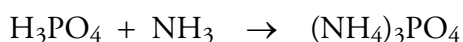
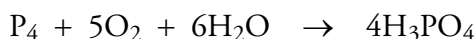
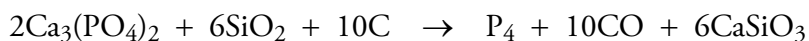


## 9.2 Oxidation Numbers

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.



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**.

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).

OBJECTIVE 4

OBJECTIVE 5

OBJECTIVE 6

**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,  $\text{H}_2\text{O}_2$ , 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**

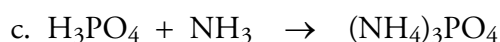
Guidelines for Assigning Oxidation Numbers

	Oxidation number	Examples	Exceptions
Pure element	0	The oxidation number for each atom in $\text{Zn}$ , $\text{H}_2$ , and $\text{S}_8$ is zero.	none
Monatomic ions	charge on ion	$\text{Cd}$ in $\text{CdCl}_2$ is $+2$ . $\text{Cl}$ in $\text{CdCl}_2$ is $-1$ . $\text{H}$ in $\text{LiH}$ is $-1$ .	none
Fluorine in the combined form	$-1$	$\text{F}$ in $\text{AlF}_3$ is $-1$ . $\text{F}$ in $\text{CF}_4$ is $-1$ .	none
Oxygen in the combined form	$-2$	$\text{O}$ in $\text{ZnO}$ is $-2$ . $\text{O}$ in $\text{H}_2\text{O}$ is $-2$ .	$\text{O}$ is $-1$ in peroxides, such as $\text{H}_2\text{O}_2$
Hydrogen in the combined form	$+1$	$\text{H}$ in $\text{H}_2\text{O}$ is $+1$ .	$\text{H}$ is $-1$ when combined with a metal.

Example 9.1 shows how we can use our new tools.

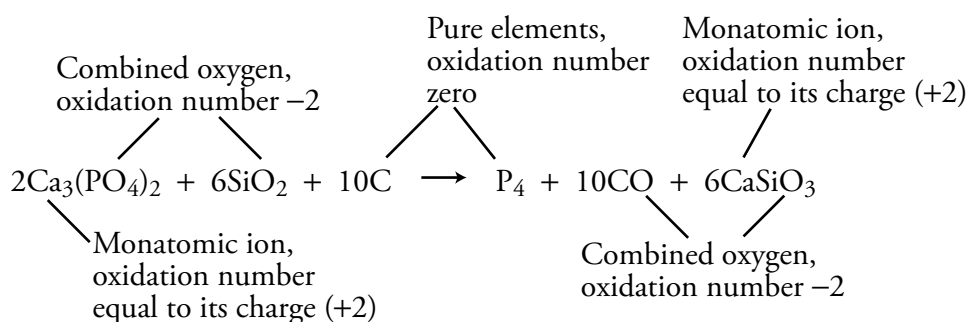
### EXAMPLE 9.1 - Oxidation Numbers and Redox Reactions

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.



*Solution*

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



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  $\text{SiO}_2$ :

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

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

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

Calcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , is an ionic compound that contains monatomic calcium ions,  $\text{Ca}^{2+}$ , and polyatomic phosphate ions,  $\text{PO}_4^{3-}$ . 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.

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

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

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

OBJECTIVE 3

OBJECTIVE 4

OBJECTIVE 5

OBJECTIVE 6

The oxidation number for the phosphorus atom in  $\text{PO}_4^{3-}$  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.

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

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

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

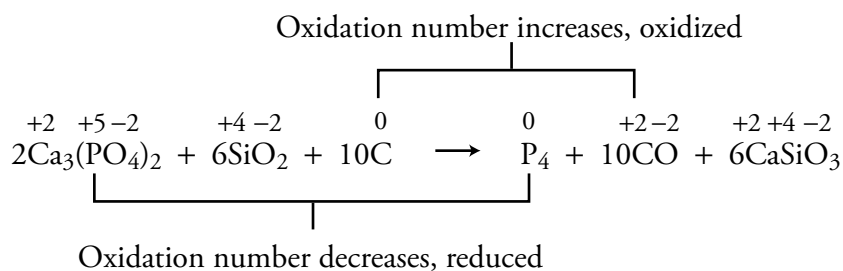
The silicon atoms in  $\text{CaSiO}_3$  must have an oxidation number of +4.

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

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

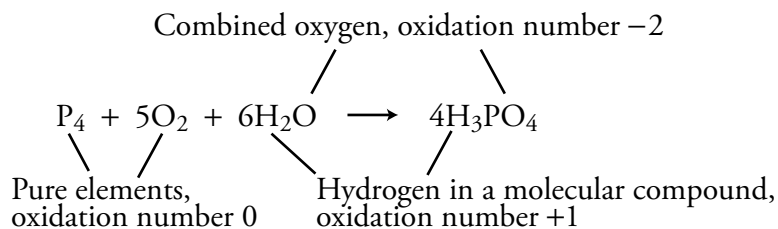
$$(\text{ox \# Si}) = +4$$

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



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  $\text{Ca}_3(\text{PO}_4)_2$  are reduced, and  $\text{Ca}_3(\text{PO}_4)_2$  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.



The following shows how we can determine the oxidation number of the phosphorus atom in  $\text{H}_3\text{PO}_4$ :

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

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

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



## OBJECTIVE 3

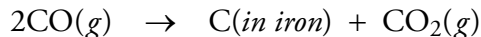
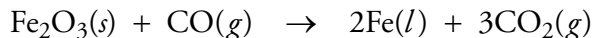
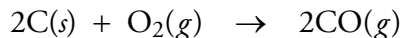
## OBJECTIVE 4

## OBJECTIVE 5

## OBJECTIVE 6

**EXERCISE 9.1 - Oxidation Numbers**

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.



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.