

Chapter 9

Ionic and Covalent Bonding

Concept Check 9.1

The following are electron configurations of some ions. Which ones would you expect to see in chemical compounds? State the concept or rule you used to decide for or against any ion.

- $\text{Fe}^{2+} [\text{Ar}]3d^44s^2$
- $\text{N}^{2-} [\text{He}]2s^22p^5$
- $\text{Zn}^{2+} [\text{Ar}]3d^{10}$
- $\text{Na}^{2+} [\text{He}]2s^22p^5$
- $\text{Ca}^{2+} [\text{Ne}]3s^23p^6$

Solution

- 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 $[\text{Ar}]3d^64s^2$, would be expected to lose the two $4s$ electrons to give the configuration $[\text{Ar}]3d^6$ 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.
- Nitrogen, whose ground-state atomic configuration is $[\text{He}]2s^22p^3$, 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 $[\text{He}]2s^22p^6$. You would not expect to see the anion N^{2-} in compounds.
- The zinc atom has the ground-state configuration $[\text{Ar}]3d^{10}4s^2$. The element is often considered to be a transition element. In any case, you expect the atom to form compounds by losing its $4s$ electrons to give Zn^{2+} with the pseudo-noble-gas configuration $[\text{Ar}]3d^{10}$. This is the ion configuration given in the problem.
- The configuration of the ground-state sodium atom is $[\text{He}]2s^22p^63s^1$. You would expect the atom to lose one electron to give the Na^+ ion with the noble-gas configuration $[\text{He}]2s^22p^6$. You would not expect to see compounds with the Na^{2+} ion.

- e. The ground state of the calcium atom is $[\text{Ne}]3s^23p^64s^2$. You would expect the atom to lose its two outer electrons to give the Ca^{2+} ion with noble-gas configuration $[\text{Ne}]3s^23p^6$, which is the configuration given in the problem.

Concept Check 9.2

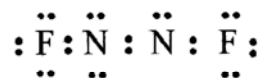
Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2 . Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?

- a. $\begin{array}{cccc} \ddot{\text{F}} & \ddot{\text{N}} & \ddot{\text{N}} & \ddot{\text{F}} \\ \vdots & \vdots & \vdots & \vdots \\ \text{:} & \text{:} & \text{:} & \text{:} \\ \vdots & \vdots & \vdots & \vdots \\ \ddot{\text{F}} & \ddot{\text{N}} & \ddot{\text{N}} & \ddot{\text{F}} \end{array}$
- b. $\begin{array}{cccc} \ddot{\text{F}} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \ddot{\text{F}} \\ \vdots & \vdots & & \vdots & \vdots \\ \text{:} & \text{:} & \text{:} & \text{:} & \text{:} \\ \vdots & \vdots & & \vdots & \vdots \\ \ddot{\text{F}} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \ddot{\text{F}} \end{array}$
- c. $\begin{array}{cccc} \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{F}} \\ \vdots & & \vdots & & \vdots & & \vdots \\ \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} \\ \vdots & & \vdots & & \vdots & & \vdots \\ \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{F}} \end{array}$
- d. $\begin{array}{cccc} \ddot{\text{F}} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \ddot{\text{F}} \\ \vdots & \vdots & & \vdots & \vdots \\ \text{:} & \text{:} & \text{:} & \text{:} & \text{:} \\ \vdots & \vdots & & \vdots & \vdots \\ \ddot{\text{F}} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \ddot{\text{F}} \end{array}$
- e. $\begin{array}{cccc} \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} & \text{:} & \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} \\ \vdots & & \vdots & & & \vdots & & \vdots & \\ \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} \\ \vdots & & \vdots & & & \vdots & & \vdots & \\ \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} & \text{:} & \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} \end{array}$
- f. $\begin{array}{cccc} \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{F}} \\ \vdots & & \vdots & & \vdots & & \vdots \\ \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} & \text{:} \\ \vdots & & \vdots & & \vdots & & \vdots \\ \ddot{\text{F}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{N}} & \text{:} & \ddot{\text{F}} \end{array}$

Solution

- 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 shells of the atoms (5 for each nitrogen atom and 7 for each fluorine atom), which is $(2 \times 5) + (2 \times 7) = 24$, or 12 pairs. The number showing in the formula here is 13, 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 9 electron pairs (3 for the single bonds and 3 for each F atom to fill out its octet). This leaves 3 pairs, which you might distribute as follows:

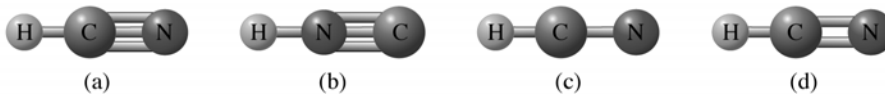


One of the nitrogen atoms (the one on the right) does not have an octet. The lack of an octet on this atom suggests that you try for a double bond. This suggests that you move one of the lone pairs on the left N atom into one of the adjacent bonding regions. Moving this lone pair into the N—N region 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.

- 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 charges. Rule A says that whenever you can write several Lewis formulas for a molecule, 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.
- 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.
- This formula does not have the correct skeleton structure.
- 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.

Concept Check 9.3

Which of the models shown below most accurately represents the hydrogen cyanide molecule, HCN? Write the electron-dot formula that most closely agrees with this model. State any concept or rule you used in arriving at your answer.



Solution

- This model and corresponding Lewis structure, $\text{H:C}::\text{N}$;, 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.
- 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.
- If you draw the Lewis structure, you will see that each atom has an octet, but the formula has too many electron pairs (7 instead of 5). You can remove two pairs and still retain octets if you move two lone pairs into the bonding region, giving a triple bond.
- 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 charges for each atom, such high formal charges for the atoms in formula d. mean that it is not a very good representation of the molecule.

Conceptual Problem 9.19

You land on a distant planet in another universe and find that the $n = 1$ level can hold a maximum of 4 electrons, the $n = 2$ level can hold a maximum of 5 electrons, and the $n = 3$ level can hold a maximum of 3 electrons. Like our universe, protons have a charge of +1, electrons have a charge of -1, and opposite charges attract. Also, a filled shell results in greater stability of an atom, so the atom tends to gain or lose electrons to give a filled shell. Predict the formula of a compound that results from the reaction of a neutral metal atom X, which has 7 electrons, and a neutral nonmetal atom Y, which has three electrons.

Solution

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 .

Conceptual Problem 9.20

Which of the following represent configurations of thallium ions in compounds? Explain your decision in each case.

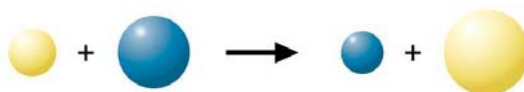
- $Tl^{2+} [Xe]4f^{14}5d^{10}6p^1$
- $Tl^{3+} [Xe]4f^{14}5d^{10}$
- $Tl^{4+} [Xe]4f^{14}5d^9$
- $Tl^+ [Xe]4f^{14}5d^{10}6s^2$

Solution

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 configurations in d. and b., respectively. The +2 ion given in a. represents a loss of the two outer s electrons, leaving the outer p electron 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.

Conceptual Problem 9.21

Below on the left side are models of two atoms, one from a metal, the other from a nonmetal. On the right side are corresponding monatomic ions of those atoms. Decide which of these ions is the cation and which is the anion. Label atoms as “metal” or “nonmetal” as appropriate.



Solution

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).

Conceptual Problem 9.22

Predict a possible monatomic ion for Element 117, Unus. Given the spherical models below, which should be labeled “atom” and which should be labeled “ion”?

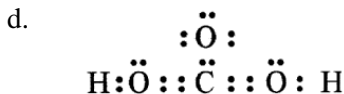
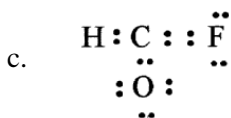
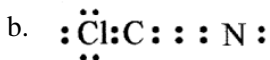
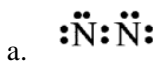


Solution

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.

Conceptual Problem 9.23

Examine each of the following electron-dot formulas and decide whether the formula is correct, or whether you could write a formula that better approximates the electron structure of the molecule. State which concepts or rules you use in each case to arrive at your conclusion.



Solution

- 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.

Conceptual Problem 9.24

For each of the following molecular models, write an appropriate Lewis formula.



(a)



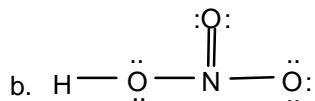
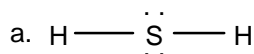
(b)

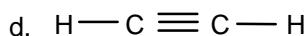
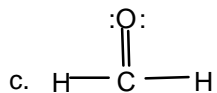


(c)



(d)

Solution



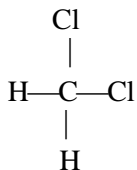
Conceptual Problem 9.25

For each of the following molecular formulas, draw the most reasonable skeleton structure.

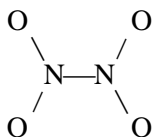
- CH_2Cl_2
- HNO_2
- NOF
- N_2O_4

Solution

- 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.

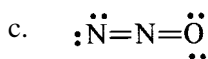
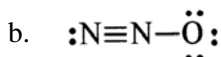
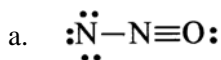


- HNO_2 is an oxyacid in which O atoms bond to the central atom, with the H bonded to O. The central atom must be N (the only other atom), so the skeleton structure is
 $\text{H}-\text{O}-\text{N}-\text{O}$
- You place the least electronegative atom (N) as the central atom and bond it to the other atoms.
 $\text{F}-\text{N}-\text{O}$
- N is less electronegative than O. The most symmetrical structure would have the two N atoms in the center with two O atoms bonded to each N atom.



Conceptual Problem 9.24

Below are a series of resonance formulas for N_2O (nitrous oxide). Rank these in terms of how closely you think each one represents the true electron structure of the molecule. State the rules and concepts you use to do this ranking.



Solution

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

- 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.
- 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.
- This formula has -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.