

4.10: Oxidation-Reduction Reactions

An oxidation-reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species. An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

📌 Rules for Assigning Oxidation States

The oxidation state (OS) of an element corresponds to the number of electrons, e^- , that an atom loses, gains, or appears to use when joining with other atoms in compounds. In determining the oxidation state of an atom, there are seven guidelines to follow:

1. The oxidation state of an individual atom is 0.
2. The total oxidation state of all atoms in: a *neutral species* is 0 and in an *ion* is equal to the ion charge.
3. Group 1 metals have an oxidation state of +1 and Group 2 an oxidation state of +2
4. The oxidation state of fluorine is -1 in compounds
5. Hydrogen generally has an oxidation state of +1 in compounds
6. Oxygen generally has an oxidation state of -2 in compounds
7. In binary metal compounds, Group 17 elements have an oxidation state of -1, Group 16 elements of -2, and Group 15 elements of -3.

*The **sum** of the oxidation states is equal to zero for neutral compounds and equal to the **charge** for polyatomic ion species.*

✓ Example 4.10.1: Assigning Oxidation States

Determine the Oxidation States of each element in the following reactions:

- a. $\text{Fe}(s) + \text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(g)$
- b. $\text{Fe}^{2+}(aq)$
- c. $\text{Ag}(s) + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S}(g) + \text{H}_2(g)$

Solutions

- A. Fe and O_2 are free elements; therefore, they each have an oxidation state of 0 according to Rule #1. The product has a total oxidation state equal to 0, and following Rule #6, O has an oxidation state of -2, which means Fe has an oxidation state of +3.
- B. The oxidation state of Fe ions just corresponds to its charge since it is a single element species; therefore, the oxidation state is +2.
- C. Ag has an oxidation state of 0, H has an oxidation state of +1 according to Rule #5, H_2 has an oxidation state of 0, S has an oxidation state of -2 according to Rule #7, and hence Ag in Ag_2S has an oxidation state of +1.

✓ Example 4.10.2: Assigning Oxidation States

Determine the oxidation states of the phosphorus atom bold element in each of the following species:

- a. Na_3PO_3
- b. H_2PO_4^-

Solutions

- a. The oxidation numbers of Na and O are +1 and -2. Because sodium phosphite is neutral species, the sum of the oxidation numbers must be zero. Letting x be the oxidation number of phosphorus, $0 = 3(+1) + x + 3(-2)$. $x = \text{oxidation number of P} = +3$.
- b. Hydrogen and oxygen have oxidation numbers of +1 and -2. The ion has a charge of -1, so the sum of the oxidation numbers must be -1. Letting y be the oxidation number of phosphorus, $-1 = y + 2(+1) + 4(-2)$, $y = \text{oxidation number of P} = +5$.

✓ Example 4.10.3: Identifying Reduced and Oxidized Elements

Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

- $\text{Zn} + 2 \text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$
- $2 \text{Al} + 3 \text{Cu}^{2+} \longrightarrow 2 \text{Al}^{3+} + 3 \text{Cu}$
- $\text{CO}_3^{2-} + 2 \text{H}^+ \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$

Solutions

- Zn is oxidized (Oxidation number: 0 \rightarrow +2); H^+ is reduced (Oxidation number: +1 \rightarrow 0)
- Al is oxidized (Oxidation number: 0 \rightarrow +3); Cu^{2+} is reduced (+2 \rightarrow 0)
- This is not a redox reaction because each element has the same oxidation number in both reactants and products: O = -2, H = +1, C = +4.

An atom is oxidized if its oxidation number increases, the reducing agent, and an atom is reduced if its oxidation number decreases, the oxidizing agent. The atom that is oxidized is the reducing agent, and the atom that is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound).

Oxidation-Reduction Reactions

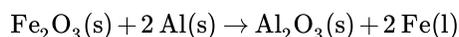
Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases, while the oxidized half loses electrons and the oxidation number increases. Simple ways to remember this include the mnemonic devices **OIL RIG**, meaning "*oxidation is loss*" and "*reduction is gain*." There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

The two species that exchange electrons in a redox reaction are given special names:

- The ion or molecule that accepts electrons is called the **oxidizing agent** - by accepting electrons it oxidizes other species.
- The ion or molecule that donates electrons is called the **reducing agent** - by giving electrons it reduces the other species.

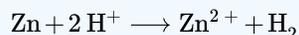
Hence, what is oxidized is the reducing agent and what is reduced is the oxidizing agent. (Note: the oxidizing and reducing agents can be the same element or compound, as in disproportionation reactions discussed below).

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3 .



✓ Example 4.10.4: Identifying Oxidizing and Reducing Agents

Determine what is the oxidizing and reducing agents in the following reaction.

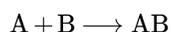


Solution

The oxidation state of H changes from +1 to 0, and the oxidation state of Zn changes from 0 to +2. Hence, Zn is oxidized and acts as the *reducing agent*. H^+ ion is reduced and acts as the *oxidizing agent*.

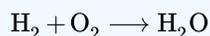
Combination Reactions

Combination reactions are among the simplest redox reactions and, as the name suggests, involves "combining" elements to form a chemical compound. As usual, oxidation and reduction occur together. The general equation for a combination reaction is given below:



✓ Example 4.10.5: Combination Reaction

Consider the combination reaction of hydrogen and oxygen



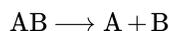
Solution

$$0 + 0 \rightarrow (2)(+1) + (-2) = 0$$

In this reaction both H_2 and O_2 are free elements; following Rule #1, their oxidation states are 0. The product is H_2O , which has a total oxidation state of 0. According to Rule #6, the oxidation state of oxygen is usually -2. Therefore, the oxidation state of H in H_2O must be +1.

Decomposition Reactions

A **decomposition** reaction is the reverse of a combination reaction, the breakdown of a chemical compound into individual elements:



✓ Example 4.10.6: Decomposition Reaction

Consider the following reaction:

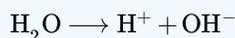


This follows the definition of the decomposition reaction, where water is "decomposed" into hydrogen and oxygen.

$$(2)(+1) + (-2) = 0 \rightarrow 0 + 0$$

As in the previous example the H_2O has a total oxidation state of 0; thus, according to Rule #6 the oxidation state of oxygen is usually -2, so the oxidation state of hydrogen in H_2O must be +1.

Note that the autoionization reaction of water is **not** a redox nor decomposition reaction since the oxidation states do not change for any element:



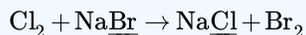
Single Replacement Reactions

A **single replacement** reaction involves the "replacing" of an element in the reactants with another element in the products:



✓ Example 4.10.7: Single Replacement Reaction

Equation:



Calculation:

$$(0) + ((+1) + (-1) = 0) \rightarrow ((+1) + (-1) = 0) + 0$$

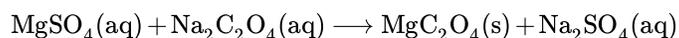
In this equation, Br is replaced with Cl, and the Cl atoms in Cl_2 are reduced, while the Br ion in NaBr is oxidized.

Double Replacement Reactions

A double replacement reaction is similar to a single replacement reaction, but involves "replacing" two elements in the reactants, with two in the products:

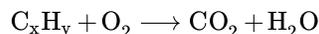


An example of a double replacement reaction is the reaction of magnesium sulfate with sodium oxalate

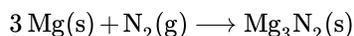
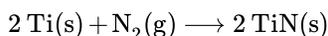


Combustion Reactions

Combustion is the formal terms for "burning" and typically involves a substance reacts with oxygen to transfer energy to the surroundings as light and heat. Hence, combustion reactions are almost always exothermic. For example, internal combustion engines rely on the combustion of organic hydrocarbons C_xH_y to generate CO_2 and H_2O :



Although combustion reactions typically involve redox reactions with a chemical being oxidized by oxygen, many chemicals can "burn" in other environments. For example, both titanium and magnesium metals can burn in nitrogen as well:



Moreover, chemicals can be oxidized by other chemicals than oxygen, such as Cl_2 or F_2 ; these processes are also considered combustion reactions.

✓ Example 4.10.8: Identifying Combustion Reactions

Which of the following are combustion reactions?

- a. $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$
- b. $4 \text{Fe} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3$
- c. $2 \text{AgNO}_3 + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + 2 \text{HNO}_3$
- d. $2 \text{Al} + \text{N}_2 \rightarrow 2 \text{AlN}_3$

Solution

Both reaction b and reaction d are combustion reactions, although with different oxidizing agents. Reaction b is the conventional combustion reaction using O_2 and reaction uses N_2 instead.

Disproportionation Reactions

In disproportionation reactions, a single substance can be both oxidized and reduced. These are known as disproportionation reactions, with the following general equation:



where n is the number of electrons transferred. Disproportionation reactions do not need begin with neutral molecules, and can involve more than two species with differing oxidation states (but rarely).

✓ Example 4.10.9: Disproportionation Reaction

Disproportionation reactions have some practical significance in everyday life, including the reaction of hydrogen peroxide, H_2O_2 poured over a cut. This a decomposition reaction of hydrogen peroxide, which produces oxygen and water. Oxygen is present in all parts of the chemical equation and as a result it is both oxidized and reduced. The reaction is as follows:



Discussion

On the reactant side, H has an oxidation state of +1 and O has an oxidation state of -1, which changes to -2 for the product H_2O (oxygen is reduced), and 0 in the product O_2 (oxygen is oxidized).

? Exercise 4.10.9

Which element undergoes a bifurcation of oxidation states in this disproportionation reaction:



Answer

The N atom undergoes disproportionation. You can confirm that by identifying the oxidation states of each atom in each species.

References

1. Petrucci, et al. *General Chemistry: Principles & Modern Applications*. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.
2. Sadava, et al. *Life: The Science of Biology*. 8th ed. New York, NY. W.H. Freeman and Company, 2007

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