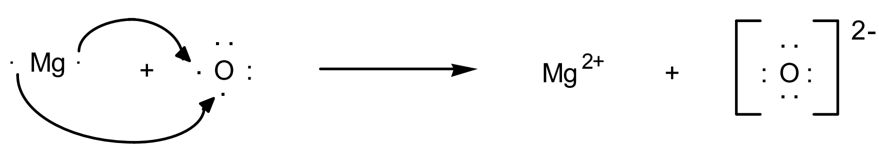
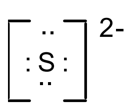
9. IONIC AND COVALENT BONDING

■ Solutions to Exercises

9.1 The Lewis symbol for oxygen is $:\dot{\underset{\cdot\cdot}{\mathrm{O}}}\cdot$ and the Lewis symbol for magnesium is $\cdot\,\mathrm{Mg}\,\cdot$. The magnesium atom loses two electrons, and the oxygen atom accepts two electrons. You can represent this electron transfer as follows:



9.2 The electron configuration of the Ca atom is [Ar]4s^2. By losing two electrons, the atom assumes a 2+ charge and the argon configuration, [Ar]. The Lewis symbol is Ca^{2+}. The S atom has the configuration [Ne]3$s^2$3p^4. By gaining two electrons, the atom assumes a 2- charge and the argon configuration [Ne]3$s^2$3p^6 and is the same as [Ar]. The Lewis symbol is



9.3 The electron configuration of lead (Pb) is [Xe]4f^{14}5d^{10}6$s^2$6p^2. The electron configuration of Pb^{2+} is [Xe]4f^{14}5d^{10}6s^2.

9.4 The electron configuration of manganese (Z = 25) is [Ar]3$d^5$4s^2. To find the ion configuration, first remove the 4s electrons, then the 3d electrons. In this case, only two electrons need to be removed. The electron configuration of Mn^{2+} is [Ar]3d^5.

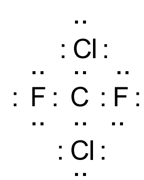
9.5 S^{2-} has a larger radius than S. The anion has more electrons than the atom. The electron-electron repulsion is greater; hence, the valence orbitals expand. The anion radius is larger than the atomic radius.

9.6 The ionic radii increase down any column because of the addition of electron shells. All of these ions are from the Group IIA family; therefore, $Mg^{2+} < Ca^{2+} < Sr^{2+}$.

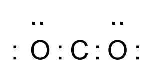
9.7 Cl^-, Ca^{2+}, and P^{3-} are isoelectronic with an electronic configuration equivalent to [Ar]. In an isoelectronic sequence, the ionic radius decreases with increasing nuclear charge. Therefore, in order of increasing ionic radius, we have Ca^{2+}, Cl^-, and P^{3-}.

9.8 The absolute value of the electronegativity differences are C-O, 1.0; C-S, 0.0; and H-Br, 0.7. Therefore, C-O is the most polar bond.

9.9 First, calculate the total number of valence electrons. C has four, Cl has seven, and F has seven. The total number is 4 + (2 x 7) + (2 x 7) = 32. The expected skeleton consists of a carbon atom surrounded by Cl and F atoms. Distribute the electron pairs to the surrounding atoms to satisfy the octet rule. All 32 electrons (16 pairs) are accounted for.



9.10 The total number of electrons in CO_2 is 4 + (2 x 6) = 16. Because carbon is more electropositive than oxygen, it is expected to be the central atom. Distribute the electrons to the surrounding atoms to satisfy the octet rule.



All sixteen electrons have been used, but notice there are only four electrons on carbon. This is four electrons short of a complete octet, which suggests the existence of double bonds. Move a pair of electrons from each oxygen to the carbon-oxygen bonds.

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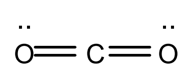
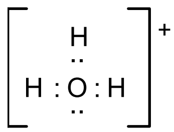
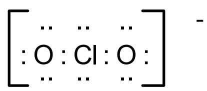


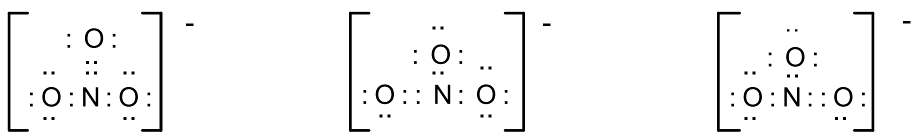
9.11 a. There are (3 x 1) + 6 = 9 valence electrons in H_3O. The H_3O^+ ion has one less electron than is provided by the neutral atoms because the charge on the ion is +1. Hence, there are eight valence electrons in H_3O^+. The electron-dot formula is



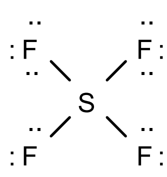
b. Cl has seven valence electrons, and O has six valence electrons. The total number of valence electrons from the neutral atoms is 7 + (2 x 6) = 19. The charge on the ClO_2^- is -1, which provides one more electron than the neutral atoms. This makes a total of twenty valence electrons. The electron-dot formula for ClO_2^- is



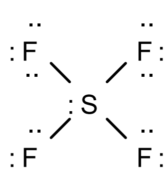
9.12 The resonance formulas for NO_3^- are



9.13 The number of valence electrons in SF_4 is 6 + (4 x 7) = 34. The skeleton structure is a sulfur atom surrounded by fluorine atoms. After the electron pairs are placed on the F atoms to satisfy the octet rule, two electrons remain.



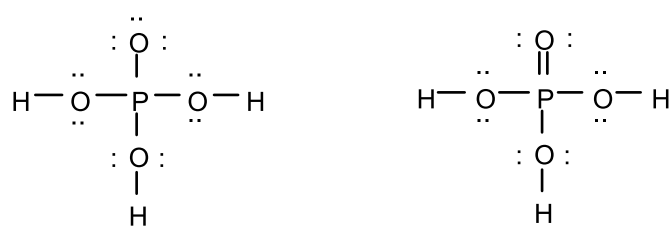
These additional two electrons are put on the sulfur atom because it had *d* orbitals and, therefore, it can expand its octet.



9.14 Be has two valence electrons, and Cl has seven valence electrons. The total number of valence electrons is 2 + (2 x 7) = 16 in the $BeCl_2$ molecule. Be, a Group IIA element, can have fewer than eight electrons around it. The electron-dot formula of $BeCl_2$ is

: C̤̈l : Be : C̤̈l :

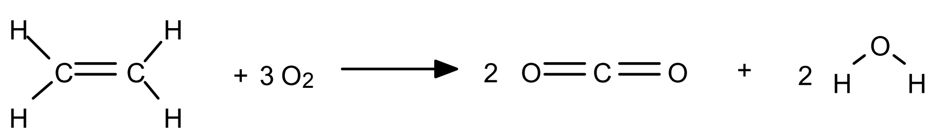
9.15 The total number of electrons in H_3PO_4 is 3 + 5 + 24 = 32. Assume a skeleton structure in which the phosphorus atom is surrounded by the more electronegative four oxygen atoms. The hydrogen atoms are then attached to the oxygen atoms. Distribute the electron pairs to the surrounding atoms to satisfy the octet rule. If you assume all single bonds (structure on the left), the formal charge on the phosphorus is +1 and the formal charge on the top oxygen is -1. Using the principle of forming a double bond with a pair of electrons on the atom with the negative formal charge, you obtain the structure on the right. The formal charge on all oxygens in this structure is zero; the formal charge on phosphorus is 5 - 5 = 0. This is the better structure.



9.16 The bond length can be predicted by adding the covalent radii of the two atoms. For O-H, we have 66 pm + 37 pm = 103 pm.

9.17 As the bond order increases, the bond length decreases. Since the C=O is a double bond, we would expect it to be the shorter one, 123 pm.

9.18



One C=C bond, four C-H bonds, and three O_2 bonds are broken. There are four C=O bonds and four O-H bonds formed.

$$\Delta H = \{[602 + (4 \times 411) + (3 \times 494)] - [(4 \times 799) + (4 \times 459)]\} \text{ kJ} = -1304 \text{ kJ}$$

■ Answers to Concept Checks

9.1 a The +2 ions are common in transition elements, but it is the outer *s* electrons that are lost to form these ions in compounds. Iron, whose configuration is [Ar]3$d^6$4s^2, would be expected to lose two 4*s* electrons to give the configuration [Ar]3d^6 for the Fe^{2+} ion in compounds. The configuration given in the problem is for an excited state; you would not expect to see it in compounds.

b. Nitrogen, whose ground-state atomic configuration is [He]2$s^2$2p^3, would be expected to form an anion with a noble-gas configuration by gaining three electrons. This would give the anion N^{3-} with the configuration [He]2$s^2$2p^6. You would not expect to see the anion N^{2-} in compounds.

c. The zinc atom has the ground-state configuration [Ar]3d^{10}4s^2. The element is often considered to be a transition element. In any case, you would expect the atom to form compounds by losing its 4*s* electrons to give Zn^{2+} with the pseudo-noble-gas configuration [Ar]3d^{10}. This is the ion configuration given in the problem.

d. The configuration of the ground-state sodium atom is [He]2$s^2$2$p^6$3s^1. You would expect the atom to lose one electron to give the Na^+ ion with the noble-gas configuration [He]2$s^2$2p^6. You would not expect to see compounds with the Na^{2+} ion.

e. The ground state of the calcium atom is [Ne]3$s^2$3$p^6$4s^2. You would expect the atom to lose its two outer electrons to give the Ca^{2+} with the noble-gas configuration [Ne]3$s^2$3p^6, which is the configuration given in the problem.

9.2 a. There are two basic points to consider in assessing the validity of each of the formulas given in the problem. One is whether the formula has the correct skeleton structure. You expect the F atoms to be bonded to the central N atoms because the F atoms are more electronegative. The second point is the number of dots in the formula. This should equal the total number of electrons in the valence shell of the atoms (five for each nitrogen atom and seven for each fluorine atom), which is (2 x 5) + (2 x 7) = 24, or twelve pairs. The number showing in the formula here is thirteen, which is incorrect.

b. This formula has the correct skeleton structure and the correct number of dots. All of the atoms have octets, so the formula would appear to be correct. As a final check, however, you might try drawing the formula beginning with the skeleton structure. In drawing an electron-dot formula, after connecting atoms by single bonds (a single electron pair), you would place electron pairs around the outer atoms (the F atoms in this formula) to give octets. After doing that, you would have used up nine electron pairs (three for the single bonds and three for each F atom to fill out its octet). This leaves three pairs, which you might distribute as follows:

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 ..   ..  ..  ..
:F :  N : N : F :
 ..   ..      ..
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(continued)

One of the nitrogen atoms (the one on the right) does not have an octet. The lack of an octet on this atom suggests you try for a double bond. This suggests you move one of the lone pairs on the left N atom into one of the adjacent bonding regions. Moving this lone pair into the N—N region would give a symmetrical result, whereas moving the lone pair into the F—N region would not. The text notes that the atoms often showing multiple bonds are C, N, O, and S. The formula given here with a nitrogen-nitrogen double bond appears quite reasonable.

c. This formula is similar to the previous one, b, but the double bond is between the F and N atoms. Multiple bonds to F are less likely than those between two N atoms. So this is not the preferred formula. You could also apply the rules of formal charge in this case, and you would come to the same conclusion. The formula here gives a -1 charge to the left F atom and a +1 charge to the right N atom, whereas each of the atoms in the b formula has zero formal charge. Rule A says that whenever you can write several Lewis formulas for a molecule, you should choose the formula having the lowest magnitudes of formal charges. In this case, this is the formula b. Strictly speaking, both b and c could be regarded as resonance formulas, but b would have much more importance than c in describing the electronic structure of the molecule.

d. This formula is similar to the one you drew earlier in describing how you would get to the formula in b. The left N atom does not have an octet, which suggests you move a lone pair on the other N atom into the N—N bond region to give a double bond.

e. This formula does not have the correct skeleton structure.

f. This formula has the correct skeleton structure and the correct total number of electron dots, but neither N atom has an octet. In fact, there is no bond between the two N atoms.

9.3 a. This model and corresponding Lewis structure, H:C:::N:, has the expected skeleton structure. (H must be an exterior atom, but either C or N might be in the center; however, you expect the more electropositive, or less electronegative atom, C, to be in this position). This formula also has the correct number of electron dots (1 + 4 + 5 = 10, or 5 pairs). Finally, the formal charge of each atom is zero. Therefore, this model should be an accurate representation of the HCN molecule.

b. This structure has the more electronegative atom, N, in the central position; you don't expect this to be the correct structure. You can also look at this from the point of view of formal charges. This formula has a +1 charge on the N atom and a -1 charge on the C atom. You would not expect the more electronegative atom to have the positive formal charge. Moreover, the previous formula, a, has zero charges for each atom, which would be preferred.

c. If you draw the Lewis structure, you will see that each atom has an octet, but the formula has too many electron pairs (seven instead of five). You can remove two pairs and still retain octets if you move two lone pairs into the bonding region, to give a triple bond.

(continued)

d. If you draw the Lewis structure, you will find the H atom has a bond and a lone pair attached to it, so this is not a reasonable structure. You would arrive at the same conclusion using formal charges. The formal charges are -2 for H, +1 for C, and +1 for N. Since you already know that formula a has zero formal charge for each atom, such high formal charges for the atoms in formula d mean it is not a very good representation of the molecule.

■ Answers to Review Questions

9.1 As an Na atom approaches a Cl atom, the outer electron of the Na atom is transferred to the Cl atom. The result is an Na^+ and a Cl^- ion. Positively charged ions attract negatively charged ions, so, finally, the NaCl crystal consists of Na^+ ions surrounded by six Cl^- ions surrounded by six Na^+ ions.

9.2 Ions tend to attract as many ions of opposite charge about them as possible. The result is that ions tend to form crystalline solids rather than molecular substances.

9.3 The energy terms involved in the formation of an ionic solid from atoms are the ionization energy of the metal atom, the electron affinity of the nonmetal atom, and the energy of the attraction of the ions forming the ionic solid. The energy of the solid will be low if the ionization energy of the metal is low, the electron affinity of the nonmetal is high, and the energy of the attraction of the ions is large.

9.4 The lattice energy for potassium bromide is the change in energy that occurs when KBr(s) is separated into isolated $K^+(g)$ and $Br^-(g)$ ions in the gas phase.

$$KB(s) \rightarrow K^+(g) + Br^-(g)$$

9.5 A monatomic cation with a charge equal to the group number corresponds to the loss of all valence electrons. This loss of electrons would give a noble-gas configuration, which is especially stable. A monatomic anion with a charge equal to the group number minus eight would have a noble-gas configuration.

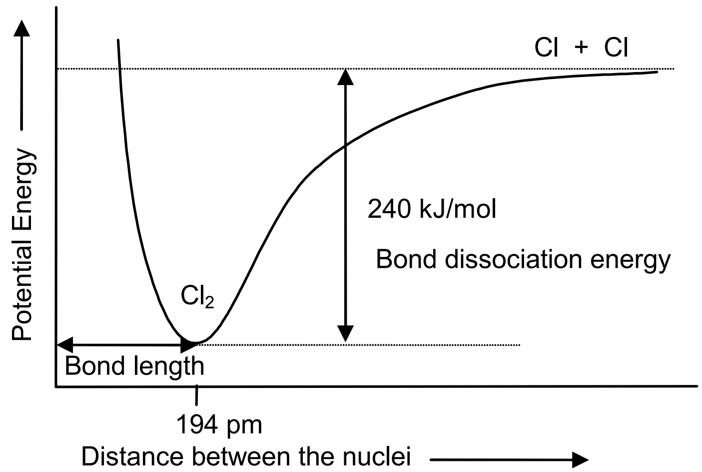
9.6 Most of the transition elements have configurations in which the outer *s* subshell is doubly occupied. These electrons will be lost first, and we might expect each to be lost with almost equal ease, resulting in +2 ions.

9.7 If we assume the ions are spheres that are just touching, the distances between centers of the spheres will be related to the radii of the spheres. For example, in LiI, we assume that the -1 ions are large spheres that are touching. The distance between centers of the I^- ions equals two times the radius of the I^- ion.

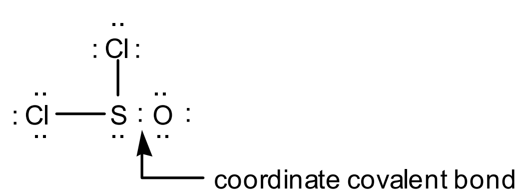
9.8 In going across a period, the cations decrease in radius. When we reach the anions, there is an abrupt increase in radius, and then the radii again decrease. Ionic radii increase going down any column of the periodic table.

9.9 As the H atoms approach one another, their 1*s* orbitals begin to overlap. Each electron can then occupy the space around both atoms; that is, the two electrons are shared by the atoms.

9.10



9.11 An example is thionyl chloride, $SOCl_2$:



Note that the O atom has eight electrons around it; that is, it has two more electrons than the neutral atom. These two electrons must have come from the S atom. Thus, this bond is a coordinate covalent bond.

9.12 In many atoms of the main-group elements, bonding uses an *s* orbital and the three *p* orbitals of the valence shell. These four orbitals are filled with eight electrons, thus accounting for the octet rule.

9.13 Electronegativity increases from left to right (with the exception of the noble gases) and decreases from top to bottom in the periodic table.

9.14 The absolute difference in the electronegativities of the two atoms in a bond gives a rough measure of the polarity of the bond.

9.15 Resonance is used to describe the electron structure of a molecule in which bonding electrons are delocalized. In a resonance description, the molecule is described in terms of two or more Lewis formulas. If we want to retain Lewis formulas, resonance is required because each Lewis formula assumes that a bonding pair of electrons occupies the region between two atoms. We must imagine that the actual electron structure of the molecule is a composite of all resonance formulas.

9.16 Molecules having an odd number of electrons do not obey the octet rule. An example is nitrogen monoxide, NO. The other exceptions fall into two groups. In one group are molecules with an atom having fewer than eight valence electrons around it. An example is borane,BH_3. In the other group are molecules with an atom having more than eight valence electrons around it. An example is sulfur hexafluoride, SF_6.

9.17 As the bond order increases, the bond length decreases. For example, the average carbon-carbon single-bond length is 154 pm, whereas the carbon-carbon double-bond length is 134 pm, and the carbon-carbon triple-bond length is 120 pm.

9.18 Bond energy is the average enthalpy change for the breaking of a bond in a molecule. The enthalpy of a reaction for gaseous reactions can be determined by summing the bond energies of all the bonds that are broken and subtracting the sum of the bond energies of all the bonds that are formed.

■ Answers to Conceptual Problems

9.19 Because the compound that forms is a combination of a metal and a nonmetal, we would expect it to be ionic. If we assume that metal atoms tend to lose electrons to obtain filled shells, then the metal atom X would lose three electrons from the n = 2 level, forming the X^{3+} cation. We can expect the nonmetal atom Y to gain electrons to obtain a filled shell, so it requires an additional electron to fill the n = 1 level, forming the Y^- anion. To produce an ionic compound with an overall charge of zero, the compound formed from these two elements would be XY_3.

9.20 Elements in higher periods in Group IIIA tend to form ions by losing either the outer *p* electron to form +1 ions or by losing the outer *s* and *p* electrons to form +3 ions. In the case of thallium, these ions have the configuration in d and b respectively. The +2 ion given in a represents a loss of the two outer *s* electrons, leaving the outer *p* electrons of higher energy. This configuration would represent an excited state of the +2 ion. You would not expect a +2 ion in thallium compounds, and an excited configuration is even less likely. The +4 ion given in c is formed by loss of the outer *s* and *p* electrons plus a *d* electron from the closed *d* subshell. This would be an unlikely ion for thallium compounds.

9.21 The smaller atom on the left (yellow) becomes a larger ion on the right, while the larger atom on the left (blue) becomes the smaller ion on the right. Since cations are smaller than the parent atom, and anions are larger than their parent atom, the cation on the right is the smaller ion (blue), and the anion is the larger ion (yellow). Finally, since metals tend to form cations, and nonmetals form anions, the metal on the left is the larger atom (blue), and the nonmetal is the smaller atom (yellow).

9.22 Element 117 would fall in Group VII A, the halogens. The monatomic ion for this element would probably be like the other halogens, an anion with a -1 charge. Since anions are larger than the parent atom, the larger sphere (on the right) would be the ion, and the smaller sphere (on the left) would be the atom.

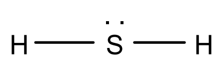
9.23 a. Incorrect. The atoms in this formula do not obey the octet rule. The formula has the correct number of valence electrons, so this suggests a multiple bond between the N atoms.

b. Correct. The central atom is surrounded by more electronegative atoms as you would expect, and each atom obeys the octet rule.

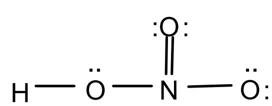
c. Incorrect. The skeleton structure is acceptable (the central atom is surrounded by more electronegative atoms), but you would expect the double bond to be between C and O rather than C and F (C, N, O, and S form multiple bonds). You would come to this same conclusion using rules of formal charge. (The formula has a formal charge of +1 on F and -1 on O whereas you would expect these formal charges to be interchanged, with the negative charge on the F atom, which is more electronegative.)

d. Incorrect. The skeleton structure is OK, but the carbon atom has ten valence electrons about it. This suggests that you replace the two carbon-oxygen double bonds by one carbon-oxygen double bond (because there is one extra pair of electrons on the C atom). The most symmetrical location of the double bond uses the oxygen atom not bonded to an H atom. Also, only this formula has zero formal charges on all atoms.

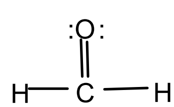
9.24 a.



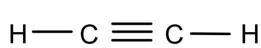
b.



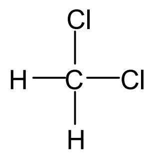
c.



d.



9.25 a. To arrive at a skeleton structure, you decide which is the central atom. (It cannot be H). The C atom is less electronegative than the Cl atom, so you place it as the central atom and surround it by the other atoms.



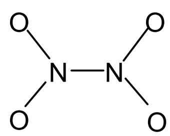
b. HNO_2 is an oxyacid in which O atoms bond to the central atom with the H bonded to O. The central atom must be N (the only other atom), so the skeletal structure is

H—O—N—O

c. You place the least electronegative atom (N) as the central atom and bond it to the other atoms

F—N—O

d. N is less electronegative than O. The most symmetrical structure would be the two N atoms in the center with two O atoms bonded to each N atom.



9.26 The ranking is a, c, b (best) for the following reasons:

a. This formula has a -2 formal charge on the outer N and +1 charges on the other two atoms. This formula has a larger magnitude of formal charges than either of the other two formulas, so it ranks last as a representation of the electron structure of the N_2O molecule.

b. This formula has a -1 formal charge on O and a +1 formal charge on the central N. This places the negative formal charge on the more electronegative atom, O, making this the best representation of the electron structure of the molecule.

c. This formula has a -1 formal charge on the outer N atom and +1 formal charge on the central N atom. This is better than resonance formula a, but not as good as b.

9.27 a. In order to be a neutral ionic compound, element X must have a charge of -3. In an ionic compound, calcium forms the Ca^{2+} cation. The combination of Ca^{2+} and X^{3-} would form the ionic compound with the formula Ca_3X_2.

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b. Since element X formed an ionic compound with sodium metal, it is probably a nonmetal with a high electron affinity. When a nonmetal with a high electron affinity combines with a metal such as calcium, an ionic compound is formed.

9.28 a. In general, the enthalpy of a reaction is (approximately) equal to the sum of the bond energies for the bonds broken minus the sum of the bond energies for the bonds formed. Therefore, the bond energy (BE) for each of the reactions can be calculated by the following relationships

$$\Delta H = BE(X\text{-}X) + BE(O{=}O) - 2 \times BE(X\text{-}O) - BE(O\text{-}O)$$

$$\Delta H = BE(Y\text{-}Y) + BE(O{=}O) - 2 \times BE(Y\text{-}O) - BE(O\text{-}O)$$

$$\Delta H = BE(Z\text{-}Z) + BE(O{=}O) - 2 \times BE(Z\text{-}O) - BE(O\text{-}O)$$

Using information that the bond energies of X-O, Y-O, and Z-O are all equal, the difference in the values of ΔH for each reaction is solely a function of the X-X, Y-Y, or Z-Z bonds. Therefore, the compound with the most positive value of ΔH has the strongest bonds. The strongest to weakest bond ranking is Y-Y > Z-Z > X-X.

b. Since the bond strengths of each product are equal, the same amount of energy would be required to dissociate each of the products into atoms.

c. In this case, less energy would be required to break the bonds, so the ΔH for each reaction would decrease.

■ Solutions to Practice Problems

9.29 a. P has the electron configuration [Ne]$3s^2 3p^3$. It has five electrons in its valence shell. The Lewis formula is

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b. P^{3-} has three more valence electrons than P. It now has eight electrons in its valence shell. The Lewis formula is

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 ┌ . . ┐3-
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c. Ga has the electron configuration [Ar]$3d^{10}4s^2 4p^1$. It has three electrons in its valence shell. The Lewis formula is

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· Ga ·
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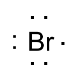
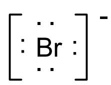
d. Ga^{3+} has three less valence electrons than Ga. It now has zero electrons in its valence shell. The Lewis formula is

Ga^{3+}

9.30 a. Br has the valence configuration [Ar]3d^{10}4$s^2$4p^5. It has seven electrons in its valence shell. The Lewis formula is



b. Br^- has one more electron than Br. It now has eight electrons in its valence shell. The Lewis formula is



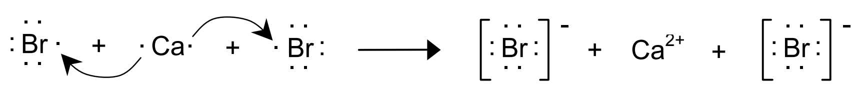
c. Strontium has the electron configuration [Kr]5s^2. It has two valence electrons in its valence shell. The Lewis formula is

· Sr ·

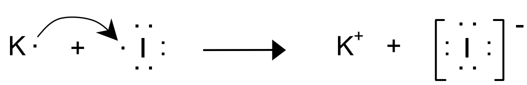
d. Sr^{2+} has two less electron than Sr. It now has zero electrons in its valence shell. The Lewis formula is

Sr^{2+}

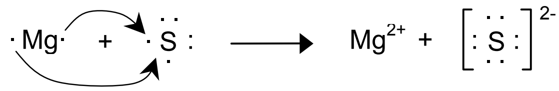
9.31 a. If the calcium atom loses two electrons, and the bromine atoms gain one electron each, all three atoms will assume noble-gas configurations. This can be represented as follows.



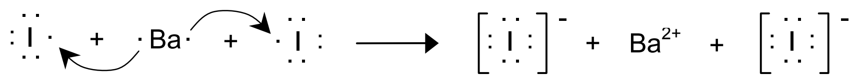
b. If the potassium atom loses one electron, and the iodine atom gains one electron, both atoms will assume a noble-gas configuration. This can be represented as follows

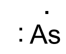


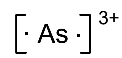
9.32 a. If the magnesium atom loses two electrons, and the sulfur atom gains two electrons, both atoms will assume a noble-gas configuration. This can be represented as follows:

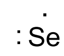


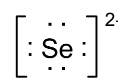
b. If the barium atom loses two electrons, and both iodine atoms gain one electron, all three atoms will have noble-gas configurations. This can be represented as follows.

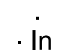


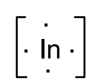
9.33 a. As: $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$ 

b. As^{3+}: $1s^22s^22p^63s^23p^63d^{10}4s^2$ 

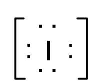
c. Se: $1s^22s^22p^63s^23p^63d^{10}4s^24p^4$ 

d. Se^{2-}: $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ 

9.34 a. In: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^1$ 

b. In^-: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$ 

c. K^+: $1s^22s^22p^63s^23p^6$ K^+

d. I^-: $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$ 

9.35 a. Bi: $[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$

b. Bi^{3+}: The three 6*p* electrons are lost from the valence shell.
$[Xe]4f^{14}5d^{10}6s^{2}$

9.36 a. Sn: $[Kr]4d^{10}5s^{2}5p^{2}$

b. Sn^{2+}: The two 5*p* electrons are lost from the valence shell.
$[Kr]4d^{10}5s^{2}$

9.37 The +2 ion is formed by the loss of electrons from the 4*s* subshell.

Ni^{2+}: $[Ar]3d^{8}$

The +3 ion is formed by the loss of electrons from the 4*s* and 3*d* subshells.

Ni^{3+}: $[Ar]3d^{7}$

9.38 The +1 ion is formed by the loss of the one electron in the 4*s* subshell.

Cu^{+}: $[Ar]3d^{10}$

The +2 ion is formed by the loss of a 4*s* and a 3*d* electron.

Cu^{2+}: $[Ar]3d^{9}$

9.39 a. $Sr^{2+} < Sr$

The cation is smaller than the neutral atom because it has lost all its valence electrons; hence, it has one less shell of electrons. The electron-electron repulsion is reduced, so the orbitals shrink because of the increased attraction of the electrons to the nucleus.

b. $Br < Br^{-}$

The anion is larger than the neutral atom because it has more electrons. The electron-electron repulsion is greater, so the valence orbitals expand to give a larger radius.

9.40 a. $Te < Te^{2-}$

The anion is larger than the neutral atom because it has more electrons. The electron-electron repulsion is greater, so the valence orbitals expand to give a larger radius.

b. $Al^{3+} < Al$

The cation is smaller than the neutral atom because it has lost all its valence electrons; hence, it has one less shell of electrons. The electron-electron repulsion is reduced, so the orbitals shrink because of the increased attraction of the electrons to the nucleus.

9.41 $S^{2-} < Se^{2-} < Te^{2-}$

All have the same number of electrons in the valence shell. The radius increases with the increasing number of filled shells.

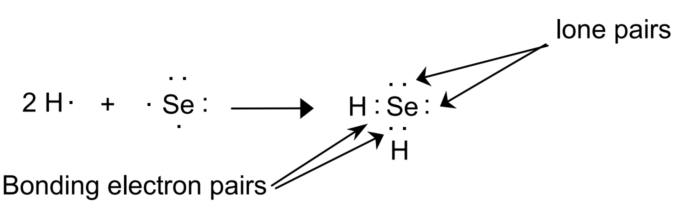
9.42 P^{3-} is larger. It has the same number of valence electrons as N^{3-}, but the valence shell has n = 3 for P^{3-} and n = 2 for N^{3-}. The radius increases with the increasing number of filled shells.

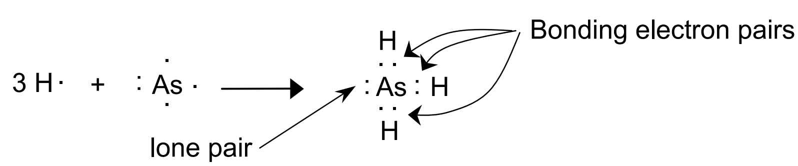
9.43 Smallest Na^+ (Z = 11), F^- (Z = 9), N^{3-} (Z = 7) Largest

These ions are isoelectronic. The atomic radius increases with the decreasing nuclear charge (Z).

9.44 Smallest Cs^+ (Z = 55), I^- (Z = 53), Te^{2-} (Z = 52) Largest

These ions are isoelectronic. The atomic radius increases with the decreasing nuclear charge (Z).

9.45 

9.46 

9.47 Arsenic is in Group VA on the periodic table and has five valence electrons. Bromine is in Group VIIA and has seven valence electrons. Arsenic forms three covalent bonds, and bromine forms one covalent bond. Therefore, the simplest compound would be $AsBr_3$.

9.48 Germanium is in Group IVA on the periodic table and has four valence electrons. Fluorine is in Group VIIA and has seven valence electrons. Germanium forms four covalent bonds, and bromine forms one covalent bond. Therefore, the simplest compound would be GeF_4.

9.49 a. P, N, O

Electronegativity increases from left to right and bottom to top in the periodic table.

b. Na, Mg, Al

Electronegativity increases from left to right within a period.

c. Al, Si, C

Electronegativity increases from left to right and bottom to top in the periodic table.

9.50 a. Cs, Ba, Sr

Electronegativity increases from left to right and bottom to top in the periodic table.

b. Ca, Ga, Ge

Electronegativity increases from left to right within a period.

c. As, P, S

Electronegativity increases from left to right and bottom to top in the periodic table.

9.51 $X_O - X_P = 3.5 - 2.1 = 1.4$

$X_{Cl} - X_C = 3.0 - 2.5 = 0.5$

$X_{Br} - X_{As} = 2.8 - 2.0 = 0.8$

The bonds arranged by increasing difference in electronegativity are C-Cl, As-Br, P-O.

9.52 $X_S - X_H = 2.5 - 2.1 = 0.4$

$X_{Cl} - X_{Si} = 3.0 - 1.8 = 1.2$

$X_{Cl} - X_N = 3.0 - 3.0 = 0.0$

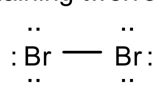
The difference in electronegativity is smallest for the N-Cl bond; hence, it is the least polar.

9.53 a. P—O ($\delta+$ $\delta-$) b. C—Cl ($\delta+$ $\delta-$) c. As—Br ($\delta+$ $\delta-$)

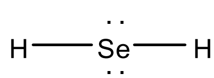
9.54 The atom with the greater electronegativity has the partial negative charge.

a. H—S ($\delta+$ $\delta-$) b. Si—Cl ($\delta+$ $\delta-$) c. Nonpolar

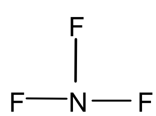
9.55 a. Total number of valence electrons = 7 + 7 = 14. Br—Br is the skeleton. Distribute the remaining twelve electrons.



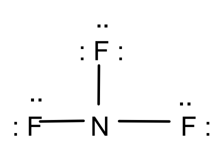
b. Total valence electrons = (2 x 1) + 6 = 8. The skeleton is H—Se—H. Distribute the remaining four electrons.



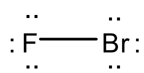
c. Total valence electrons = (3 x 7) + 5 = 26. The skeleton is



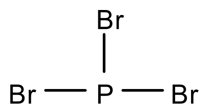
Distribute the remaining twenty electrons.



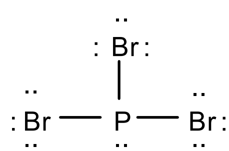
9.56 a. Total valence electrons = 7 + 7 = 14. F—Br is the skeleton. Distribute the remaining twelve electrons.



b. Total valence electrons = 5 + (3 x 7) = 26. The skeleton is

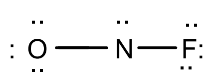


Distribute the remaining twenty electrons.

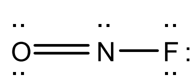


c. Total valence electrons = 7 + 5 + 6 = 18. The skeleton is

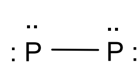
Distribute the remaining fourteen electrons so the O and F atoms have an octet.



Draw a N-O double bond to achieve an N octet.



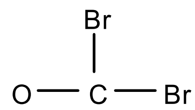
9.57 a. Total valence electrons = 2 x 5 = 10. The skeleton is P-P. Distribute the remaining electrons symmetrically:



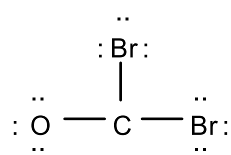
Neither P atom has an octet. There are four fewer electrons than needed. This suggests the presence of a triple bond. Make one lone pair from each P a bonding pair.

(continued)

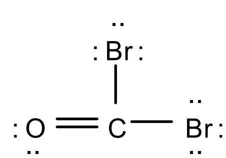
b. Total valence electrons = 4 + 6 + (2 x 7) = 24. The skeleton is



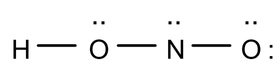
Distribute the remaining eighteen electrons.



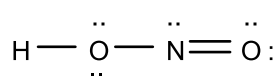
Notice that carbon is two electrons short of an octet. This suggests the presence of a double bond. The most likely double bond is between C and O.



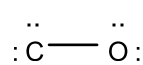
c. Total valence electrons = 1 + 5 + (2 x 6) = 18. The skeleton is most likely H-O-N-O. Distribute the remaining twelve electrons:



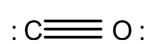
Notice the N atom does not have an octet. It is two electrons short. The most likely double bond is between N and O.



9.58 a. Total valence electrons = 4 + 6 = 10. The skeleton is C-O. Distribute the remaining eight electrons:

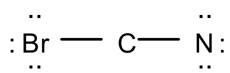


Neither atom has an octet. There are four fewer electrons than needed. This suggests a triple bond.

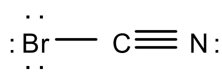


(continued)

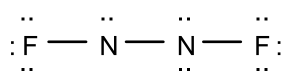
b. Total valence electrons = 7 + 4 + 5 = 16. The skeleton is Br-C-N. Distribute the remaining twelve electrons:



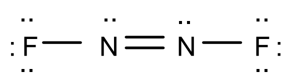
Notice the carbon atom is four electrons short of an octet. Make a triple bond between C and N from the four nonbonding electrons on nitrogen.



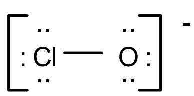
c. Total valence electrons = (2 x 5) + (2 x 7) = 24. The skeleton is F-N-N-F. Distribute the remaining eighteen electrons.



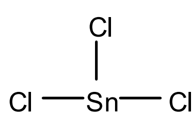
Notice one of the nitrogens is two electrons short of an octet. This suggests the presence of a double bond. The most likely double bond is between the nitrogens.



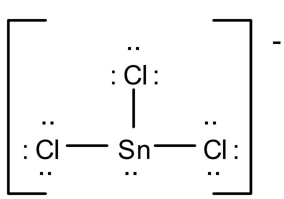
9.59 a. Total valence electrons = 7 + 6 + 1 = 14. The skeleton is Cl-O. Distribute the remaining twelve electrons.



b. Total valence electrons = 4 + (3 x 7) + 1 = 26. The skeleton is

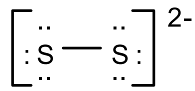


Distribute the remaining twenty electrons so that each atom has an octet.

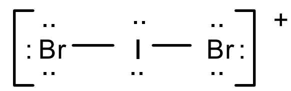


(continued)

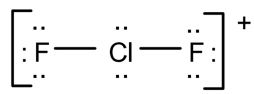
c. Total valence electrons = (2 x 6) + 2 = 14. The skeleton is S-S. Distribute the remaining twelve electrons.



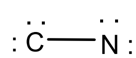
9.60 a. Valence electrons = 7 + (2 x 7) - 1 = 20. The skeleton is Br-I-Br. Distribute the remaining sixteen electrons.



b. Total valence electrons = 7 + (2 x 7) - 1 = 20. The skeleton is F-Cl-F. Distribute the remaining sixteen electrons.

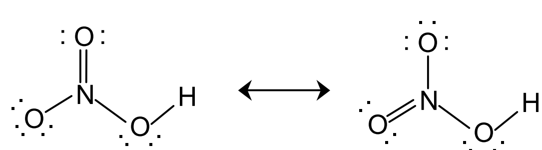


c. Total valence electrons = 4 + 5 + 1 = 10. The skeleton is C-N. Distribute the remaining eight electrons.



Notice neither atom has an octet. There are four fewer electrons than needed, suggesting a triple bond:

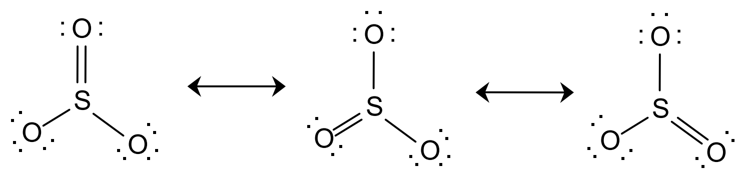
9.61 a. There are two possible resonance structures for HNO_3.



One electron pair is delocalized over the nitrogen atom and the two oxygen atoms.

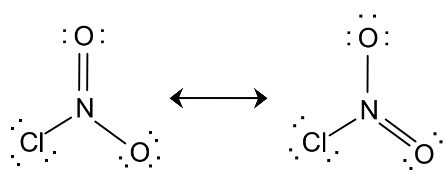
(continued)

b. There are three possible resonance structures for SO_3.



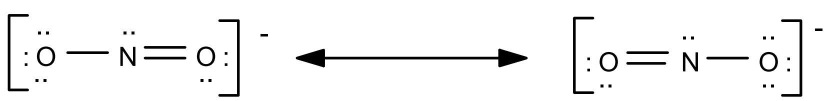
One pair of electrons is delocalized over the region of the three sulfur-oxygen bonds.

9.62 a. There are two possible resonance structures for $ClNO_2$.

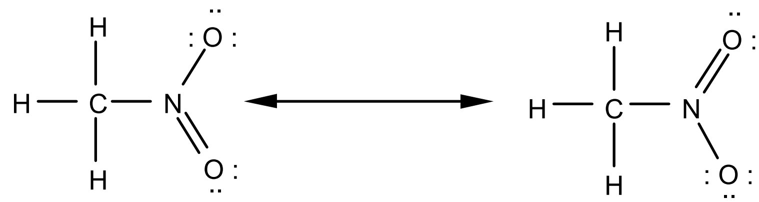


One electron pair is delocalized over the nitrogen atom and the two oxygen atoms.

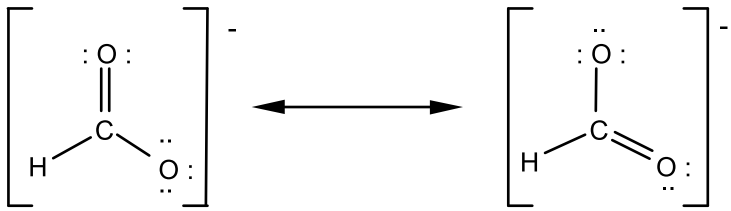
b. There are two resonance forms for NO_2^-.



One pair of electrons is delocalized over the region of both nitrogen-oxygen bonds.

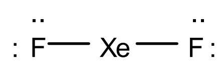
9.63 

One pair of electrons is delocalized over the O-N-O bonds.

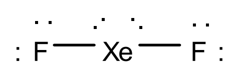
9.64 

The two carbon-oxygen bonds are expected to be the same. This means one pair of electrons is delocalized over the region of the O-C-O bonds.

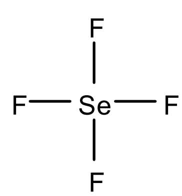
9.65 a. Total valence electrons = 8 + (2 x 7) = 22. The skeleton is F-Xe-F. Place six electrons around each fluorine atom to satisfy its octet.



There are three electron pairs remaining. Place them on the xenon atom.

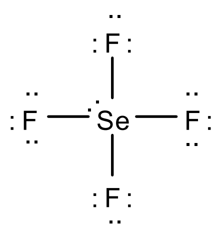


b. Total valence electrons = 6 + (4 x 7) = 34. The skeleton is

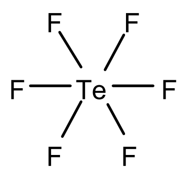


(continued)

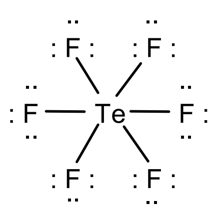
Distribute twenty four of the remaining twenty six electrons on the fluorine atoms. The remaining pair of electrons is placed on the selenium atom.



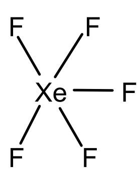
c. Total valence electrons = 6 + (6 x 7) = 48. The skeleton is



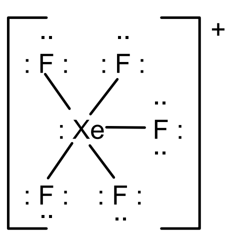
Distribute the remaining thirty six electrons on the fluorine atoms.



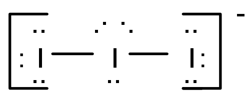
d. Total valence electrons = 8 + (5 x 7) - 1 = 42. The skeleton is



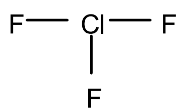
Use thirty of the remaining thirty two electrons on the fluorine atoms to complete their octets. The remaining two electrons form a lone pair on the xenon atom.



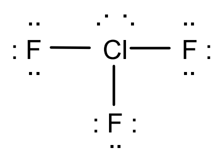
9.66 a. Total valence electrons = (3 x 7) + 1 = 22. The skeleton is **I-I-I**. Distribute the remaining eighteen electrons. The central iodine atom may expand its octet.



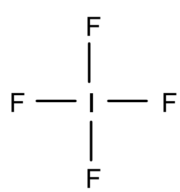
b. Total valence electrons = 7 + (3 x 7) = 28. The skeleton is



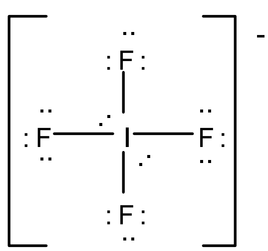
Distribute eighteen of the remaining twenty two electrons to complete the octets of the fluorine atoms. The four remaining electrons form two sets of lone pairs on the chlorine atom.



c. Total valence electrons = 7 + (4 x 7) + 1 = 36. The skeleton is

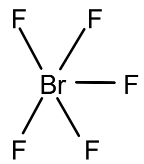


Distribute twenty four of the twenty eight remaining electrons to complete the octets of the fluorine atoms. The four electrons remaining form two sets of lone pairs on the iodine atom.

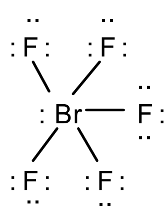


(continued)

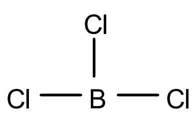
d. Total valence electrons = 7 + (5 x 7) = 42. The skeleton is



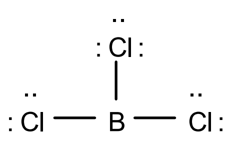
Use thirty of the remaining thirty two electrons to complete the octets of the fluorine atoms. The two electrons remaining form a lone pair on the bromine atom.



9.67 a. Total valence electrons = 3 + (3 x 7) = 24. The skeleton is

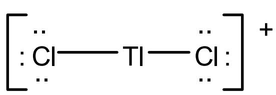


Distribute the remaining eighteen electrons.



Although boron has only six electrons, it has the normal number of covalent bonds.

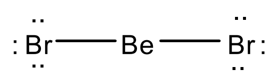
b. Total valence electrons = 3 + (2 x 7) - 1 = 16. The skeleton is Cl-Tl-Cl. Distribute the remaining twelve electrons.



Tl has only four electrons around it.

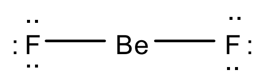
(continued)

c. Total valence electrons = 2 + (2 x 7) = 16. The skeleton is Br-Be-Br. Distribute the remaining twelve electrons.



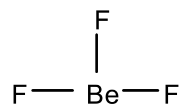
In covalent compounds, beryllium frequently has two bonds, even though it does not have an octet.

9.68 a. Total valence electrons = 2 + (2 x 7) = 16. The skeleton is F-Be-F. Distribute the remaining twelve electrons.

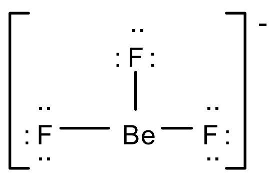


In covalent compounds, beryllium commonly has two bonds, even though it does not have an octet.

b. Total valence electrons = 2 + (3 x 7) + 1 = 24. The skeleton is

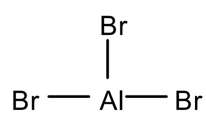


Distribute the remaining eighteen electrons on the fluorine atoms.

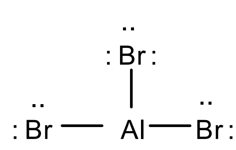


This ion is isoelectronic with BF_3, and the beryllium, like boron, has only six electrons around it.

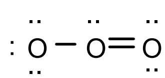
c. Total valence electrons = 3 + (3 x 7) = 24. The skeleton is



Distribute the remaining eighteen electrons to the bromine atoms.

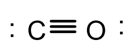


9.69 a. The total number of electrons in O_3 is 3 x 6 = 18. Assume a skeleton structure in which one oxygen atom is singly bonded to the other two oxygen atoms. This requires six electrons for the three single bonds, leaving twelve electrons to be used. It is impossible to fill the outer octets of all three oxygen atoms by writing three electron pairs around each, so a double bond must be written between the central oxygen and one of the other oxygen atoms. Then, distribute the electron pairs to the oxygen atoms to satisfy the octet rule. As shown below, there are three bonds and six lone pairs of electrons, or eighteen electrons, in the structure. Thus, all eighteen electrons are accounted for. One of the possible resonance structures is shown below; the other structure would have the double bond written between the left and central oxygen atoms.



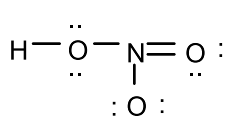
Starting with the left oxygen, the formal charge of this oxygen is 6 - 1 - 6 = -1. The formal charge of just the central oxygen is 6 - 3 - 2 = +1. The formal charge of the right oxygen is 6 - 2 - 4 = 0. The sum of all three is 0.

b. The total number of electrons in CO is 4 + 6 = 10. Assume a skeleton structure in which the oxygen atom is singly bonded to carbon. This requires two electrons for the single bond, and leaves eight electrons to be used. It is impossible to fill the outer octets of the carbon and oxygen by writing four electron pairs around each, so a triple bond must be written between the carbon and oxygen. Then, distribute the electron pairs to both atoms to satisfy the octet rule. As shown below, there are one triple bond and two lone pairs of electrons, or ten electrons, in the structure. Thus, all ten electrons are accounted for. The structure is



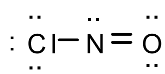
The formal charge of the carbon is 4 - 3 - 2 = -1. The formal charge of the oxygen is 6 - 3 - 2 = +1. The sum of both is 0.

c. The total number of electrons in HNO_3 is 1 + 5 + 18 = 24. Assume a skeleton structure in which the nitrogen atom is singly bonded to two oxygen atoms and doubly bonded to one oxygen. This requires two electrons for the O—H single bond, and leaves eight electrons to be used for the N bonds.



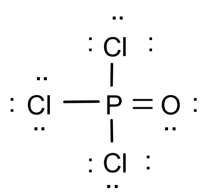
The formal charge of the nitrogen is 5 - 4 - 0 = +1. The formal charge of the hydrogen is 1 - 1 - 0 = 0. The formal charge of the oxygen bonded to the hydrogen is 6 - 2 - 4 = 0. The formal charge of the other singly bonded oxygen is 6 - 1 - 6 = -1. The formal charge of the doubly bonded oxygen is 6 - 2 - 4 = 0.

9.70 a. The total number of electrons in ClNO is 7 + 5 + 6 = 18. Assume a skeleton structure in which one chlorine atom is singly bonded to the nitrogen atom. If a N-O single bond is assumed, twenty electrons are needed to fill the outer octets. Hence, a N=O double bond must be used, the structure being



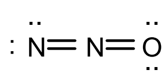
The formal charge of the chlorine is 7 - 1 - 6 = 0. The formal charge of the nitrogen is 5 - 3 - 2 = 0. The formal charge of the oxygen is 6 - 2 - 4 = 0.

b. The total number of electrons in $POCl_3$ is 5 + 6 + 21 = 32. Assume a skeleton structure in which the phosphorus atom is singly bonded to each of the three chlorines and doubly bonded to the oxygen. This structure has a lower formal charge than one with a single P-O bond.



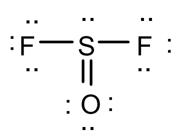
The formal charge of phosphorus is 5 - 5 - 0 = 0. The formal charge on each chlorine is 7 - 1 - 6 = 0. The formal charge of oxygen is 6 - 2 - 4 = 0.

c. The total number of electrons in N_2O is 2 x 5 + 6 = 16. Assume a skeleton structure in which the two nitrogen atoms are double bonded to each other. The oxygen atom can be singly bonded or doubly bonded to the central nitrogen. Using a N=O double bond gives the lowest formal charge.



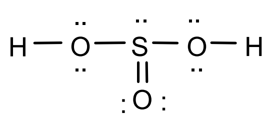
The formal charge of the end nitrogen is 5 - 2 - 4 = -1. The formal charge of the nitrogen between the end nitrogen and oxygen is 5 - 4 = +1. The formal charge of the oxygen is 6 - 2 - 4 = 0.

9.71 a. The total number of electrons in SOF_2 is 6 + 6 + 14 = 26. Assume a skeleton structure in which the sulfur atom is singly bonded to the two fluorine atoms. If a S-O single bond is assumed, twenty six electrons are needed. However, there would be formal charges of +1 on the sulfur and -1 on the oxygen. Using a S=O double bond requires only twenty six electrons and results in zero formal charge.



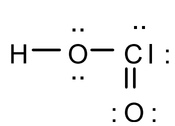
The formal charge on each of the two fluorine atoms is 7 - 1 - 6 = 0. The formal charge on the oxygen is 6 - 2 - 4 = 0. The formal charge on the sulfur is 6 - 4 - 2 = 0.

b. The total number of electrons in H_2SO_3 is 2 + 6 + 18 = 26. Assume a skeleton structure in which the sulfur atom is singly bonded to the three oxygen atoms. Then, form single bonds from the two hydrogen atoms to each of two oxygen atoms. If a S-O single bond is assumed, twenty six electrons are needed. However, there would be formal charges of +1 on the sulfur and -1 on the oxygen. A S=O double bond also requires twenty six electrons but results in zero formal charge on all atoms.



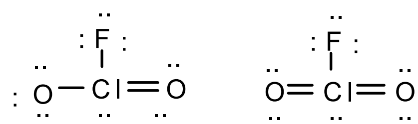
The formal charge of each hydrogen is 1 - 1 = 0. The formal charge of each oxygen bonded to a hydrogen is 6 - 2 - 4 = 0. The formal charge of the oxygen doubly bonded to the sulfur is 6 - 2 - 4 = 0. The formal charge of the sulfur is 6 - 4 - 2 = 0.

c. The total number of electrons in $HClO_2$ is 1 + 7 + 12 = 20. Assume a skeleton structure in which the chlorine atom is singly bonded to the two oxygen atoms, and the hydrogen is singly bonded to one of the oxygen atoms. If all Cl-O single bonds are assumed, twenty electrons are needed, but the chlorine exhibits a formal charge of +1 and one oxygen exhibits a formal charge of -1. Hence, a pair of electrons on the oxygen without the hydrogen is used to form a Cl=O double bond.



The formal charge of hydrogen is 1 - 1 = 0. The formal charge of the oxygen bonded to hydrogen is 6 - 2 - 4 = 0. The formal charge of the oxygen that is not bonded to the hydrogen is 6 - 2 - 4 = 0. The formal charge of the chlorine is 7 - 3 - 4 = 0.

9.72 a. The total number of electrons in ClO_2F is 7 + 12 + 7 = 26. Assume a skeleton structure in which the chlorine atom is singly bonded to the two oxygen atoms and the fluorine atom. If all single bonds are assumed, the chlorine has a formal charge of +2, and each oxygen has a formal charge of -1. The general principle to be followed whenever two atoms on a bond have opposite charges is to move an electron pair on the atom with the negative charge into the bond and form a double bond. Doing this once gives the structure on the left below. In this structure, the chlorine now has a formal charge of +1 and the oxygen on the left has a formal charge of -1. Following the general principle again results in the formation of a second double bond as shown in the structure on the right.



In the structure on the right, the formal charge of each oxygen is 6 - 2 - 4 = 0. The formal charge of the fluorine is 7 - 1 - 6 = 0. The formal charge of the chlorine is 7 - 5 - 2 = 0.

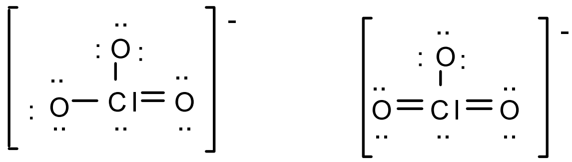
b. The total number of electrons in SO_2 is 6 + 12 = 18. Assume a skeleton structure in which the sulfur atom is singly bonded to the two oxygen atoms. If all single bonds are assumed, the sulfur atom has a formal charge of +2, and each of the oxygen atoms has a formal charge of -1. As in part a, the general principle to be followed whenever two atoms on a bond have opposite charges is to move an electron pair on the atom with the negative charge into the bond and form a double bond. Doing this once gives the structure on the left below. In this structure, the sulfur now has a formal charge of +1 and the oxygen on the left has a formal charge of -1. Following the general principle again results in the formation of a second double bond as shown in the structure on the right.

The formal charge of both oxygen atoms in the structure on the right is 6 - 2 - 4 = 0. The formal charge of the sulfur is 6 - 4 - 2 = 0.

c. The total number of electrons in ClO_3^-, including the charge, is twenty six. Assume a skeleton structure in which the chlorine atom is singly bonded to the three oxygen atoms. If all single bonds are assumed, the chlorine atom has a formal charge of +2, and each of the oxygen atoms has a formal charge of -1. As in part a, the general principle to be followed whenever two atoms on a bond have opposite charges is to move an electron pair on the atom with the negative charge into the bond and form a double bond. Doing this once gives the structure on the left below. In this structure, the chlorine now has a formal charge of +1, and, the two oxygen atoms have a formal charge of -1.

(continued)

Following the general principle again results in the formation of a second double bond, as shown in the structure on the right.



In the right-hand structure, the formal charge of the two doubly bonded oxygen atoms is 6 - 2 - 4 = 0. The formal charge of the singly bonded oxygen is 6 - 1 - 6 = -1 (= negative charge of -1). The formal charge of the chlorine is 7 - 5 - 2 = 0.

9.73 $r_F = 64$ pm

$r_P = 110$ pm

$d_{P\text{-}F} = r_F + r_P = 64 \text{ pm} + 110 \text{ pm} = 174 \text{ pm}$

9.74 $r_B = 88$ pm

$r_{Cl} = 99$ pm

$d_{B\text{-}Cl} = r_B + r_{Cl} = 88 \text{ pm} + 99 \text{ pm} = 187 \text{ pm}$

9.75 a. $d_{C\text{-}H} = r_C + r_H = 77 \text{ pm} + 37 \text{ pm} = 114 \text{ pm}$

b. $d_{S\text{-}Cl} = r_S + r_{Cl} = 104 \text{ pm} + 99 \text{ pm} = 203 \text{ pm}$

c. $d_{Br\text{-}Cl} = r_{Br} + r_{Cl} = 114 \text{ pm} + 99 \text{ pm} = 213 \text{ pm}$

d. $d_{Si\text{-}O} = r_{Si} + r_O = 117 \text{ pm} + 66 \text{ pm} = 183 \text{ pm}$

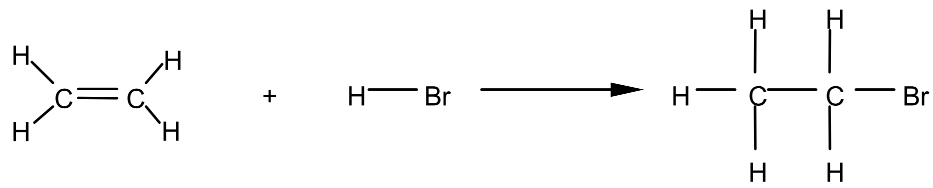
9.76 $d_{C\text{-}H} = r_C + r_H = 77 \text{ pm} + 37 \text{ pm} = 114 \text{ pm}$ $\quad d_{exp} = 107 \text{ pm}$

$d_{C\text{-}Cl} = r_C + r_{Cl} = 77 \text{ pm} + 99 \text{ pm} = 176 \text{ pm}$ $\quad d_{exp} = 177 \text{ pm}$

The calculated bond distances agree very well with the experimental values.

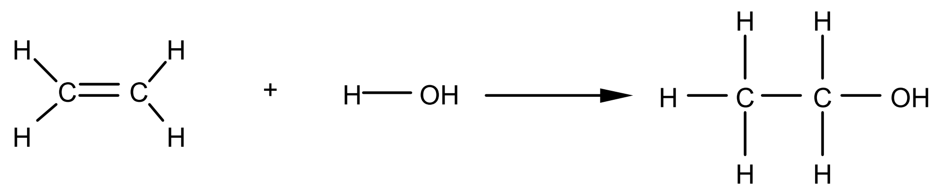
9.77	Methylamine	147pm	Single C-N bond is longer.
	Acetonitrile	116pm	Triple C-N bond is shorter.

9.78 Formaldehyde has a shorter carbon-oxygen bond than methanol. In methanol, the carbon-oxygen bond is a single bond, and in formaldehyde it is a double bond.

9.79 

In the reaction, a C=C double bond is converted to a C-C single bond. An H-Br bond is broken, and one C-H bond and one C-Br bond are formed.

$$\Delta H \cong BE(C{=}C) + BE(H\text{-}Br) - BE(C\text{-}C) - BE(C\text{-}H) - BE(C\text{-}Br)$$
$$= (602 + 362 - 346 - 411 - 285)\ kJ = -78\ kJ$$

9.80 

In the reaction, a C=C bond and an O-H bond are converted to a C-C single bond, a C-O bond, and a C-H bond.

$$\Delta H \cong [BE(C{=}C) + BE(O\text{-}H)] - [BE(C\text{-}C) + BE(C\text{-}O) + BE(C\text{-}H)]$$
$$= [(602 + 459) - (346 + 358 + 411)]\ kJ = -54\ kJ$$

■ Solutions to General Problems

9.81 a. Strontium is a metal, and oxygen is a nonmetal. The binary compound is likely to be ionic. Strontium, in Group IIA, forms Sr^{2+} ions; oxygen, from Group VIA, forms O^{2-} ions. The binary compound has the formula SrO and is named strontium oxide.

b. Carbon and bromine are both nonmetals; hence, the binary compound is likely to be covalent. Carbon usually forms four bonds, and bromine usually forms one bond. The formula for the binary compound is CBr_4. It is called carbon tetrabromide.

(continued)

c. Gallium is a metal, and fluorine is a nonmetal. The binary compound is likely to be ionic. Gallium is in Group IIIA and forms Ga^{3+} ions. Fluorine is in Group VIIA and forms F^- ions. The binary compound is GaF_3 and is named gallium(III) fluoride.

d. Nitrogen and bromine are both nonmetals; hence, the binary compound is likely to be covalent. Nitrogen usually forms three bonds, and bromine usually forms one bond. The formula for the binary compound is NBr_3. It is called nitrogen tribromide.

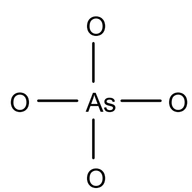
9.82 a. Sodium is a metal, and sulfur is a nonmetal. The binary compound is likely to be ionic. Sodium, in Group IA, forms Na^+ ions. Sulfur, in Group VIA, forms S^{2-} ions. The binary compound is Na_2S. It is named sodium sulfide.

b. Aluminum is a metal, and fluorine is a nonmetal. The binary compound is likely to be ionic. Aluminum, in Group IIIA, forms Al^{3+} ions. Fluorine, in Group VIIA, forms F^- ions. The binary compound is AlF_3. It is named aluminum fluoride.

c. Calcium is a metal, and chlorine is a nonmetal. The binary compound is likely to be ionic. Calcium, in Group IIA, forms Ca^{2+} ions. Chlorine, in Group VIIA, forms Cl^- ions. The binary compound is $CaCl_2$. It is named calcium chloride.

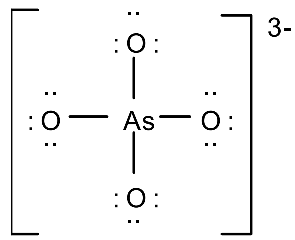
d. Silicon and bromine are both nonmetals; hence, the binary compound is likely to be covalent. Silicon usually forms four bonds, and bromine usually forms one bond. The formula for the binary compound is $SiBr_4$. It is called silicon tetrabromide.

9.83 Total valence electrons = 5 + (4 x 6) + 3 = 32. The skeleton is

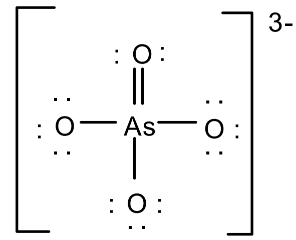


Distribute the remaining twenty four electrons to complete the octets around the oxygen atoms.

(continued)

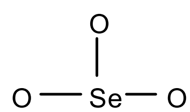


or

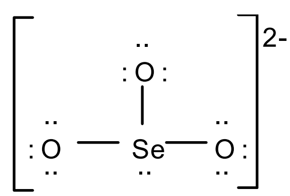


The formula for lead(II) arsenate is $Pb_3(AsO_4)_2$. The structure on the right has no formal charge.

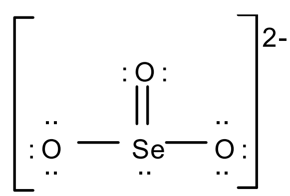
9.84 Total valence electrons = 6 + (3 x 6) + 2 = 26. The skeleton is



Distribute the remaining twenty electrons to complete the octets of oxygen and selenium atoms.

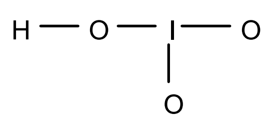


or

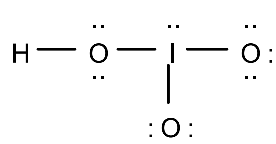


The formula for aluminum selenite is $Al_2(SeO_3)_3$. The structure on the right has no formal charge.

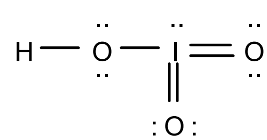
9.85 Total valence electrons = 1 + 7 + (3 x 6) = 26. The skeleton is



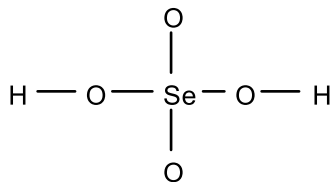
Distribute the remaining eighteen electrons to satisfy the octet rule. The structure on the right has no formal charge.



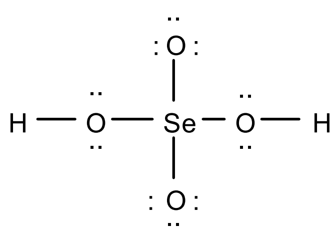
or



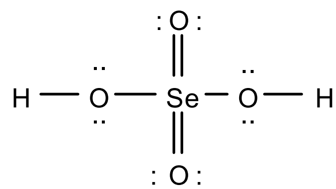
9.86 Total valence electrons = (2 x 1) + 6 + (4 x 6) = 32. The skeleton is



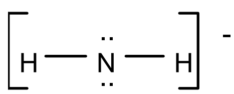
Distribute the remaining twenty electrons to satisfy the octet rule. The structure on the right has no formal charge.



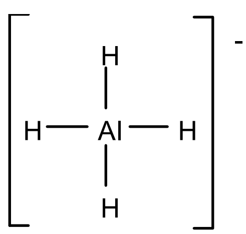
or



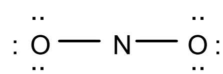
9.87 Total valence electrons = 5 + (2 x 1) + 1 = 8. The skeleton is H-N-H. Distribute the remaining four electrons to complete the octet of the nitrogen atom.



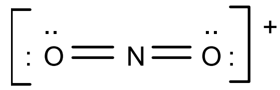
9.88 Total valence electrons = 3 + (4 x 1) + 1 = 8. The skeleton structure will use all the electrons. Because there are no electrons left, the Lewis structure is



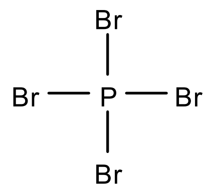
9.89 Total valence electrons = 5 + (2 x 6) - 1 = 16. The skeleton is O-N-O. Distribute the remaining electrons on the oxygen atoms.



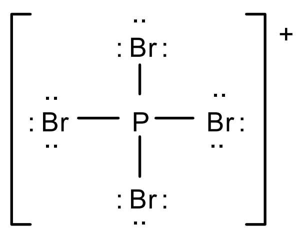
The nitrogen atom is short four electrons. Use two double bonds, one with each oxygen.

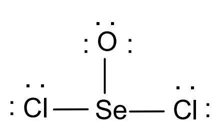
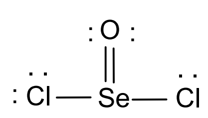
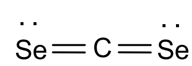


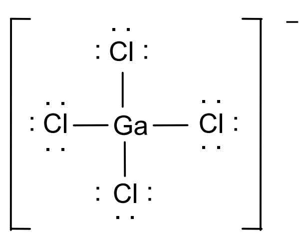
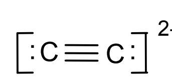
9.90 Total valence electrons = 5 + (4 x 7) - 1 = 32. The skeleton is

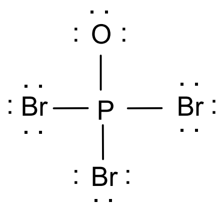
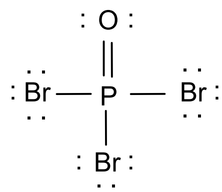


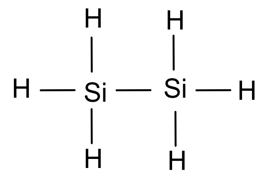
Distribute the twenty four remaining electrons to complete the octets on the bromine atoms.

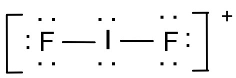


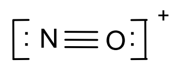
9.91 a.  or  b. 

c.  d. 

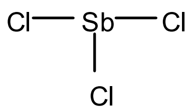
9.92 a.  or 

b. 

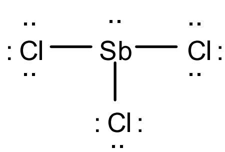
c. 

d. 

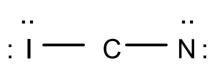
9.93 a. Total valence electrons = 5 + (3 x 7) = 26. The skeleton is



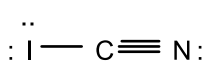
Distribute the remaining twenty electrons to the chlorine atoms and the antimony atom to complete their octets.



b. Total valence electrons = 7 + 4 + 5 = 16. The skeleton is I-C-N. Distribute the remaining twelve electrons.

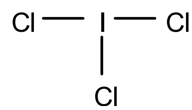


Notice the carbon atom is four electrons short of an octet. Make a triple bond between C and N from the four nonbonding electrons on the nitrogen.

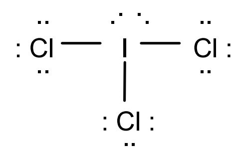


(continued)

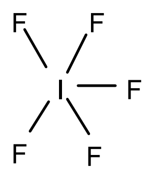
c. Total valence electrons = 7 + (3 x 7) = 28. The skeleton is



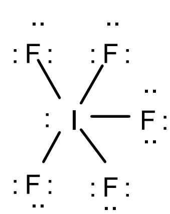
Distribute eighteen of the remaining twenty two electrons to complete the octets of the chlorine atoms. The four remaining electrons form two sets of lone pairs on the iodine atom.



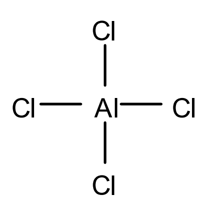
d. Total valence electrons = 7 + (5 x 7) = 42. The skeleton is



Use thirty of the remaining thirty two electrons to complete the octets of the fluorine atoms. The two electrons remaining form a lone pair on the iodine atom:

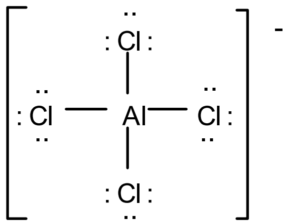


9.94 a. Total valence electrons = 3 + (4 x 7) + 1 = 32. The skeleton is

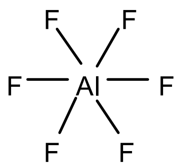


(continued)

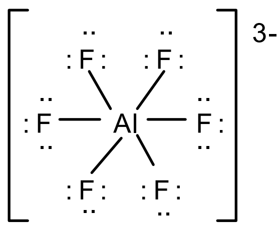
Distribute the remaining twenty four electrons to complete the octets of the Cl atoms.



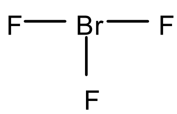
b. Total valence electrons = 3 + (6 x 7) + 3 = 48. The skeleton is



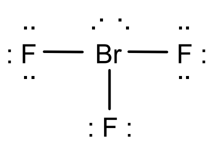
Distribute the remaining thirty six electrons to complete the octets of the F atoms.



c. Total valence electrons = 7 + (3 x 7) = 28. The skeleton is

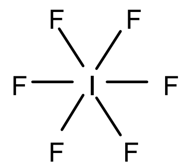


Distribute eighteen of the remaining twenty two electrons to complete the octets of the fluorine atoms. The four remaining electrons form two sets of lone pairs on the bromine atom.

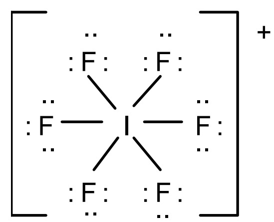


(continued)

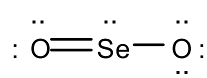
d. Total valence electrons = 7 + (6 x 7) - 1 = 48. The skeleton is



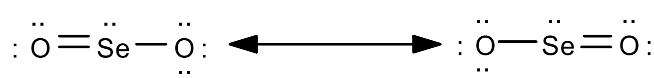
Distribute the remaining thirty six electrons to complete the octets of the fluorine atoms.



9.95 a. One possible electron-dot structure is

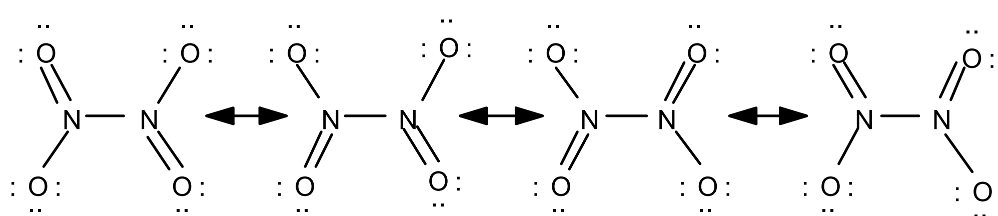


Because the selenium-oxygen bonds are expected to be equivalent, the structure must be described in resonance terms.



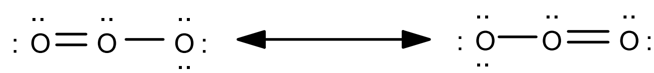
One electron pair is delocalized over the selenium atom and the two oxygen atoms.

b. The possible electron-dot structures are



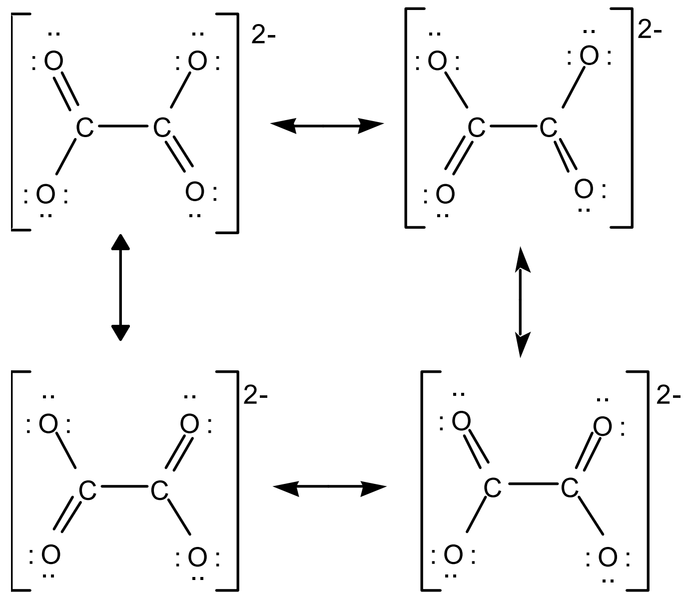
At each end of the molecule, a pair of electrons is delocalized over the region of the nitrogen atom and the two oxygen atoms.

9.96 a. The possible electron-dot structures are



A pair of electrons is delocalized over the region of the oxygen-oxygen bonds.

b. The possible electron-dot structures are

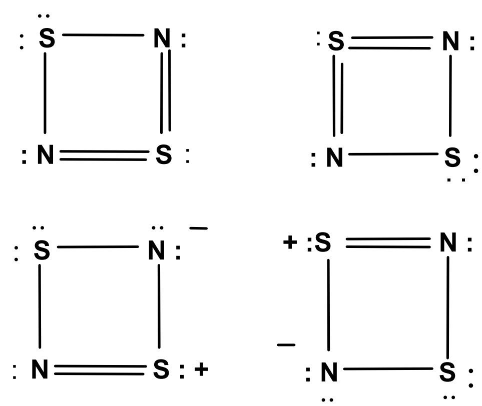


At each end of the molecule, a pair of electrons is delocalized over the region of the two carbon-oxygen bonds.

9.97 The compound S_2N_2 will have a four-membered ring structure. Calculate the total number of valence electrons of sulfur and nitrogen, which will be 6 + 6 + 5 + 5 = 22. Writing the skeleton of the four-membered ring with single S-N bonds will use up eight electrons, leaving fourteen electrons for electron pairs. After writing an electron pair on each atom, there will be six electrons left for three electron pairs. No matter where these electrons are written, either a nitrogen or a sulfur will be left with less than eight electrons. This suggests one or more double bonds are needed. If only one S=N double bond is written, writing the remaining twelve electrons as six electron pairs will give the sulfur in the S=N double bond a formal charge of +1 (see second line of formulas on next page). Writing two S=N double bonds using the same sulfur for both double bonds will give a formal charge of zero for all four atoms (see first line of formulas).

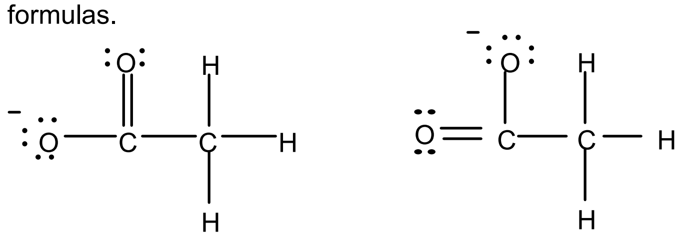
(continued)

The first two resonance formulas below have a zero formal charge on all atoms. However, one of the sulfur atoms does not obey the octet rule.



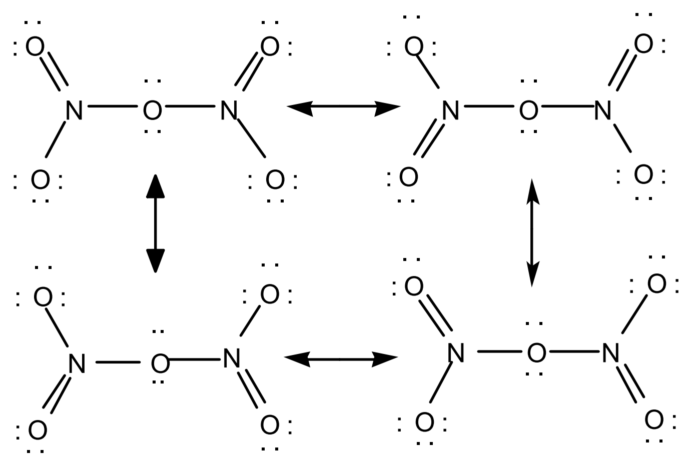
In the two resonance formulas immediately above, all of the atoms obey the octet rule, but there is a positive formal charge on one sulfur atom, and a negative formal charge on one nitrogen atom.

9.98 If you try to write an electron-dot formula for the acetate ion, you will find you can write two formulas.



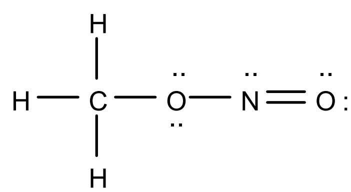
According to theory, the C=O double bond is delocalized; that is, a bonding pair of electrons is spread over the carbon atom and the two oxygen atoms rather than localized between a carbon and one oxygen. This results in both bonds being of identical length.

9.99 The possible electron-dot structures are



Because double bonds are shorter, the terminal N-O bonds are 118 pm, and the central N-O bonds are 136 pm.

9.100 The only possible electron-dot structure is



Because double bonds are shorter, the terminal N=O bond is 122 pm and the inner N-O bond is 137 pm.

9.101 $\Delta H = BE(H\text{-}H) + BE(O{=}O) - 2BE(H\text{-}O) - BE(O\text{-}O)$

$= (432 + 494 - 2 \times 459 - 142)\text{ kJ} = -134\text{ kJ}$

9.102 $\Delta H = 2BE(H\text{-}H) + BE(N{\equiv}N) - BE(N\text{-}N) - 4BE(N\text{-}H)$

$= (2 \times 432 + 942 - 167 - 4 \times 386)\text{ kJ} = +95\text{ kJ}$

9.103 $\Delta H = BE(N{=}N) + BE(F\text{-}F) - BE(N\text{-}N) - 2BE(N\text{-}F)$

$= (418 + 155 - 167 - 2 \times 283)\text{ kJ} = -1.60 \times 10^2\text{ kJ}$

9.104 $\Delta H = BE(C\equiv N) + 2BE(H\text{-}H) - BE(C\text{-}N) - 2BE(C\text{-}H) - 2BE(N\text{-}H)$

$$= (887 + 2 \times 432 - 305 - 2 \times 411 - 2 \times 386)\text{ kJ} = -148\text{ kJ}$$

■ Solutions to Cumulative-Skills Problems

Note on significant figures: The final answer to each cumulative-skills problem is given first with one nonsignificant figure (the rightmost significant figure is underlined) and then is rounded to the correct number of figures. Intermediate answers usually also have at least one nonsignificant figure. Atomic weights are rounded to two decimal places except for that of hydrogen.

9.105 The electronegativity differences and bond polarities are:

P- H	0.0	nonpolar
O- H	1.4	polar (acidic)

$$H_3PO_3(aq) + 2NaOH(aq) \rightarrow Na_2HPO_3(aq) + 2H_2O(l)$$

$$\frac{\text{mol}}{\text{L}} = \frac{0.1250\text{ mol NaOH}}{\text{L NaOH}} \times 0.02250\text{ L NaOH} \times \frac{1}{0.2000\text{ L }H_3PO_3}$$

$$\times \frac{1\text{ mol }H_3PO_3}{2\text{ mol NaOH}} \quad 0.00703\underline{1}2 = 0.007031\text{ M }H_3PO_3$$

9.106 The electronegativity differences and bond polarities are:

P- H	0.0	nonpolar
O- H	1.4	polar (acidic)

$$H_3PO_2(aq) + NaOH(aq) \rightarrow NaH_2PO_2(aq) + H_2O(l)$$

$$\frac{\text{mol}}{\text{L}} = \frac{0.1250\text{ mol NaOH}}{\text{L NaOH}} \times 0.02250\text{ L NaOH} \times \frac{1}{0.2000\text{ L }H_3PO_2}$$

$$\times \frac{1\text{ mol }H_3PO_2}{1\text{ mol NaOH}} = 0.0140\underline{6}2 = 0.01406\text{ M }H_3PO_2$$

9.107 After assuming a 100.0 g sample, convert to moles:

$$10.9 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.3 \text{ g Mg}} = 0.44\underline{8}5 \text{ mol Mg}$$

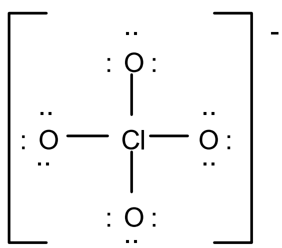
$$31.8 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.453 \text{ g Cl}} = 0.89\underline{6}96 \text{ mol Cl}$$

$$57.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.5\underline{8}1 \text{ mol O}$$

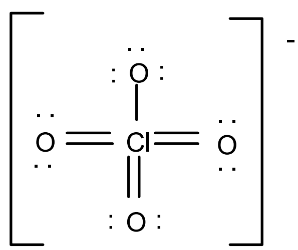
Divide by 0.4485:

$$\text{Mg: } \frac{0.4485}{0.4485} = 1; \text{ Cl: } \frac{0.89696}{0.4485} = 2.00; \text{ O: } \frac{3.581}{0.4485} = 7.98$$

The simplest formula is $MgCl_2O_8$. However, since $Cl_2O_8^{2-}$ is not a well known ion, write the simplest formula as $Mg(ClO_4)_2$, magnesium perchlorate. The Lewis formulas are Mg^{2+} and



or



9.108 After assuming a 100.0 g sample, convert to moles:

$$30.3 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{40.08 \text{ g Ca}} = 0.75\underline{5}9 \text{ mol Ca}$$

$$21.2 \text{ g N} \times \frac{1 \text{ mol N}}{14.01 \text{ g N}} = 1.5\underline{1}3 \text{ mol N}$$

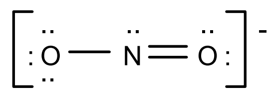
$$48.5 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.0\underline{3}1 \text{ mol O}$$

(continued)

Divide by 0.7559:

$$\text{Ca: } \frac{0.7559}{0.7559} = 1; \text{ N: } \frac{1.513}{0.7559} = 2.00; \text{ O: } \frac{3.031}{0.7559} = 4.01$$

The simplest formula is CaN_2O_4. However, since $N_2O_4^{2-}$ is not a well known ion, write the simplest formula as $Ca(NO_2)_2$, calcium nitrite. The Lewis formulas are Ca^{2+} and



9.109 After assuming a 100.0 g sample, convert to moles:

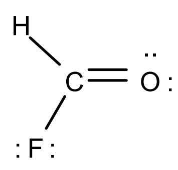
$$25.0 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 2.0\underline{8}1 \text{ mol C}$$

$$2.1 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 2.\underline{0}8 \text{ mol H}$$

$$39.6 \text{ g F} \times \frac{1 \text{ mol F}}{18.99 \text{ g F}} = 2.0\underline{8}5 \text{ mol F}$$

$$33.3 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.0\underline{8}1 \text{ mol O}$$

The simplest formula is CHOF. Because the molecular mass of 48.0 divided by the formula mass of 48.0 is one, the molecular formula is also CHOF. The Lewis formula is



9.110 After assuming a 100.0 g sample, convert to moles:

$$14.5 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 1.2\underline{0}7 \text{ mol C}$$

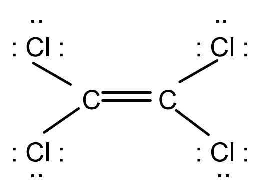
$$85.5 \text{ g Cl} \times \frac{1 \text{ mol Cl}}{35.453 \text{ g Cl}} = 2.4\underline{1}16 \text{ mol Cl}$$

(continued)

Divide by 1.207:

$$C: \frac{1.207}{1.207} = 1; \quad Cl: \frac{2.4116}{1.207} = 1.998$$

The simplest formula is CCl_2. Dividing the molecular mass by the formula mass gives 166 amu ÷ 82.92 amu = 2.0. The molecular formula is C_2Cl_4. The Lewis formula is



9.111 First, calculate the number of moles in one liter:

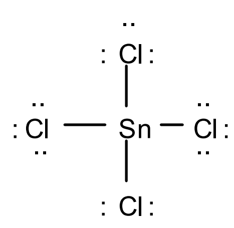
$$n = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 1.00 \text{ L}}{0.0821 \text{ L} \bullet \text{atm}/(\text{K} \bullet \text{mol}) \times 424 \text{ K}} = 0.028\underline{7}27 \text{ mol}$$

$$MW = \frac{g}{mol} = \frac{7.49 \text{ g}}{0.028727 \text{ mol}} = 26\underline{0}.7 \text{ g/mol}$$

$$MW = 260.7 \text{ amu} = 118.69 \text{ amu Sn} + n \times (35.453 \text{ amu Cl})$$

$$n = \frac{260.7 - 118.69}{35.453} = 4.0\underline{0}55$$

The formula is $SnCl_4$, which is molecular because the electronegativity difference is 1.2. The Lewis formula is



9.112 First, calculate the number of moles present:

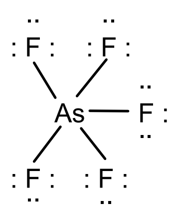
$$n = \frac{PV}{RT} = \frac{(765/760)\ \text{atm x } 0.0142\ \text{L}}{0.0821\ \text{L}\bullet\text{atm}/(\text{K}\bullet\text{mol}) \text{ x } 296\ \text{K}} = 5.8\underline{8}16 \text{ x } 10^{-4}\ \text{mol}$$

$$\text{MW} = \frac{\text{g}}{\text{mol}} = \frac{0.100\ \text{g}}{5.8816 \text{ x } 10^{-4}\ \text{mol}} = 17\underline{0}.02\ \text{g/mol}$$

MW = 170.02 amu = 74.92 amu As + n(18.998 amu F)

$$n = \frac{170.02 - 74.92}{18.998} = 5.0\underline{0}57$$

The formula is AsF_5. The Lewis formula is



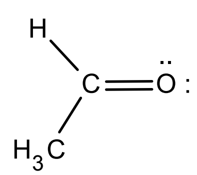
9.113 HCN(g) → H(g) + C(g) + N(g)

(135 218 715.0 473) ΔH_f (kJ/mol)

ΔH_{rxn} = 1271 kJ/mol

BE(C≡N) = ΔH - BE(C-H) = [1271 - 411] kJ/mol

= 860 kJ/mol (Table 9.5 has 887 kJ/mol.)

9.114  ⟶ 4 H (g) + 2 C (g) + O (g)

(-166 4 x 218 2 x 715 249.2) ΔH_f (kJ/mol)

ΔH_{rxn} = 2717.2 kJ/mol

BE(C=O) = ΔH - [4 x BE(C-H)] - BE(C-C)

= [2717.2 - (4 x 411) - 346] kJ/mol

= $72\underline{7}.2$ kJ/mol (Table 9.5 has 727 kJ/mol.)

9.115 Use the O-H bond and its bond energy of 459 kJ/mol to calculate X_o.

$$BE(O\text{-}H) = 1/2[BE(H\text{-}) + BE(O\text{-})] + k(X_O - X_H)^2$$

$$459 \text{ kJ/mol} = 1/2(432 \text{ kJ/mol} + 142 \text{ kJ/mol}) + 98.6 \text{ kJ } (X_O - X_H)^2$$

Collecting the terms gives

$$\frac{459 - 287}{98.6} = (X_o - X_H)^2$$

Taking the square root of both sides gives

$$1.3\underline{2}07 = 1.32 = (X_O - X_H)$$

Because $X_H = 2.1$, $X_O = 2.1 + 1.32 = 3.42 = 3.4$.

9.116 $BE(N\text{-}I) = 1/2[BE(N\text{-}N) + BE(I\text{-}I)] + k(X_N - X_I)^2$

$BE(N\text{-}I) = 1/2(167 + 149) + 98.6\,(3.0 - 2.5)^2$

$BE(N\text{-}I) = 158 + 24.65 = 18\underline{2}.65 = 183$ kJ/mol

9.117 $$X = \frac{\text{I.E.} - \text{E.A.}}{2} = \frac{[1250 - (-349)] \text{ kJ/mol}}{2} = 79\underline{9}.5 \text{ kJ/mol}$$

$$\frac{799.5 \text{ kJ/mol}}{230 \text{ kJ/mol}} = 3.47 \text{ (Pauling's X = 3.0)}$$

9.118 $$X = \frac{\text{I.E.} - \text{E.A.}}{2} = \frac{[1314 - (-141)] \text{ kJ/mol}}{2} = 72\underline{7}.5 \text{ kJ/mol}$$

$$\frac{727.5 \text{ kJ/mol}}{230 \text{ kJ/mol}} = 3.16 \text{ (Pauling's X = 3.5)}$$

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