9.2 Oxidation Numbers

Phosphates, like ammonium phosphate, are important components of fertilizers used to stimulate the growth of agricultural crops and to make our gardens green. Their commercial synthesis requires elemental phosphorus, which can be acquired by heating phosphate rock (containing calcium phosphate) with sand (containing silicon dioxide) and coke (a carbon-rich mixture produced by heating coal). This method for isolating phosphorus, called the *furnace process*, is summarized in the first equation below. The other equations show how phosphorus can be converted into ammonium phosphate.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 10CO + 6CaSiO_3$$

$$P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4$$

$$H_3PO_4 + NH_3 \rightarrow (NH_4)_3PO_4$$

Are these reactions oxidation-reduction reactions? Are electrons transferred? Simply reading a chemical equation does not always tell us whether oxidation and reduction have occurred, so chemists have developed a numerical system to help identify a reaction as redox. For redox reactions, this system also shows us which element is oxidized, which is reduced, what the oxidizing agent is, and what the reducing agent is.

The first step in this system is to assign an **oxidation number** to each atom in the reaction equation. As you become better acquainted with the procedure, you will gain a better understanding of what the numbers signify, but for now, just think of them as tools for keeping track of the flow of electrons in redox reactions. Oxidation numbers are also called **oxidation states**.

OBJECTIVE 4
OBJECTIVE 5
OBJECTIVE 6

If any element undergoes a change of oxidation number in the course of a reaction, the reaction is a redox reaction. If an element's oxidation number increases in a reaction, that element is oxidized. If an element's oxidation number decreases in a reaction, that element is reduced. The reactant containing the element that is oxidized is the reducing agent. The reactant containing the element that is reduced is the oxidizing agent (Table 9.1).

Table 9.1
Questions Answered by the Determination of Oxidation Numbers

OBJECTIVE 4 OBJECTIVE 5 OBJECTIVE 6

Question	Answer
Is the reaction redox?	If any atoms change their oxidation number, the reaction is redox.
Which element is oxidized?	The element that increases its oxidation number is oxidized.
Which element is reduced?	The element that decreases its oxidation number is reduced.
What's the reducing agent?	The reactant that contains the element that is oxidized is the reducing agent.
What's the oxidizing agent?	The reactant that contains the element that is reduced is the oxidizing agent.

Study Sheet 9.1 on the next page describes how you can assign oxidation numbers to individual atoms.

Sample Study Sheet 9.1 Assignment of Oxidation Numbers

OBJECTIVE 3

TIP-OFF You are asked to determine the oxidation number of an atom, or you need to assign oxidation numbers to atoms to determine whether a reaction is a redox reaction, and if it is, to identify which element is oxidized, which is reduced, what the oxidizing agent is, and what the reducing agent is.

GENERAL STEPS

Use the following guidelines to assign oxidation numbers to as many atoms as you can. (Table 9.2 provides a summary of these guidelines with examples.)

- The oxidation number for each atom in a pure element is zero.
- The oxidation number of a monatomic ion is equal to its charge.
- When fluorine atoms are combined with atoms of other elements, their oxidation number is −1.
- When oxygen atoms are combined with atoms of other elements, their oxidation number is −2, except in peroxides, such as hydrogen peroxide, H_2O_2, where their oxidation number is −1. (*There are other exceptions that you will not see in this text.*)
- The oxidation number for each hydrogen atom in a molecular compound or a polyatomic ion is +1.

If a compound's formula contains one element for which you cannot assign an oxidation number using the guidelines listed above, calculate the oxidation number according to the following rules.

- The sum of the oxidation numbers for the atoms in an uncharged formula is equal to zero.
- The sum of the oxidation numbers for the atoms in a polyatomic ion is equal to the overall charge on the ion.

EXAMPLE See Example 9.1.

Table 9.2
Guidelines for Assigning Oxidation Numbers

	Oxidation number	Examples	Exceptions
Pure element	0	The oxidation number for each atom in Zn, H_2, and S_8 is zero.	none
Monatomic ions	charge on ion	Cd in $CdCl_2$ is +2. Cl in $CdCl_2$ is −1. H in LiH is −1.	none
Fluorine in the combined form	−1	F in AlF_3 is −1. F in CF_4 is −1.	none
Oxygen in the combined form	−2	O in ZnO is −2. O in H_2O is −2.	O is −1 in peroxides, such as H_2O_2
Hydrogen in the combined form	+1	H in H_2O is +1.	H is −1 when combined with a metal.

Example 9.1 shows how we can use our new tools.

Example 9.1 - Oxidation Numbers and Redox Reactions

Objective 3
Objective 4
Objective 5
Objective 6

The following equations represent the reactions that lead to the formation of ammonium phosphate for fertilizers. Determine the oxidation number for each atom in the formulas. Decide whether each reaction is a redox reaction, and if it is, identify what element is oxidized, what is reduced, what the oxidizing agent is, and what the reducing agent is.

a. $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 10CO + 6CaSiO_3$

b. $P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4$

c. $H_3PO_4 + NH_3 \rightarrow (NH_4)_3PO_4$

Solution

a. The first step is to determine the oxidation number for each atom in the reaction. Let's consider the first equation above:

Combined oxygen, oxidation number –2

Pure elements, oxidation number zero

Monatomic ion, oxidation number equal to its charge (+2)

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 10CO + 6CaSiO_3$$

Monatomic ion, oxidation number equal to its charge (+2)

Combined oxygen, oxidation number –2

Because the sum of the oxidation numbers for the atoms in an uncharged molecule is zero, the oxidation number of the carbon atom in CO is +2:

$$(\text{ox \# C}) + (\text{ox \# O}) = 0$$

$$(\text{ox \# C}) + -2 = 0$$

$$(\text{ox \# C}) = +2$$

Using a similar process, we can assign a +4 oxidation number to the silicon atom in SiO_2:

$$(\text{ox \# Si}) + 2(\text{ox \# O}) = 0$$

$$(\text{ox \# Si}) + 2(-2) = 0$$

$$(\text{ox \# Si}) = +4$$

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound that contains monatomic calcium ions, Ca^{2+}, and polyatomic phosphate ions, PO_4^{3-}. The oxidation number of each phosphorus atom can be determined in two ways. The following shows how it can be done considering the whole formula.

$$3(\text{ox \# Ca}) + 2(\text{ox \# P}) + 8(\text{ox \# O}) = 0$$

$$3(+2) + 2(\text{ox \# P}) + 8(-2) = 0$$

$$(\text{ox \# P}) = +5$$

The oxidation number for the phosphorus atom in PO_4^{3-} is always the same, no matter what the cation is that balances its charge. Thus we could also have determined the oxidation number of each phosphorus atom by considering the phosphate ion separately from the calcium ion.

$$(\text{ox \# P}) + 4(\text{ox \# O}) = -3$$

$$(\text{ox \# P}) + 4(-2) = -3$$

$$(\text{ox \# P}) = +5$$

The silicon atoms in $CaSiO_3$ must have an oxidation number of +4.

$$(\text{ox \# Ca}) + (\text{ox \# Si}) + 3(\text{ox \# O}) = 0$$

$$(+2) + (\text{ox \# Si}) + 3(-2) = 0$$

$$(\text{ox \# Si}) = +4$$

The oxidation numbers for the individual atoms in the first reaction are below.

Oxidation number increases, oxidized

$$\overset{+2}{2Ca_3}(\overset{+5}{P}O_4)_2 + 6\overset{+4}{Si}O_2 + 10\overset{0}{C} \longrightarrow \overset{0}{P_4} + 10\overset{+2}{C}O + 6\overset{+4}{Ca}\overset{+2}{Si}O_3$$

Oxidation number decreases, reduced

Phosphorus atoms and carbon atoms change their oxidation numbers, so **the reaction is redox**. Each phosphorus atom changes its oxidation number from +5 to zero, so the **phosphorus atoms in $Ca_3(PO_4)_2$ are reduced, and $Ca_3(PO_4)_2$ is the oxidizing agent**. Each carbon atom changes its oxidation number from zero to +2, so the **carbon atoms are oxidized, and carbon is the reducing agent**.

b. Now, let's consider the second reaction.

Combined oxygen, oxidation number −2

$$P_4 + 5O_2 + 6H_2O \longrightarrow 4H_3PO_4$$

Pure elements, oxidation number 0

Hydrogen in a molecular compound, oxidation number +1

The following shows how we can determine the oxidation number of the phosphorus atom in H_3PO_4:

$$3(\text{ox \# H}) + (\text{ox \# P}) + 4(\text{ox \# O}) = 0$$

$$3(+1) + (\text{ox \# P}) + 4(-2) = 0$$

$$(\text{ox \# P}) = +5$$

The oxidation numbers for the individual atoms in the second reaction are below.

Oxidation number increases, oxidized

$$\overset{0}{P_4} + 5\overset{0}{O_2} + 6\overset{+1\ -2}{H_2O} \longrightarrow 4\overset{+1\ +5\ -2}{H_3PO_4}$$

Oxidation number decreases, reduced

Phosphorus atoms and oxygen atoms change their oxidation numbers, so **the reaction is redox**. Each phosphorus atom changes its oxidation number from zero to +5, so the **phosphorus atoms in P_4 are oxidized, and P_4 is the reducing agent**. Each oxygen atom in O_2 changes its oxidation number from zero to −2, so the **oxygen atoms in O_2 are reduced, and O_2 is the oxidizing agent**.

c. Finally, let's consider the third reaction.

Hydrogen in a molecule, oxidation number +1 — Hydrogen in a polyatomic ion, oxidation number +1

$$H_3PO_4 + NH_3 \longrightarrow (NH_4)_3PO_4$$

Combined oxygen, oxidation number −2

We know from part (b) that the oxidation number of the phosphorus atoms in H_3PO_4 is +5.

The oxidation number of the nitrogen atom in NH_3 is calculated below.

$$(\text{ox \# N}) + 3(\text{ox \# H}) = 0$$

$$(\text{ox \# N}) + 3(+1) = 0$$

$$(\text{ox \# N}) = -3$$

We can determine the oxidation number of each nitrogen atom in $(NH_4)_3PO_4$ in two ways, either from the whole formula or from the formula for the ammonium ion alone.

$$3(\text{ox \# N}) + 12(\text{ox \# H}) + (\text{ox \# P}) + 4(\text{ox \# O}) = 0$$

$$3(\text{ox \# N}) + 12(+1) + (+5) + 4(-2) = 0$$

$$(\text{ox \# N}) = -3$$

or $(\text{ox \# N}) + 4(\text{ox \# H}) = +1$

$$(\text{ox \# N}) + 4(+1) = +1$$

$$(\text{ox \# N}) = -3$$

The oxidation numbers for the individual atoms in this reaction are below.

$$\overset{+1\ +5\ -2}{H_3PO_4} + \overset{-3\ +1}{NH_3} \longrightarrow \overset{-3\ +1}{(NH_4)_3}\overset{+5\ -2}{PO_4}$$

None of the atoms change their oxidation number, so **the reaction is not redox.**

Exercise 9.1 - Oxidation Numbers

Objective 3
Objective 4
Objective 5
Objective 6

In one part of the steel manufacturing process, carbon is combined with iron to form pig iron. Pig iron is easier to work with than pure iron because it has a lower melting point (about 1130 °C compared to 1539 °C for pure iron) and is more pliable. The following equations describe its formation. Determine the oxidation number for each atom in the formulas. Decide whether each reaction is a redox reaction, and if it is, identify what is oxidized, what is reduced, what the oxidizing agent is, and what the reducing agent is.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

$$Fe_2O_3(s) + CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

$$2CO(g) \rightarrow C(\textit{in iron}) + CO_2(g)$$

Equations for redox reactions can be difficult to balance, but your ability to determine oxidation numbers can help. You can find a description of the process for balancing redox equations at the textbook's Web site.