

Electrolytic Cells

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Voltaic cells are driven by a *spontaneous* chemical reaction that produces an electric current through an outside circuit. These cells are important because they are the basis for the batteries that fuel modern society. But they are not the only kind of electrochemical cell. **The reverse reaction in each case is non-spontaneous** and requires electrical energy to occur.

Introduction

The general form of the reaction can be written as:

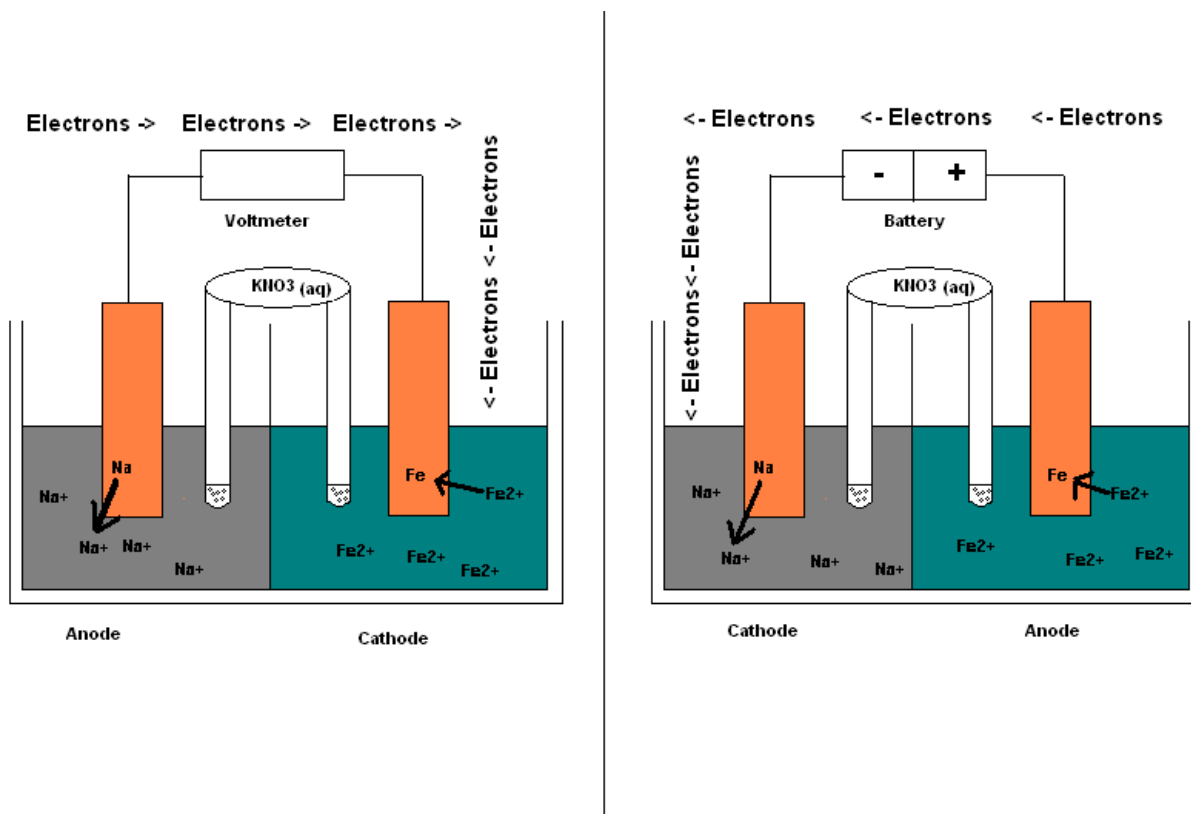
Spontaneous ----->				
Reactants		Products	+	Electrical Energy
<----- Non spontaneous				

It is possible to construct a cell that does work on a chemical system by driving an electric current through the system. These cells are called **electrolytic cells**, and operate through **electrolysis**. Electrolysis is used to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously by *driving an electric current through the system* while doing work on the chemical system itself, and therefore is *non-spontaneous*.

Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell. The direction of electron flow in electrolytic cells, however, may be reversed from the direction of spontaneous electron flow in galvanic cells, but the definition of both cathode and anode remain the same, where

reduction takes place at the cathode and oxidation occurs at the anode. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

Similarities and Differences Galvanic and Electrolytic Cell:



Electrolytic cells are very similar to voltaic (galvanic) cells in the sense that both require a salt bridge, both have a cathode and anode side, and both have a consistent flow of electrons from the anode to the cathode. However, there are also striking differences between the two cells. The main differences are outlined below:

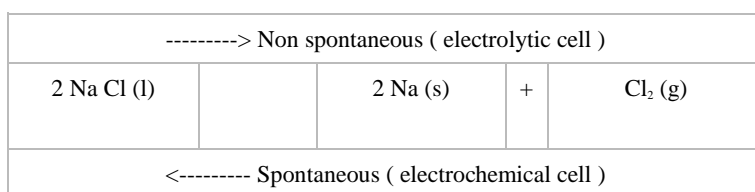
Differences between a Galvanic cell and an Electrolytic cell

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode.	Here, the anode is positive and cathode is the negative

Electrochemical cell (Galvanic Cell)	Electrolytic cell
The reaction at the anode is oxidation and that at the cathode is reduction.	electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.	The external battery supplies the electrons. They enter through the cathode and come out through the anode.

Electrolytic Cell

To explain what happens in an electrolytic cell let us examine the decomposition of molten sodium chloride into sodium metal and chlorine gas. The reaction is written below.

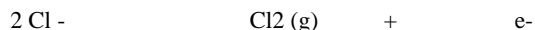


If molten NaCl (l) is placed into the container and inert electrodes of C(s) are inserted, attached to the + and - terminals of a battery, an electrolytic reaction will occur. Examine the diagram here <http://library.thinkquest.org/C00666...ectrolytic.gif>

1. Electrons from the negative terminal travel to the cathode and are used to reduce sodium ions into sodium atoms. The sodium will plate onto the cathode as it forms. The sodium ion are migrating towards the cathode.



2. The negative Chlorine ions migrate towards the anode and release electrons as they oxidize to form chlorine atoms. The chlorine atoms will combine together to form chlorine gas which will bubble away.



3. Note that the site of oxidation is still the anode and the site of reduction is still the cathode, but the charge on these two electrodes are reversed. Anode is now + charged and the cathode has a - charged.

4. **The conditions under which the electrolyte cell operates are very important.** The substance that is the strongest reducing agent (the substance with the highest standard cell potential value in the table) will undergo oxidation. The substance that is the strongest oxidizing agent will be reduced. If a solution of sodium chloride

(containing water) was used in the above system, hydrogen would undergo reduction instead of sodium, because it is a stronger reducing agent than sodium.

Predicting Electrolysis Reaction

There are four factors that determine whether or not electrolysis will take place even if the external voltage exceeds the calculated amount:

- 1) An overpotential or voltage excess is sometimes needed to overcome interactions at the electrode surface. This case happens more frequently with gases.

Ex1) $\text{H}_2(\text{g})$: 1.5 V overpotential

Pt (s) : 0 V overpotential

- 2) There might be more than one electrode reaction that occurs meaning that there may be more than one half-reaction leaving two or more possibilities for the cell reaction.

- 3) The reactants may be in nonstandard conditions which means that the voltage for the half cells may be less or more than the standard condition amount

Ex1) Concentration of chloride ion = 5.5M not the unit activity of 1M. This means that the reduction of chloride = 1.31V not 1.36V

Ex2) The standard condition is to have a pH of 4 in the anode half cell but sometimes during nonstandard states, the pH may be higher or lower changing the voltage.

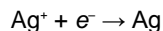
- 4) An *inert* electrode's ability to electrolysis depend on the reactants in the electrolyte solution while an *active* electrode can run on its own to perform the oxidation or reduction half reaction.

If all four of these factors are accounted for, we can successfully predict electrode half reactions and overall reactions in electrolysis.

Example) Predict the electrode reactions and the overall reaction when the anode is made of (a) copper and (b) platinum.

Quantitative Aspects of Electrolysis

Michael Faraday discovered in 1833 that there is always a simple relationship between the amount of substance produced or consumed at an electrode during electrolysis and the quantity of electrical charge Q which passes through the cell. For example, the half-equation



tells us that when 1 mol Ag^+ is plated out as 1 mol Ag, 1 mol e^- must be supplied from the cathode. Since the negative charge on a single electron is known to be 1.6022×10^{-19} C, we can multiply by the Avogadro constant to obtain the charge per mole of electrons. This quantity is called the **Faraday Constant**, symbol F :

$$F = 1.6022 \times 10^{-19} \text{ C} \times 6.0221 \times 10^{23} \text{ mol}^{-1} = 9.649 \times 10^4 \text{ C mol}^{-1}$$

Thus in the case of Eq. (1), 96 490 C would have to pass through the cathode in order to deposit 1 mol Ag. For any electrolysis the electrical charge Q passing through an electrode is related to the amount of electrons n_{e^-} by

$$F = \frac{Q}{n_{e^-}}$$

Thus F serves as a conversion factor between n_{e^-} and Q .

Often the electrical current rather than the quantity of electrical charge is measured in an electrolysis experiment. Since a **coulomb** is defined as the quantity of charge which passes a fixed point in an electrical circuit when a current of one ampere flows for one second, the charge in coulombs can be calculated by multiplying the measured current (in amperes) by the time (in seconds) during which it flows:

$$Q = It$$

In this equation I represents current and t represents time. If you remember that

$$\text{coulomb} = 1 \text{ ampere} \times 1 \text{ second} \quad 1 \text{ C} = 1 \text{ A s}$$

you can adjust the time units to obtain the correct result. Now that we can predict the electrode half-reactions and overall reactions in electrolysis, it is also important to be able to calculate the quantities of reactants consumed and the products produced. For these calculations we will be using the Faraday constant:

$$1 \text{ mol of electron} = 96,485 \text{ C}$$

$$\text{charge (C)} = \text{current (C/s)} \times \text{time (s)}$$

$$(C/s) = 1 \text{ coulomb of charge per second} = 1 \text{ ampere (A)}$$

Simple conversion for any type of problem:

1. Convert any given time to seconds
2. Take the current given (**A**) over the seconds, [$1\text{ C} = (\text{A})/(\text{s})$]
3. Finally use the stoichiometry conversion of 1 mol of electron = 96,485 **C (Faraday's Constant)**

Example) The electrolysis of dissolved Bromine sample can be used to determine the amount of Bromine content in sample. At the cathode, the reduction half reaction is $\text{Br}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow 2\text{Br}$. What mass of Bromine can be deposited in 3.00 hours by a current of 1.18 A?

$$\text{Sol)} 3.00\text{ hours} \times 60\text{ min/hour} \times 60\text{ sec/1 min} \times 1.18\text{ C(A)} / 1\text{ sec} \times 1\text{ mol e}^{-}/96,485\text{ C}$$

$$= 0.132\text{ mol e}^{-}$$

Outside links

- http://en.wikipedia.org/wiki/Electrolytic_cell
- <http://hyperphysics.phy-astr.gsu.edu...lectrolyt.html>
- <http://www.chem.purdue.edu/gchelp/ho...Potentials.htm>
- <http://chemistryh2t13.blogspot.com/2...anic-cell.html>
- <http://www.sparknotes.com/chemistry/.../section1.html>
- Anderson, Guy E. "Small Scale Electrolytic Cells." *J. Chem. Educ.* **1996**, *73*, A170.
- Probst, Donald A.; Henderson, Giles. "Zinc Electrodes and the Thermodynamics of a Galvanic Cell." *J. Chem. Educ.* **1996** *73* 962.
- Zhou, Rei, "How to Offer the Optimal Demonstration of the Electrolysis of Water" *J. Chem. Ed.* **1996**: *73*, 786

References

1. Petrucci, et al. *General Chemistry: Principles & Modern Applications*. 9th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2007.
2. Kolbe, Hermann. *The Electrolysis of Organic Compounds*. Edinburgh : E. & S. Livingstone, 1947.
3. Stuart, A.T. "Electrolysis of water." *Hydrogen Production* 2001 May 13
4. All of the aforementioned "Outside Links" as well.

Contributors

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Source: http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Electrolytic_Cells