A monatomic ion has an oxidation number equal to the charge of the ion. For example, the ions Na^+, Ca^{2+}, and Cl^- have oxidation numbers of +1, +2, and −1, respectively.

Let's examine the assignment of oxidation numbers to the atoms in two molecular compounds, hydrogen fluoride, HF, and water, H_2O. Both compounds have polar-covalent bonds. In HF, the fluorine atom should have an oxidation number of −1 (see Rule 3 on the previous page). Rule 5 tells us that hydrogen should have an oxidation number of +1. This makes sense because fluorine is more electronegative than hydrogen, and in a polar-covalent bond, shared electrons are assumed to belong to the more-electronegative element. For water, Rules 4 and 5 tell us that the oxidation number of oxygen should be −2 and the oxidation number of each hydrogen atom should be +1. Again, oxygen is more electronegative than hydrogen, so the shared electrons are assumed to belong to oxygen.

Because the sum of the oxidation numbers of the atoms in a compound must satisfy Rule 6 or 7 of the guidelines on the previous page, it is often possible to assign oxidation numbers when they are not known. This is illustrated in Sample Problem E.

SAMPLE PROBLEM E

Assign oxidation numbers to each atom in the following compounds or ions:

a. UF_6

b. H_2SO_4

c. ClO_3^-

SOLUTION

a. Start by placing known oxidation numbers above the appropriate elements. From the guidelines, we know that fluorine always has an oxidation number of −1.

$$\mathrm{U}\overset{-1}{\mathrm{F}}_6$$

Multiply known oxidation numbers by the appropriate number of atoms and place the totals underneath the corresponding elements. There are six fluorine atoms, 6 × −1 = −6.

$$\mathrm{U}\underset{-6}{\overset{-1}{\mathrm{F}}}_6$$

The compound UF_6 is molecular. According to the guidelines, the sum of the oxidation numbers must equal zero. The total of positive oxidation numbers is therefore +6.

$$\underset{+6}{\mathrm{U}}\underset{-6}{\overset{-1}{\mathrm{F}}}_6$$

Divide the total calculated oxidation number by the appropriate number of atoms. There is only one uranium atom in the molecule, so it must have an oxidation number of +6.