Using Everyday Examples in Engineering (E_3)

Oxidation reaction: Why is the Statue of Liberty blue-green? How does rust work?

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Engage:

Take a piece of rusted iron into class.

Explore

First, ask the student to raise their hands if they have seen the Statue of Liberty either in person or on pictures. Ask students what color the Statue of Liberty is. Students usually give the right answer: that it is blue. Then ask them why it is blue-green. Students generally have no clue. Now, the instructor may address that it is because of oxidation of copper. In the meantime, show them the piece of rusted metal and point out that the brick red of rust is caused by the oxidation of iron.

Photo Credit: National Park Services

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Explain

Chemical reactions can be divided into two classes: redox (reduction-oxidation) reactions and nonredox reactions based on whether electron transfer process is involved or not. A redox reaction consists of two half reactions: a reductive half-reaction in which a reactant accepts electrons and an oxidative half-reaction in which a reactant donates electrons. The nature of a redox reaction is that one reactant donates its electrons to the other reagent. For example, in the oxidation of copper by oxygen (equation 1), copper atoms donate electrons to an oxygen molecule so copper is oxidized while oxygen is reduced [1].

$$\mathbf{2Cu + O_2 \rightarrow Cu_2O} \qquad \text{equation 1}$$

Elaborate

The Statue of Liberty gets its blue-green color from patina formed on its copper surface mainly through oxidation along with several other chemical reactions. The main constituent of patina contains a mixture of 3 compounds: $Cu_4SO_4(OH)_6$ in green; $Cu_2CO_3(OH)_2$ in green; and $Cu_3(CO_3)_2(OH)_2$ in blue. The following reactions are involved.

The oxidation starts with the formation of copper (I) oxide (Cu_2O), which is red or pink in color (equation 1), when copper atoms initially react with oxygen molecules in the air. Copper (I) oxide is further oxidized to copper (II) oxide (CuO), which is black in color (equation 2). In the 19th and early 20th century, coal was the major fuel source for American industry and it usually contains sulfur. Thus, the black copper (II) sulfide (CuS) also forms (equation 3). Over the years, CuO

$$\mathbf{2Cu_2O + O_2 \rightarrow 4CuO} \qquad \text{equation 2}$$
$$\mathbf{Cu + S \rightarrow 4CuS} \qquad \text{equation 3}$$

and CuS slowly reacts with carbon dioxide (CO_2) and hydroxide ions (OH^-) in water from the air to eventually form $Cu_2CO_3(OH)_2$ (equation 4) , $Cu_3(CO_3)_2(OH)_2$ (equation 5) and $Cu_4SO_4(OH)_6$ (equation 6), which constitute the patina. The extent of humidity and the level of sulfur-related air pollution have a significant impact on how fast the patina develops, as well as the relative ratio of the three components [2, 3].

$$\mathbf{2CuO + CO_2 + H_2O \rightarrow Cu_2CO_3(OH)_2} \qquad \text{equation 4}$$
$$\mathbf{3CuO + 2CO_2 + H_2O \rightarrow Cu_3(CO_3)_2(OH)_2} \qquad \text{equation 5}$$
$$\mathbf{4CuO + SO_3 + 3H_2O \rightarrow Cu_4SO_4(OH)_6} \qquad \text{equation 6}$$

On the other hand, rust gets its brick-red color from iron oxide formed on its iron surface mainly through oxidation of iron along with several acid-base reactions. Rust consists of mainly two forms: iron (III) oxide Fe_2O_3 and iron (III) hydroxide $Fe(OH)_3$[4].

The oxidation starts with the formation of iron (II) ion in the acidic condition (equation 6).

$$\mathbf{2\ Fe_{(s)} + O_{2(g)} + 4\ H^+_{(aq)} \rightarrow 2\ H_2O_{(l)} + 2Fe^{2+}_{(aq)}} \qquad \text{equation 6}$$

Fe^{2+} can be further oxidized to Fe^{3+} over the time (equation7).

$$4\ Fe^{2+} + O_2 \rightarrow 4\ Fe^{3+} + 2\ O^{2-} \qquad \text{equation 7}$$

The following acid-base reaction (equation 8) followed by a dehydration reaction (equation 9) completes rust formation (figure 1) [4, 5].

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \qquad \text{equation 8}$$
$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \qquad \text{equation 9}$$

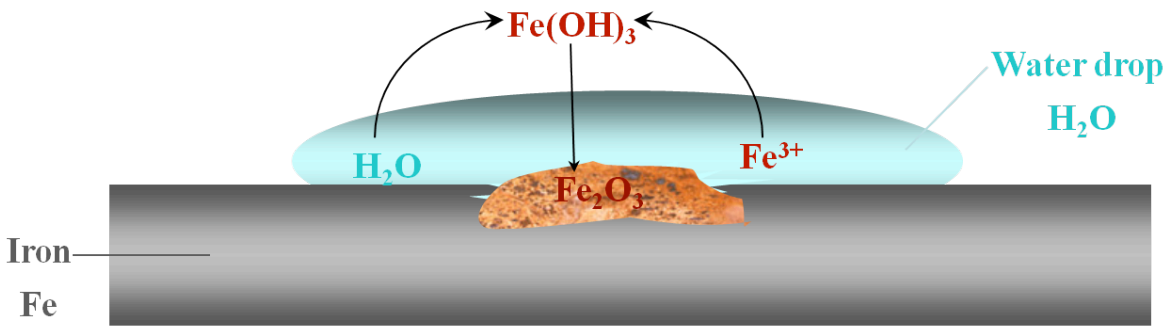

Figure 1. Formation of rust. (Created utilizing Microsoft PowerPoint™)

References

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