Electrolytic cells and batteries

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In this tutorial, we will learn about a second type of electrochemical cell: electrolytic cells. We will also learn broadly about the concept of electrolysis, how it applies to electrolytic cells and chemistry, and its real-world applications. You will also learn the difference between galvanic cells (like a battery) and electrolytic cells.

In the cover image, a manufacturing facility is shown that produces caustic soda (sodium hydroxide), hydrogen and chlorine gas from salt (sodium chloride) and electricity. This is an example of electrolysis at an industrial scale. Let’s explore the chemistry behind these types of processes.

An electrolytic cell, much like a galvanic cell, has two separate half-cells: a reduction half-cell and an oxidation half-cell. In an electrolytic cell, an external source of electricity (such as a battery) is used to drive electron flow from the anode, where oxidation occurs, to the cathode, where reduction occurs. An external source of electrical energy is needed because the reaction that occurs in electrolytic cells is non-spontaneous.

Basically, an electrolytic cell turns electrical energy into chemical energy; this is the opposite of galvanic cells, which turn chemical energy into electrical energy. This makes sense, as in electrolytic cells, electrons flow in the opposite direction from galvanic cells.

Electrolysis is the name given to the process that occurs in an electrolytic cell, where an electrical current is used to start a non-spontaneous reaction. Electrolysis, and thus an electrolytic cell, is often used in real applications for separating a substance--two common examples are the decomposition of NaCl and of H2O. We will look at the decomposition of NaCl in greater depth below. Additionally, electrolysis is often used in the real world for electroplating jewelry, though this can be extended to any metal.

If sodium chloride is melted into a liquid, you can pass an electric current through the molten salt to decompose it. In this example, molten NaCl decomposes into solid sodium and chlorine gas. The positive sodium ions are attracted to the negative cathode and the negative chlorine ions are attracted to the positive anode. Thus, the half-reaction at the cathode is: and the balanced half-reaction at the anode is: . Thus, the net reaction for this reaction is: .

To analyze this reaction further, we can consult the standard reduction potentials, similarly to the process by which we determine the potential of a voltaic cell. We take the two half-reactions and write them as reduction reactions:

Keeping in mind that the chlorine half-reaction actually undergoes oxidation, not reduction, we flip the sign for its potential, making it . Adding those together, we get a total potential of for the reaction. This means that the external battery source needs to have a potential of at least for the decomposition of molten NaCl to occur.

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Faraday’s law of electrolysis states that the amount of a substance that is consumed/produced at one of the electrodes of an electrolytic cell is directly proportional to the amount of electricity passing through the cell. In order to utilize this, we need to remember the relationships:

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