

Electrochemistry

Electrochemistry is the study of electricity and how it relates to chemical reactions. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as redox or oxidation-reduction reaction.

Electrolysis is the process by which ionic substances are decomposed (broken down) into simpler substances when an electric current is passed through them.

Electrochemical cells: An electrochemical cell is a device that can generate electrical energy from the chemical reactions occurring in it, or use the electrical energy supplied to it to facilitate chemical reactions in it. These devices are capable of converting chemical energy into electrical energy, or vice versa.

Such cells capable of generating an electric current from the chemical reactions occurring in them are called Galvanic cells or Voltaic cells. Alternatively, the cells which cause chemical reactions to occur in them when an electric current is passed through them are called electrolytic cells.

The main components of an electrochemical cell are:

1. **Electrodes:** The solid electrical conductor composed of metals in an electrochemical cell are known as electrodes. They are of two types:
 - a. **The Anode:** The cell compartment where oxidation takes place.
 - b. **The Cathode:** The cell compartment where reduction takes place.

The key features of the cathode and the anode are tabulated below.

2. **Electrolyte** These are the substances which allow the electric current to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition.
3. **Salt Bridge:** This connects the oxidation half and reduction half of an electrochemical cell and completes the electrochemical circuit.

Cathode	Anode
Denoted by a positive sign since electrons are consumed here	Denoted by a negative sign since electrons are liberated here
A reduction reaction occurs in the cathode of an electrochemical cell	An oxidation reaction occurs here
Electrons move into the cathode	Electrons move out of the anode

Half-Cells and Cell Potential

- Electrochemical Cells are made up of two half-cells, each consisting of an electrode which is dipped in an electrolyte. The same electrolyte can be used for both half cells.
- These half cells are connected by a salt bridge which provides the platform for ionic contact between them without allowing them to mix with each other. An

example of a salt bridge is a filter paper which is dipped in a potassium nitrate or sodium chloride solution.

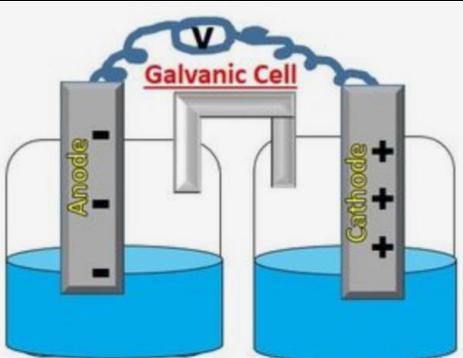
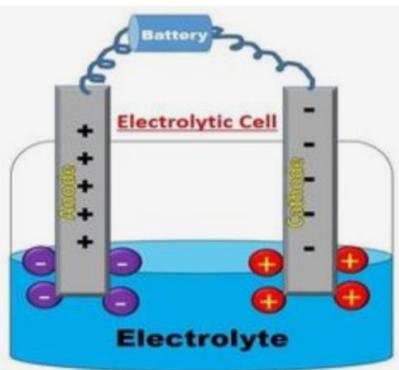
- One of the half cells of the electrochemical cell loses electrons due to oxidation and the other gains electrons in a reduction process. It can be noted that an equilibrium reaction occurs in both the half cells, and once the equilibrium is reached, the net voltage becomes 0 and the cell stops producing electricity.
- The tendency of an electrode which is in contact with an electrolyte to lose or gain electrons is described by its electrode potential. The values of these potentials can be used to predict the overall cell potential. Generally, the electrode potentials are measured with the help of the standard hydrogen electrode as a reference electrode (an electrode of known potential).

Types of Electrochemical Cells

The two primary types of electrochemical cells are

1. Galvanic cells (also known as Voltaic cells)
2. Electrolytic cells

The key differences between Galvanic cells and electrolytic cells are tabulated below.

Galvanic Cell / Voltaic Cell	Electrolytic Cell
Chemical energy is transformed into electrical energy in these electrochemical cells.	Electrical energy is transformed into chemical energy in these cells.
The redox reactions that take place in these cells are spontaneous in nature.	An input of energy is required for the redox reactions to proceed in these cells, i.e. the reactions are non-spontaneous.
In these electrochemical cells, the anode is negatively charged and the cathode is positively charged.	These cells feature a positively charged anode and a negatively charged cathode.
The electrons originate from the species that undergoes oxidation.	Electrons originate from an external source (such as a battery).
	

Applications of Electrochemical Cells

- Electrolytic cells are used in the electrorefining of many non-ferrous metals. They are also used in the electrowinning of these metals.
- The production of high-purity lead, zinc, aluminium, and copper involves the use of electrolytic cells.
- Metallic sodium can be extracted from molten sodium chloride by placing it in an electrolytic cell and passing an electric current through it.
- Many commercially important batteries (such as the lead-acid battery) are made up of Galvanic cells.
- Fuel cells are an important class of electrochemical cells that serve as a source of clean energy in several remote locations.

Faraday's Law

In every electrochemical process, whether spontaneous or not, a certain amount of electric charge is transferred during the oxidation and reduction. The half-reactions we have written for electrode processes include the electrons which carry that charge. It is possible to measure the rate at which the charge is transferred with a device called an ammeter.

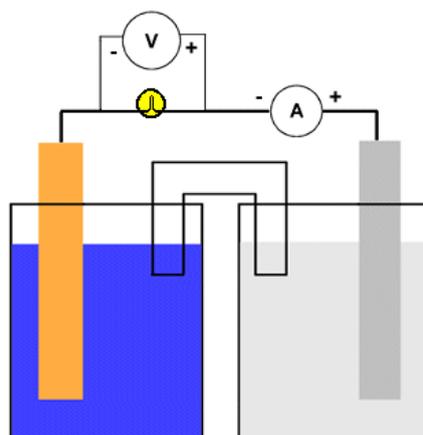
An ammeter measures the current flowing through a circuit. The units of current are amperes (A) (amps, for short). Unlike a voltmeter, ammeters allow electrons to pass and essentially "clock" them as they go by. The amount of electric charge which has passed through the circuit can then be calculated by a simple relationship:

$$\text{Charge (Coulombs)} = \text{current (amps)} \times \text{time (seconds)}$$

$$Q = I \times t$$

This enables us to connect reaction stoichiometry to electrical measurements. The principles underlying these relationships were worked out in the first half of the 19th century by the English scientist, Michael Faraday.

The diagram shows how voltage and current might be measured for a typical galvanic cell but the arrangement is the same for any electrochemical cell. Notice that the voltmeter is placed across the electron conduit (i.e., the wire) while the ammeter is part of that conduit. A good quality voltmeter can be used in this way even though it might appear to be "shorting out" the circuit. Since electrons cannot pass through the voltmeter, they simply continue along the wire.



Both the voltmeter and ammeter are polarized. They have negative and positive terminals marked on them. Electrons are "expected" only in one direction. This is important in measurements of direct current (DC) such as comes out of (or goes into) electrochemical cells.

Faraday's Constant represents the amount of electric charge carried by one mole, or Avogadro's number, of electrons. It is an important constant in chemistry, physics, and electronics and is commonly symbolized by the italic uppercase letter *F*. It is expressed in coulombs per mole (C/mol).

Faraday constant (*F*) = 96485.33289(59) C/mol

So to calculate the moles of electrons we use the equation below:

$$\text{Number of moles (mole)} = \text{Charge (Coulombs)} / \text{Faraday constant (Coulombs/mole)}$$

$$n = Q / F$$

Example: A metallic object to be plated with copper is placed in a solution of CuSO_4 . What mass of copper will be deposited if a current of 0.22 amp flows through the cell for 1.5 hours? Molecular weight of Cu = 63.54 g/mol.



Solution

The amount of charge passing through the cell is

$$(0.22 \text{ amp}) \times (5400 \text{ sec}) = 1200 \text{ c}$$

$$(1200 \text{ c}) \div (96500 \text{ c } F^{-1}) = 0.012 \text{ F}$$

Since the reduction of one mole of Cu^{2+} ion requires the addition of two moles of electrons, the mass of Cu deposited will be

$$(63.54 \text{ g mol}^{-1}) (0.5 \text{ mol Cu/F}) (0.012 \text{ F}) = 0.39 \text{ g of copper}$$

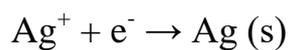
Homework:

1. Calculate the amount of copper metal (in moles) that can be generated with 300 C of electricity.



(0.00155 moles of copper are generated)

2. What is the time needed to deposit 25 g of silver from a solution of silver nitrate at 2 A?



(t = 11,194 seconds)