

Electrochemistry is a science that offers the solution to our energy needs. It is the study of oxidation-reduction reactions that deals with the relationship between chemical energy and electrical energy. This process is carried out in an **electrochemical cell** that consists of electrodes dipped into an electrolyte and in which chemical reaction either generates or uses electric current. There are two types of electrochemical cells, labeled differently based on their tasks:

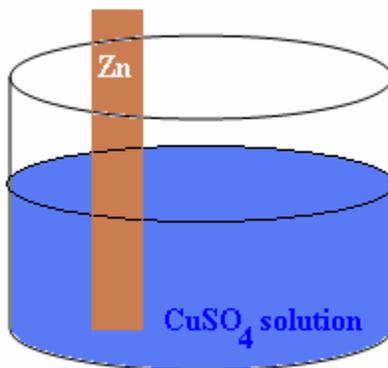
(a) *Chemical energy into electrical energy*: This process is carried out in **voltaic** or **galvanic cell** that is nothing but an electrochemical cell in which a spontaneous chemical reaction generates an electric current.

(b) *Electrical energy into chemical energy*: This process is carried out in an **electrolytic cell** that is also an electrochemical cell in which an electric current is used to drive an otherwise nonspontaneous chemical reaction. This process is known as **electrolysis**.

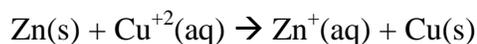
Both processes are very important industrially and make our lives more comfortable and enjoyable.

Galvanic Cells

Galvanic cell also known as voltaic cell (named after Italian scientists Luigi Galvani and Alessandro Volta) is a device in which redox reactions are carried out to generate electrical energy from chemical energy from spontaneous reactions. To illustrate the concept of galvanic cell, consider the following example of piece of zinc (Zn) metal placed in a solution of copper sulfate (CuSO_4), where Zn is oxidized Zn^{+2} and Cu^{+2} is reduced to Cu.

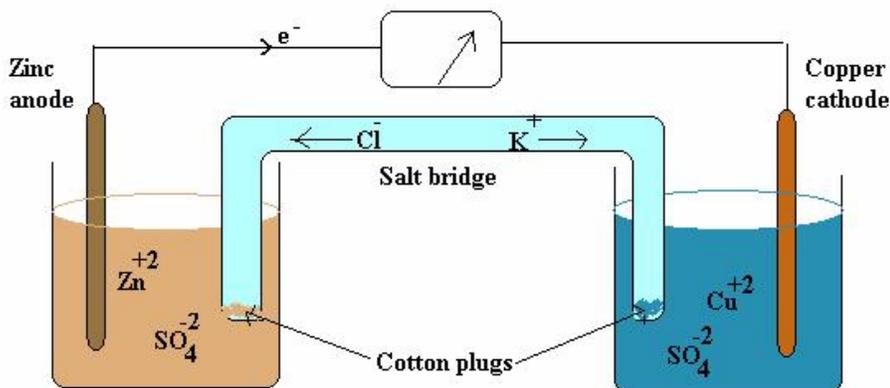


This process is described by the following redox equation:

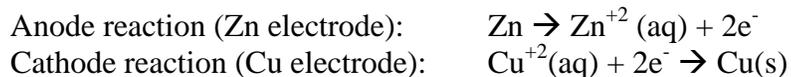


The electrons are directly transferred from the metallic Zn to Cu^{+2} ions in solution. Thus the electrons appear and disappear in solution itself, which are of little use. However, if we take the electrons out of the solution and pass them through the external wire and bring them back to solution, then in essence we are passing the current in the external wire that can be utilized for useful purpose. In order to do that the metallic Zn must be

separated from the CuSO_4 solution. This is the basis for constructing the galvanic cell apparatus. According to galvanic cell, oxidation and reduction parts are separated and carried in two separate containers. A zinc metal is placed in a ZnSO_4 solution and a copper metal is placed in a CuSO_4 solution. This particular arrangement of Zn and Cu electrodes and their corresponding ZnSO_4 and CuSO_4 solutions is labeled as **Daniell cell**.



The metallic rods in galvanic cell are known as **electrodes**. Zn metal dissolves in zinc sulfate solution by liberating electrons, which climb up the electrode and travel through the external wire, go through the voltmeter to register the voltage, enter the copper sulfate solution through copper electrode, and then reduce the Cu^{+2} ions to copper metal. Thus the oxidation occurs at Zn electrode and the reduction occurs at Cu electrode. The Zn electrode is known as an **anode** and the Cu electrode known as the **cathode**. By definition, *the anode is the electrode where oxidation (electron loss) takes place and the cathode is an electrode where reduction (electron gain) takes place*. Each reaction is one half of the entire cell reaction and hence it is called a half-cell reaction. The half-cell reactions are



There is one problem with this construction, that is, unless the electrical circuit is complete, the cell is short-lived due to build up of positive charges in anode compartment and negative charges in cathode compartment. To eliminate this problem, a salt bridge is used to connect both compartments. A **salt bridge** is a inverted U tube filled with some inert electrolyte solution, such as, NH_4NO_3 or KCl , whose ions do not react with other ions in solution or with electrodes, and some cotton placed at both ends of U tube. Only the KCl filled salt bridge is shown in the above diagram. During the operation of the cell, electrons move in the external circuit (shown by the arrow). Positive Zn ions along with K^{+} ions are transported towards the cathode compartment and negative sulfate ions along with Cl^{-} ions are transported towards anode compartment, both across the salt bridge.

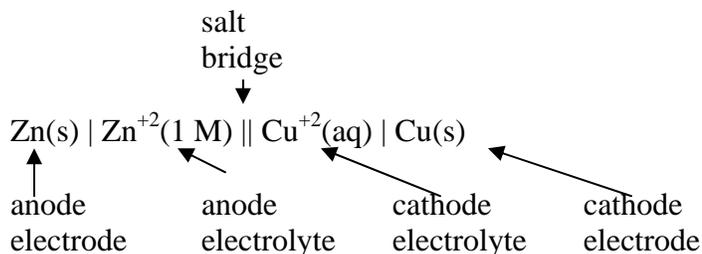
Therefore, the sole purpose of the salt bridge is to transport ions from one compartment to another compartment.

Cations move towards cathode and anions move towards anode

Electric current flows from anode to cathode due to a difference in electrical potential energy between both electrodes (electrons flow from high electrical potential to low electrical potential). This difference, experimentally, measured by a **voltmeter** is known as a **cell voltage** or a **cell potential** or a **electromotive force** (EMF) and the unit of volt is used. The cell potential, however, not only depends on the nature of electrodes and electrolytes, but also depends on the concentrations of electrolytes and the temperature.

Cell diagram

The cell diagram is the short-hand notation to represent the galvanic cell shown in the above diagram. If we assume the concentrations of both solutions are 1 M, then cell diagram for the above galvanic cell is



The single bar represents a phase boundary and the double bars the salt bridge. The anode compartment is written first followed by the cathode compartment that are separated by salt bridge to indicate the direction of flow of electrons from anode to cathode.