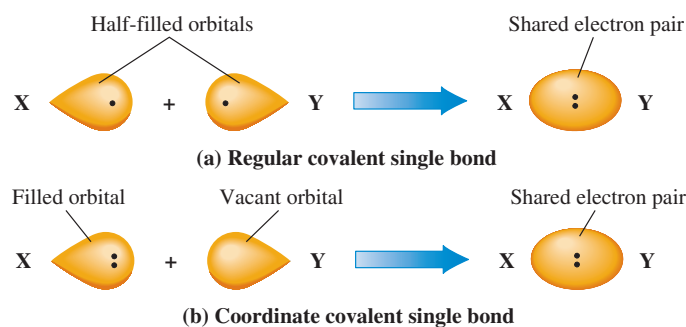


Figure 5.3 (a) A “regular” covalent single bond is the result of overlap of two half-filled orbitals. (b) A coordinate covalent single bond is the result of overlap of a filled and a vacant orbital.



In hypochlorous acid, all the bonds are “ordinary” covalent bonds. In chlorous acid, which differs from hypochlorous acid in that a second oxygen atom is present, the “new” chlorine–oxygen bond is a coordinate covalent bond. The second oxygen atom with six valence electrons (denoted by x’s) needs two more for an octet. It shares one of the nonbonding electron pairs present on the chlorine atom. (The chlorine atom does not need any of the oxygen’s electrons because it already has an octet.)

Atoms participating in coordinate covalent bonds generally deviate from the common bonding pattern (Section 5.4) expected for that type of atom. For example, oxygen normally forms two bonds; yet in the molecules N_2O and CO , which contain coordinate covalent bonds, oxygen forms one and three bonds, respectively.



Once a coordinate covalent bond is formed, there is no way to distinguish it from any of the other covalent bonds in a molecule; all electrons are identical regardless of their source. The main use of the concept of coordinate covalency is to help rationalize the existence of certain molecules and polyatomic ions whose electron-bonding arrangement would otherwise present problems. Figure 5.3 contrasts the formation of a “regular” covalent bond with that of a coordinate covalent bond.

5.6 SYSTEMATIC PROCEDURES FOR DRAWING LEWIS STRUCTURES

Could you generate the Lewis structures of HOCl , HClO_2 , N_2O , and CO given in the preceding section without any help? Drawing Lewis structures for diatomic molecules is usually straightforward and uncomplicated. However, with triatomic and even larger molecules, students often have trouble. Here is a stepwise procedure for distributing valence electrons as bonding and nonbonding pairs within a Lewis structure.

Let us apply this stepwise procedure to the molecule SO_2 , a molecule in which two oxygen atoms are bonded to a central sulfur atom (see Figure 5.4).

Step 1: Calculate the total number of valence electrons available in the molecule by adding together the valence electron counts for all atoms in the molecule. The periodic table is a useful guide for determining this number.

An SO_2 molecule has 18 valence electrons available for bonding. Sulfur (Group VIA) has 6 valence electrons, and each oxygen (also Group VIA) has 6 valence electrons. The total number is therefore $6 + 2(6) = 18$.

Step 2: Write the chemical symbols of the atoms in the molecule in the order in which they are bonded to one another, and then place a single covalent bond, involving two electrons, between each pair of bonded atoms. For SO_2 , the S atom is the central atom. Thus we have

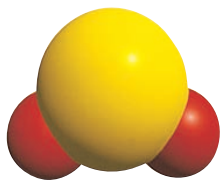


Figure 5.4 The sulfur dioxide (SO_2) molecule. A computer-generated model.

Atoms participating in coordinate covalent bonds generally do not form their normal number of covalent bonds.

Once a coordinate covalent bond forms, it is indistinguishable from other covalent bonds in a molecule.

Determining which atom is the *central atom*—that is, which atom has the most other atoms bonded to it—is the key to determining the arrangement of atoms in a molecule or polyatomic ion. Most other atoms present will be bonded to the central atom. For common binary molecular compounds, the molecular formula can help us determine the identity of the central atom. The central atom is the atom that appears only once in the formula; for example, S is the central atom in SO_3 , O is the central atom in H_2O , and P is the central atom in PF_3 . In molecular compounds containing hydrogen, oxygen, and an additional element, that additional element is the central atom; for example, N is the central atom in HNO_3 , and S is the central atom in H_2SO_4 . In compounds of this type, the oxygen atoms are bonded to the central atom, and the hydrogen atoms are bonded to the oxygens. Carbon is the central atom in nearly all carbon-containing compounds. Neither hydrogen nor fluorine is ever the central atom.

Step 3: *Add nonbonding electron pairs to the structure such that each atom bonded to the central atom has an octet of electrons. Remember that for hydrogen, an “octet” is only 2 electrons.*

For SO_2 , addition of the nonbonding electrons gives



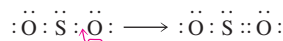
At this point, 16 of the 18 available electrons have been used.

Step 4: *Place any remaining electrons on the central atom of the structure.*
Placing the two remaining electrons on the S atom gives



Step 5: *If there are not enough electrons to give the central atom an octet, then use one or more pairs of nonbonding electrons on the atoms bonded to the central atom to form double or triple bonds.*

The S atom has only 6 electrons. Thus a nonbonding electron pair from an O atom is used to form a sulfur–oxygen double bond.



This structure now obeys the octet rule.

Step 6: *Count the total number of electrons in the completed Lewis structure to make sure it is equal to the total number of valence electrons available for bonding, as calculated in Step 1. This step serves as a “double-check” on the correctness of the Lewis structure.*

For SO_2 , there are 18 valence electrons in the Lewis structure of Step 5, the same number we calculated in Step 1.

EXAMPLE 5.2

Drawing a Lewis Structure Using Systematic Procedures

Draw Lewis structures for the following molecules.

- PF_3 , a molecule in which P is the central atom and all F atoms are bonded to it (see Figure 5.5).
- HCN , a molecule in which C is the central atom (see Figure 5.6).

Solution

- Step 1:** Phosphorus (Group VA) has 5 valence electrons, and each of the fluorine atoms (Group VIIA) has 7 valence electrons. The total electron count is $5 + 3(7) = 26$.

(continued)