

Science-1A Lecture: Week-14, Friday, April 23, 2021

Oxidation-Reduction Reactions – Electrolysis, Batteries, Electroplating, and Corrosion

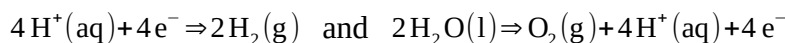
Electrolysis

In the electrolysis of water for our explosion in the 3rd week of this course, we put an electrical voltage across two stainless steel electrodes immersed in water to which some MgSO₄ salt was added. Bubbles of hydrogen gas H₂ formed at the negative electrode and oxygen gas O₂ formed at the positive electrode. The overall reaction was



As explained in an earlier lecture, (l) and (g) here indicate liquid and gas, respectively, and below (aq) is used to indicate ions in an aqueous solution.

This simple equation hides what really happens. Since the hydrogen is produced at one electrode and the oxygen is produced at a separate electrode, there are actually two reactions happening at once. One takes in electrons from the negative terminal of the electrical source (which I will call a battery here, although we actually used a power supply) and also a companion reaction that releases electrons to the positive terminal. The following half-reactions combine to give the above simplified reaction.

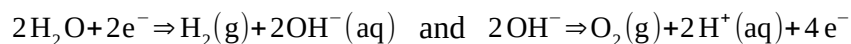


The first reaction shown above was doubled to balance the electron counts for the reaction pair. In these oxidation-reduction reactions, electric charges must be balanced as well as atom counts.

The conventional electrical current flows from the positive terminal of a battery *through the outside circuit* to its negative terminal, but in the wires it is actually the negatively-charged electrons that flow in the opposite direction. In the solution it is the flow of ions that carry the electrical current. Positive ions flow from the positive electrode to the negative electrode while negative ions flow in the opposite direction.

Within the battery, the chemical reactions with the metals of the battery electrodes pump conventional current from the negative electrode to the positive electrode.

The full story is actually more complicated since there are two other reactions that can simultaneously occur



Here OH⁻ ions flow within the solution from the hydrogen electrode to the oxygen electrode, adding to the current produced by the opposite H⁺ ion flow.

In the actual demonstration an orange chemical was also formed. It is the result of the stainless steel not being a perfect electrode. Platinum is better, but too expensive for demonstrations. I believe that the orange-colored chemicals are iron hydroxide Fe(OH)₂ and iron oxides like Fe₂O₃ which do not dissolve significantly in water and become a cloud of suspended rust “dust” in the water. Such undissolved reaction products are called **precipitates**.

This electrolysis process depends on the rate of current flow which would be extremely small for pure water because there are so few free ions in pure water. Adding the MgSO₄ adds Mg⁺⁺ and SO₄⁻⁻ ions which aid the current flow while still producing hydrogen and oxygen gas. If NaCl (ordinary table salt) were used instead, poisonous Cl₂ gas would be created instead of O₂ at the “oxygen” electrode. When I did this at home during my high school days, I did not know this, but still got a nice explosion that produced hydrochloric acid HCl as the H₂ and Cl₂ reacted. I fortunately went to the kitchen and took a Cheerios break. Don't use NaCl!

This general type of combined electron and ion flow with two separate reactions is called an oxidation-reduction reaction. I will not burden you with understanding the terms oxidation and reduction or terms for the electrodes (anode and cathode) which can be very confusing and are not crucial to understanding the content of

this note, but I think it is important to understand the four types of important oxidation-reduction reactions common in chemical engineering: **electrolysis**, **batteries**, **electroplating**, and **corrosion**. Electrolysis is using electricity to rip apart molecules as described above for the electrolysis of water. The other types of oxidation-reduction reactions are described below.

Batteries

Batteries are made using electrodes of *different* metals separately inserted into a liquid or paste, called an **electrolyte**, that supports the flow of ions. Favorite electrolytes used in elementary schools are in potatoes and oranges. The juice in them allows ions to flow from one electrode to the other to complete the battery circuit. The electrodes I use to demonstrate such a battery are pieces of copper, bought at a hardware store, and steel tuna fish can lids. Both need to be scrubbed with steel wool to remove oxide from the copper and to remove the coating on the steel used to separate the food from bare steel. Copper wires are then attached to each and the voltage measured between them with a multimeter. The voltage depends on the properties of the two metals. It will be about 0.55 V for the copper-steel combination, but it is 1.1 V for copper-zinc and 1.5 V for carbon-zinc.

To make enough voltage to power a light-emitting diode (LED), it is necessary to put 5 of these cells in series, each insulated from the others by sheets of plastic (I use baggies). The electrodes are connected with the positive (copper) from one cell attached to the negative (steel) of the next, just as one would when connecting normal batteries in series to get their voltages to add. LED's have positive and negative leads and will not light if connected backwards. If your "battery" is too good, you may need a current limiting resistor of a few hundred ohms in series with the LED to prevent it from being burned out.

When copper plumbing pipes are connected to iron pipes, a battery can be unintentionally formed. Water inside the pipes provides an electrolyte and this accidental battery will eat away at the pipes. Proper construction requires that a "dielectric union" be used between the pipes to insulate the copper from the iron. That prevents the electric current flow and therefore prevents the gradual corrosion of the pipes.

Electroplating

Gold-plated objects like finger rings have a thin layer of gold on top of a less-expensive material like brass. Electricity and very carefully-prepared solutions are used to move the gold atoms from a gold source to uniformly coat the object. We can do an unprofessional job of copper plating by just using copper sulfate CuSO_4 , a common garden root killer which has pretty blue crystals, but is toxic as explained at [https://en.wikipedia.org/wiki/Copper\(II\)_sulfate](https://en.wikipedia.org/wiki/Copper(II)_sulfate)

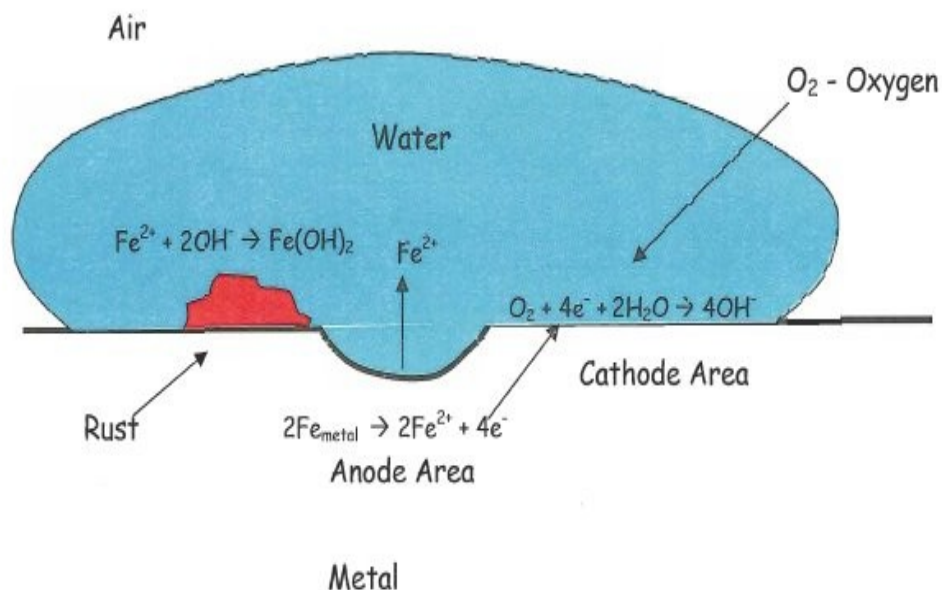
Because young children might think of it as a pretty candy, use in a classroom must be closely managed and the container stored away from the classroom by a school custodian or gardener.

The simplest demonstration using CuSO_4 starts by dissolving it in water to produce a beautiful blue liquid. If bought in crystal chunks, it will need to be ground up into a powder to dissolve in a reasonable time. Then, use steel wool to clean a nail of its oxide or other coatings so that bare steel is exposed. Finally, just dip half of the nail into the CuSO_4 solution for about 15 seconds and pull it back out. It will have become coated with an extremely thin layer of copper. Cu^{++} ions in the solution will take pairs of electrons from iron atoms at the surface of the nail to become complete Cu atoms that attached to the nail surface. The iron atoms, on the other hand, become iron ions Fe^{++} that move into the solution. Once the nail is coated, no more iron is exposed and the process stops.

If, however, a copper electrode is added to the solution, and a battery is attached between the copper electrode and nail with the positive side connected to the copper, copper ions will be continually transferred from the copper electrode to the nail to build up a thick copper coating. This is the usual process of electroplating. Doing this with our simple CuSO_4 solution will produce an ugly coating. Getting a nice smooth surface is a challenge in the art of electroplating.

Corrosion

Rusting is the most common type of corrosion. When iron rusts, it becomes a crumbly iron oxide that can weaken structures and plug up piping. The rusting of iron Fe is illustrated by the following diagram.



Here some iron metal is dissolved in a water drop producing iron ions Fe^{2+} (reaction near the bottom of the figure) and freeing up some electrons. These electrons react with water molecules and oxygen molecules O_2 dissolved in the water to produce hydroxide ions OH^{-} (reaction shown at the right side). The dissolved iron ions then can react with the hydroxide ions to form ferrous hydroxide $\text{Fe}(\text{OH})_2$ (reaction at the left). Once $\text{Fe}(\text{OH})_2$ is created, $\text{Fe}(\text{OH})_3$ and Fe_2O_3 are also formed.

The net result is that, in the presence of moisture and oxygen, iron has been removed from its strong metallic form and converted to a crumbly oxide. As the rusting proceeds, the regions identified in the figure as anode and cathode will gradually cover the entire surface of the structure. Since rust is permeable to air and water, the corrosion slowly continues into the interior of the iron until all the metallic iron has been converted to rust.

Iron construction materials exposed to moisture and air (such as roofing nails, metal fences, and water pipes) are coated with zinc metal that is relatively immune to this rusting type of reaction with water and air. This coating process is called galvanization. Even if the zinc does not coat the iron everywhere, it can still provide rust protection because it will preferably act as a "sacrificial" anode and corrode instead of the iron. To act as a "sacrificial" anode, however, the zinc must be in electrical and ionic contact with the iron and its moisture. This rust protection diminishes with time, and after a few decades Nature wins and the iron will rust.

All of these processes depend on the exact state of the surface of the metals; it is exactly at the surface that the action happens and the surface condition on an atomic scale is important.

Note: These notes prepare you for the possible extra questions you might see on the Chemistry Midterm. See pages 128-129 of the Physics Handouts or

<https://yosemitefoothills.com/Science-1A/QuizAndTestPractice/PossibleAdditionalQuestionsForChemistryTest.pdf>
and

<https://yosemitefoothills.com/Science-1A/QuizAndTestPractice/PossibleAdditionalQuestionsForChemistryTest-Solutions.pdf>