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# Galvanic cell

A **galvanic cell** or **voltaic cell**, named after Luigi Galvani or Alessandro Volta, respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals immersed in electrolytes, or of individual half-cells with different metals and their ions in solution connected by a salt bridge or separated by a porous membrane.
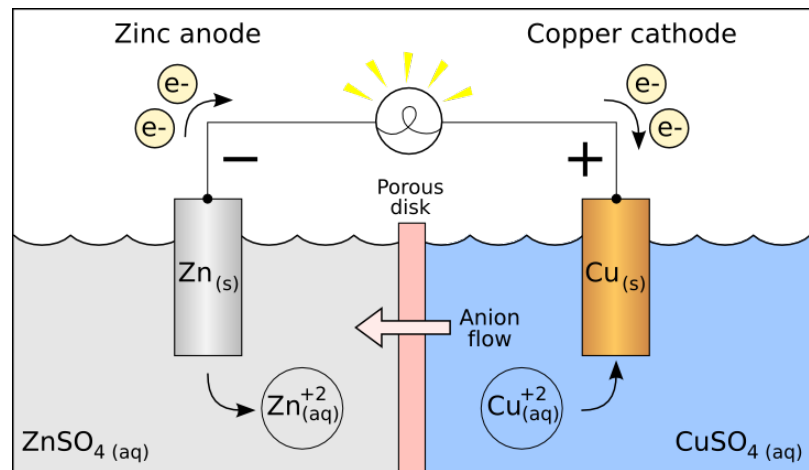

Galvanic cell with no cation flow

Volta was the inventor of the voltaic pile, the first electrical battery. In common usage, the word "battery" has come to include a single galvanic cell, but a battery properly consists of multiple cells.[1]

## Contents

# History

In 1780, Luigi Galvani discovered that when two different metals (e.g., copper and zinc) are in contact and then both are touched at the same time to two different parts of a muscle of a frog leg, to close the circuit, the frog's leg contracts.[2] He called this "animal electricity". The frog's leg, as well as being a detector of electrical current, was also the electrolyte (to use the language of modern chemistry).

A year after Galvani published his work (1790), Alessandro Volta showed that the frog was not necessary, using instead a force-based detector and brine-soaked paper (as electrolyte). (Earlier Volta had established the law of capacitance $C = \frac{Q}{V}$ with force-based detectors). In 1799 Volta invented the voltaic pile, which is a pile of galvanic cells each consisting of a metal disk, an electrolyte layer, and a disk of a different metal. He built it entirely out of non-biological material to challenge Galvani's (and the later experimenter Leopoldo Nobili)'s animal electricity theory in favor of his own metal-metal contact electricity theory.[3] Carlo Matteucci in his turn constructed a battery entirely out of biological material in answer to Volta.[4] Volta's contact electricity view characterized each electrode with a number that we would now call the work function of the electrode. This view ignored the chemical reactions at the electrode-electrolyte interfaces, which include $H_2$ formation on the more noble metal in Volta's pile.

Although Volta did not understand the operation of the battery or the galvanic cell, these discoveries paved the way for electrical batteries; Volta's cell was named an IEEE Milestone in 1999.[5]

Some forty years later, Faraday (see Faraday's laws of electrolysis) showed that the galvanic cell -- now often called a voltaic cell -- was chemical in nature. Faraday introduced new terminology to the language of chemistry: electrode (cathode and anode), electrolyte, and ion (cation and anion). Thus Galvani incorrectly thought the source of electricity (or source of emf, or seat of emf) was in the animal, Volta incorrectly thought it was in the physical properties of the isolated electrodes, but Faraday correctly identified the source of emf as the chemical reactions at the two electrode-electrolyte interfaces. The authoritative work on the intellectual history of the voltaic cell remains that by Ostwald.[6]

It was suggested by Wilhelm König in 1940 that the object known as the Baghdad battery might represent galvanic cell technology from ancient Parthia. Replicas filled with citric acid or grape juice have been shown to produce a voltage. However, it is far from certain that this was its purpose—other scholars have pointed out that it is very similar to vessels known to have been used for storing parchment scrolls.[7]
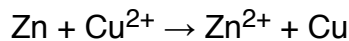
## Basic description

In its simplest form, a half-cell consists of a solid metal (called an electrode) that is submerged in a solution; the solution contains cations (+) of the electrode metal and anions (−) to balance the charge of the cations. The full cell consists of two half-cells, usually connected by a semi-permeable membrane or by a salt bridge that prevents the ions of the

more noble metal from plating out at the other electrode.

A specific example is the Daniell cell (see figure), with a zinc (Zn) half-cell containing a solution of $ZnSO_4$ (zinc sulfate) and a copper (Cu) half-cell containing a solution of $CuSO_4$ (copper sulfate). A salt bridge is used here to complete the electric circuit.

If an external electrical conductor connects the copper and zinc electrodes, zinc from the zinc electrode dissolves into the solution as $Zn^{2+}$ ions (oxidation), releasing electrons that enter the external conductor. To compensate for the increased zinc ion concentration, via



Schematic of Zn-Cu galvanic cell

the salt bridge zinc ions leave and anions enter the zinc half-cell. In the copper half-cell, the copper ions plate onto the copper electrode (reduction), taking up electrons that leave the external conductor. Since the $Cu^{2+}$ ions (cations) plate onto the copper electrode, the latter is called the cathode. Correspondingly the zinc electrode is the anode. The electrochemical reaction is:
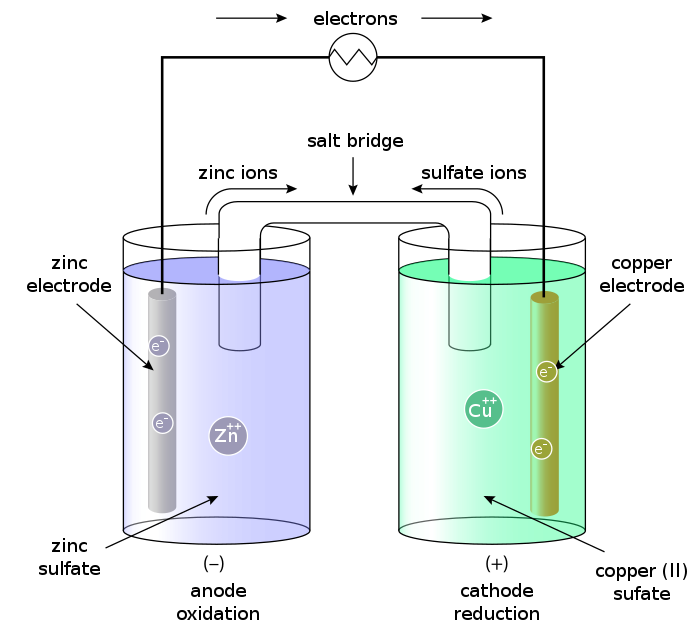
$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

In addition, electrons flow through the external conductor, which is the primary application of the galvanic cell.

As discussed under #Cell voltage, the emf of the cell is the difference of the half-cell potentials, a measure of the relative ease of dissolution of the two electrodes into the electrolyte. The emf depends on both the electrodes and on the electrolyte, an indication that the emf is chemical in nature.

# Electrochemical thermodynamics of galvanic cell reactions

The electrochemical processes in a galvanic cell occur because reactants of high free energy (e.g. metallic Zn and hydrated $Cu^{2+}$ in the Daniell cell) are converted to lower-energy products (metallic Cu and hydrated $Zn^{2+}$ in this example). The difference in the lattice cohesive energies [8] of the electrode metals is sometimes the dominant energetic driver of the reaction, specifically in the Daniell cell.[9] Metallic Zn, Cd, Li, and Na, which are not stabilized by d-orbital bonding, have higher cohesive energies (i.e. they are more weakly

bonded) than all transition metals, including Cu, and are therefore useful as high-energy anode metals.[9]

The difference between the metals' ionization energies in water [9] is the other energetic contribution that can drive the reaction in a galvanic cell; it is not important in the Daniell cell because the energies of hydrated $Cu^{2+}$ and $Zn^{2+}$ ions happen to be similar.[9] Both atom transfer, e.g. of zinc from the metal electrode into the solution, and electron transfer, from metal atoms or to metal ions, play important roles in a galvanic cell. Concentration cells, whose electrodes and ions are made of the same metal and which are driven by an entropy increase and free-energy decrease as ion concentrations equalize, show that the electronegativity difference of the metals is not the driving force of electrochemical processes.

Galvanic cells and batteries are typically used as a source of electrical power. The energy derives from a high-cohesive-energy metal dissolving while to a lower-energy metal is deposited, and/or from high-energy metal ions plating out while lower-energy ions go into solution.

Quantitatively, the electrical energy produced by a galvanic cell is approximately equal to the standard free-energy difference of the reactants and products, denoted as $\Delta_r G^0$. In the Daniell cell, most of the electrical energy of $\Delta_r G^0$ = -213 kJ/mol can be attributed to the -207 kJ/mol difference between Zn and Cu lattice cohesive energies.[9]

## Half reactions and conventions

A half-cell contains a metal in two oxidation states. Inside an isolated half-cell, there is an oxidation-reduction (redox) reaction that is in chemical equilibrium, a condition written symbolically as follows (here, "M" represents a metal cation, an atom that has a charge imbalance due to the loss of "$n$" electrons):

$M^{n+}$ (oxidized species) + $n e^-$ $\rightleftharpoons$ M (reduced species)

A galvanic cell consists of two half-cells, such that the electrode of one half-cell is composed of metal A, and the electrode of the other half-cell is composed of metal B; the redox reactions for the two separate half-cells are thus:

$A^{n+} + n e^- \rightleftharpoons A$
$B^{m+} + m e^- \rightleftharpoons B$
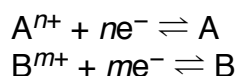
The overall balanced reaction is

$m A + n B^{m+} \rightleftharpoons n B + m A^{n+}$
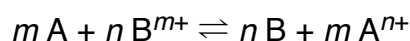
In other words, the metal atoms of one half-cell are oxidized while the metal cations of the other half-cell are reduced. By separating the metals in two half-cells, their reaction can be

controlled in a way that forces transfer of electrons through the external circuit where they can do useful work.

- The electrodes are connected with a metal wire in order to conduct the electrons that participate in the reaction.

  In one half-cell, dissolved metal-B cations combine with the free electrons that are available at the interface between the solution and the metal-B electrode; these cations are thereby neutralized, causing them to precipitate from solution as deposits on the metal-B electrode, a process known as plating.
  This reduction reaction causes the free electrons throughout the metal-B electrode, the wire, and the metal-A electrode to be pulled into the metal-B electrode. Consequently, electrons are wrestled away from some of the atoms of the metal-A electrode, as though the metal-B cations were reacting directly with them; those metal-A atoms become cations that dissolve into the surrounding solution.
  As this reaction continues, the half-cell with the metal-A electrode develops a positively charged solution (because the metal-A cations dissolve into it), while the other half-cell develops a negatively charged solution (because the metal-B cations precipitate out of it, leaving behind the anions); unabated, this imbalance in charge would stop the reaction. The solutions of the half-cells are connected by a salt bridge or a porous plate that allows ions to pass from one solution to the other, which balances the charges of the solutions and allows the reaction to continue.

By definition:

- The anode is the electrode where oxidation (loss of electrons) takes place (metal-A electrode); in a galvanic cell, it is the negative electrode, because when oxidation occurs, electrons are left behind on the electrode.[10] These electrons then flow through the external circuit to the cathode (positive electrode) (while in electrolysis, an electric current drives electron flow in the opposite direction and the anode is the positive electrode).
- The cathode is the electrode where reduction (gain of electrons) takes place (metal-B electrode); in a galvanic cell, it is the positive electrode, as ions get reduced by taking up electrons from the electrode and plate out (while in electrolysis, the cathode is the negative terminal and attracts positive ions from the solution). In both cases, the statement 'the cathode attracts cations' is true.

Galvanic cells, by their nature, produce direct current. The Weston cell has an anode composed of cadmium mercury amalgam, and a cathode composed of pure mercury. The electrolyte is a (saturated) solution of cadmium sulfate. The depolarizer is a paste of mercurous sulfate. When the electrolyte solution is saturated, the voltage of the cell is very reproducible; hence, in 1911, it was adopted as an international standard for voltage.

A battery is a set of galvanic cells that are connected together to form a single source of voltage. For instance, a typical 12V lead–acid battery has six galvanic cells connected in series with the anodes composed of lead and cathodes composed of lead dioxide, both immersed in sulfuric acid. Large battery rooms, for instance in a telephone exchange providing central office power to user's telephones, may have cells connected in both series and parallel.

# Cell voltage

The voltage (electromotive force $E^o$) produced by a galvanic cell can be estimated from the standard Gibbs free energy change in the electrochemical reaction according to
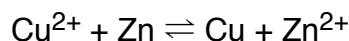
$$E^o_\text{cell} = -\Delta_r G^o / (\nu_e F)$$

where $\nu_e$ is the number of electrons transferred in the balanced half reactions, and $F$ is Faraday's constant. However, it can be determined more conveniently by the use of a standard potential table for the two half cells involved. The first step is to identify the two metals and their ions reacting in the cell. Then one looks up the standard electrode potential, $E^o$, in volts, for each of the two half reactions. The standard potential of the cell is equal to the more positive $E^o$ value minus the more negative $E^o$ value.

For example, in the figure above the solutions are $CuSO_4$ and $ZnSO_4$. Each solution has a corresponding metal strip in it, and a salt bridge or porous disk connecting the two solutions and allowing $SO_4^{2-}$ ions to flow freely between the copper and zinc solutions. To calculate the standard potential one looks up copper and zinc's half reactions and finds:

$$Cu^{2+} + 2\,e^- \rightleftharpoons Cu \qquad E^o = +0.34 \text{ V}$$
$$Zn^{2+} + 2\,e^- \rightleftharpoons Zn \qquad E^o = -0.76 \text{ V}$$
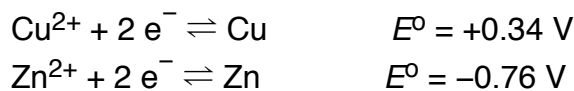
Thus the overall reaction is:

$$Cu^{2+} + Zn \rightleftharpoons Cu + Zn^{2+}$$

The standard potential for the reaction is then +0.34 V − (−0.76 V) = 1.10 V. The polarity of the cell is determined as follows. Zinc metal is more strongly reducing than copper metal because the standard (reduction) potential for zinc is more negative than that of copper. Thus, zinc metal will lose electrons to copper ions and develop a positive electrical charge. The equilibrium constant, $K$, for the cell is given by

$$\ln K = \frac{\nu_e F E^o_\text{cell}}{RT}$$

where $F$ is the Faraday constant, $R$ is the gas constant and $T$ is the temperature in kelvins. For the Daniell cell $K$ is approximately equal to $1.5 \times 10^{37}$. Thus, at equilibrium, a few electrons are transferred, enough to cause the electrodes to be charged.[11]

Actual half-cell potentials must be calculated by using the Nernst equation as the solutes are unlikely to be in their standard states,

$$E_\text{half-cell} = E^o - \frac{RT}{\nu_e F} \ln_e Q$$

where $Q$ is the reaction quotient. When the charges of the ions in the reaction are equal, this simplifies to

$$E_{\text{half-cell}} = E^o - 2.303 \frac{RT}{\nu_e F} \log_{10}\left\{M^{n+}\right\}$$

where $\{M^{n+}\}$ is the activity of the metal ion in solution. In practice concentration in mol/L is used in place of activity. The metal electrode is in its standard state so by definition has unit activity. The potential of the whole cell is obtained as the difference between the potentials for the two half-cells, so it depends on the concentrations of both dissolved metal ions. If the concentrations are the same, $E_{\text{cell}} = E^o_{\text{cell}}$ and the Nernst equation is not needed under the conditions assumed here.

The value of $2.303\frac{R}{F}$ is $1.9845 \times 10^{-4}$ V/K, so at 25 °C (298.15 K) the half-cell potential will change by only 0.05918 V/$\nu_e$ if the concentration of a metal ion is increased or decreased by a factor of 10.

$$E_{\text{half-cell}} = E^o - \frac{0.05918\ \text{V}}{\nu_e} \log_{10}\left[M^{n+}\right]$$

These calculations are based on the assumption that all chemical reactions are in equilibrium. When a current flows in the circuit, equilibrium conditions are not achieved and the cell voltage will usually be reduced by various mechanisms, such as the development of overpotentials.[12] Also, since chemical reactions occur when the cell is producing power, the electrolyte concentrations change and the cell voltage is reduced. A consequence of the temperature dependency of standard potentials is that the voltage produced by a galvanic cell is also temperature dependent.

## Galvanic corrosion

Galvanic corrosion is a process that degrades metals electrochemically. This corrosion occurs when two dissimilar metals are in contact with each other in the presence of an electrolyte, such as salt water, forming a galvanic cell with $H_2$ formation on the more noble metal. The resulting electrochemical potential then develops an electric current that electrolytically dissolves the less noble material. A concentration cell can be formed if the same metal is exposed to two different concentrations of electrolyte.

## Cell types

- Concentration cell
- Electrolytic cell
- Electrochemical cell
- Lemon battery
- Thermogalvanic cell

# See also

- Bioelectrochemical reactor
- Biological cell voltage
- Bio-nano generator
- Cell notation
- Desulfation
- Electrochemical engineering
- Electrode potential
- Electrohydrogenesis
- Electrosynthesis
- Enzymatic biofuel cell
- Galvanic series
- Isotope electrochemistry
- List of battery types
- Sacrificial anode

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12. Atkins, P; de Paula (2006). *Physical Chemistry*. J. (8th. ed.). Oxford University Press. ISBN 978-0-19-870072-2. Section 25.12 "Working Galvanic cells"

# External links

- How to build a galvanic cell battery (https://web.archive.org/web/20141124233113/http://www.miniscience.com/link/Airbattery.htm) from MiniScience.com
- Galvanic Cell (http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/galvan5.swf), an animation
- Interactive animation of Galvanic Cell (https://web.archive.org/web/20110719210759/http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfiles/electroChem/voltaicCell20.html). Chemical Education Research Group, Iowa State University.
- Electron transfer reactions and redox potentials in GALVANIc cells - what happens to the ions at the phase boundary (NERNST, FARADAY) (https://av.tib.eu/media/34660?pag=1) (Video by SciFox on TIB AV-Portal)

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