

Cells, cell potential and electrolysis

AP Chemistry · Lesson

Quick answer: Electrochemistry links redox reactions to electrical energy. In a galvanic cell a spontaneous reaction pushes electrons through a wire, and the voltage is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. In an electrolytic cell a power supply forces a non-spontaneous reaction. $\Delta G^\circ = -nFE^\circ$ and Faraday's law connect voltage, charge and the amount of product.

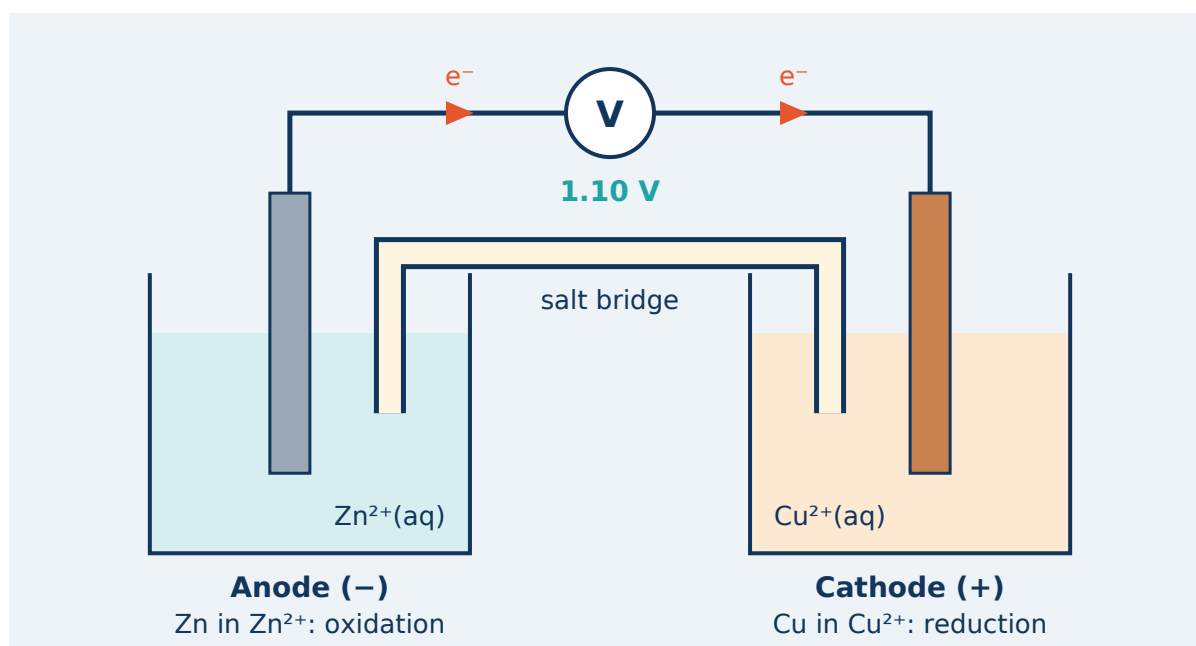
Level: AP Chemistry · **Curriculum:** AP Chem Unit 9

What is a galvanic cell and how does it work?

Definition

A **galvanic cell** (also called a voltaic cell) uses a spontaneous redox reaction to push electrons through an external circuit. **Oxidation** happens at the **anode** and **reduction** happens at the **cathode**, in every kind of cell.

Put a zinc strip in zinc sulfate solution and a copper strip in copper(II) sulfate solution. Zinc atoms give up electrons more readily than copper atoms, so the zinc half-cell is the anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. The electrons travel through the wire to the copper strip, where Cu^{2+} ions pick them up: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$. A **salt bridge** lets ions drift between the beakers so that neither side builds up charge. Anions move toward the anode, cations toward the cathode.



A zinc-copper galvanic cell: electrons leave the anode, pass through the voltmeter and reach the cathode.

Lina's tip

Remember “an ox and a red cat”: anode with oxidation, reduction at the cathode. Electrons always travel from anode to cathode through the wire.

How do you calculate a standard cell potential?

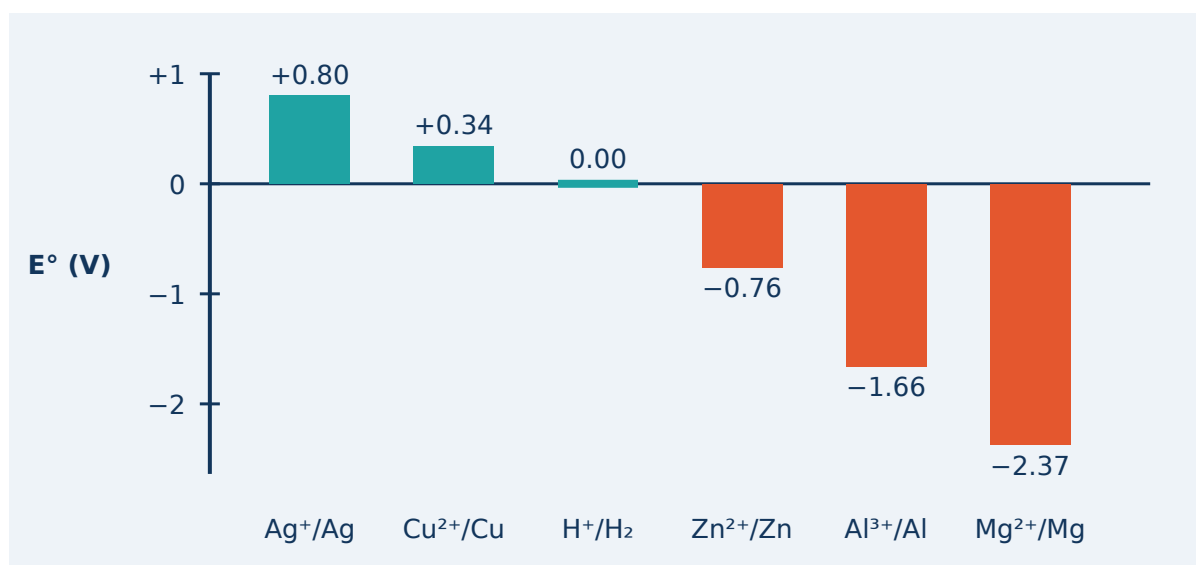
Each half-reaction has a **standard reduction potential**, E° , measured against the standard hydrogen electrode (1.0 mol/dm³ H⁺, 1 atm H₂, platinum, 25 °C), which is defined as 0.00 V. The half-cell with the higher E° is reduced, so it is the cathode.

Formula

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

E°_{cell} is in volts (V). Both values are reduction potentials taken from the table. If E°_{cell} is positive the reaction is spontaneous as written.

Half-reaction (reduction)	E° (V)
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37



Standard reduction potentials: the higher the bar, the stronger the oxidising agent on the left of the half-reaction.

Worked example

A cell joins Zn^{2+}/Zn and Ag^+/Ag half-cells. Find E°_{cell} .

Silver has the higher E° , so silver is the cathode and zinc is the anode. $E^\circ_{\text{cell}} = 0.80 - (-0.76) = \mathbf{+1.56 \text{ V}}$. The overall equation is $\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$.

Common mistake

Never multiply E° by the stoichiometric coefficient. Potentials are intensive: doubling the silver half-reaction does not double its voltage. The subtraction already handles the anode sign, so do not change it again.

How are E°_{cell} , ΔG° and K connected?

Formula

$\Delta G^\circ = -nFE^\circ_{\text{cell}}$, and $\Delta G^\circ = -RT \ln K$, so $\log K = nE^\circ_{\text{cell}} / 0.0592$ at 25 °C

n = moles of electrons transferred in the balanced equation; $F = 96\,485 \text{ C/mol}$; ΔG° in J/mol; $R = 8.314 \text{ J/(mol}\cdot\text{K)}$.

Worked example

Find ΔG° and K for the zinc-copper cell, $E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10 \text{ V}$, $n = 2$.

$\Delta G^\circ = -2 \times 96\,485 \times 1.10 = -2.12 \times 10^5 \text{ J/mol} = \mathbf{-212 \text{ kJ/mol}}$. $\log K = 2 \times 1.10 / 0.0592 = 37.2$, so $\mathbf{K \approx 10^{37}}$: the reaction goes essentially to completion.

Away from standard conditions the voltage changes with the reaction quotient Q . The **Nernst equation** at 25 °C is $E = E^\circ - (0.0592 / n) \log Q$. When the cell runs, Q grows until $Q = K$, at which point $E = 0$ and the battery is flat.

Worked example

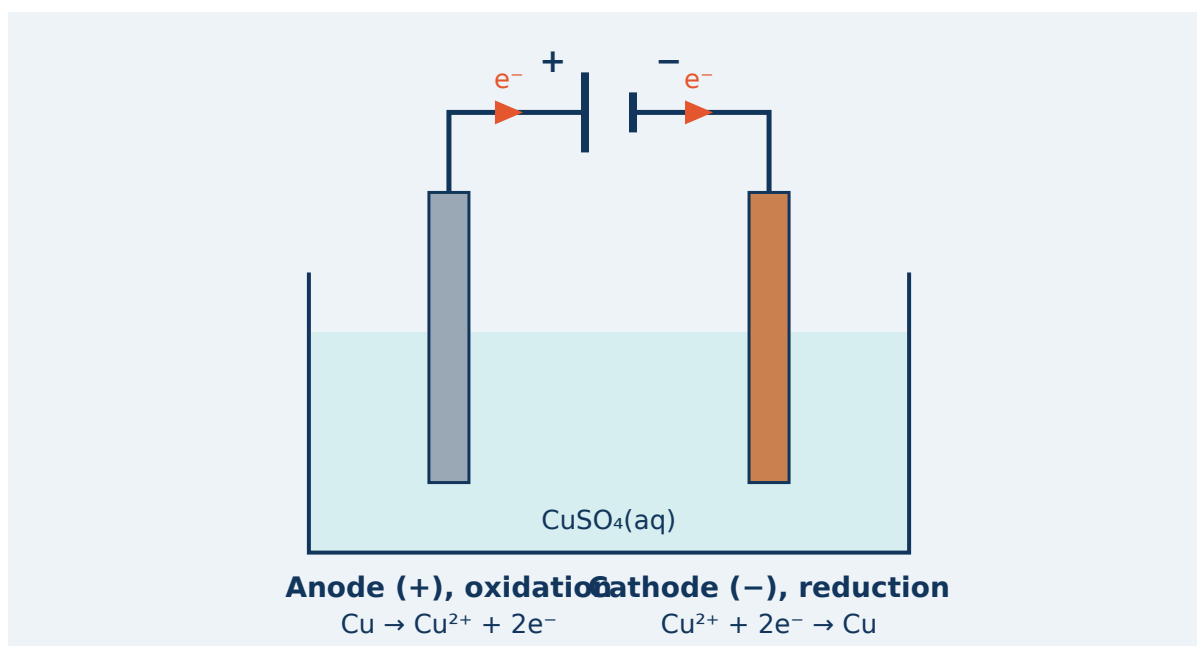
Zn/Cu cell with $[\text{Zn}^{2+}] = 1.0 \text{ mol/dm}^3$ and $[\text{Cu}^{2+}] = 0.010 \text{ mol/dm}^3$. $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 100$, $\log Q = 2$.

$E = 1.10 - (0.0592 / 2)(2) = 1.10 - 0.059 = \mathbf{1.04 \text{ V}}$. Diluting the reactant Cu^{2+} lowers the driving force, so the voltage drops.

What happens in an electrolytic cell, and what does Faraday's law say?

Definition

An **electrolytic cell** uses an external power source to force a non-spontaneous reaction. The anode is still where oxidation happens, but it is now the *positive* electrode, and the cathode is negative.



An electrolytic cell for copper plating: the battery forces electrons onto the cathode.

In aqueous solutions water can also react, so the product at each electrode is whichever half-reaction needs the smaller applied voltage. That is why aqueous sodium chloride gives hydrogen at the cathode, not sodium.

Key law

Faraday's law: the amount of substance changed at an electrode is proportional to the charge passed. $Q = It$, moles of electrons = Q / F , and moles of product = moles of electrons / z , where z is the number of electrons per ion or atom.

Worked example

A current of 2.50 A plates copper from Cu^{2+} for 40.0 min. Find the mass of copper.

$t = 40.0 \times 60 = 2400 \text{ s}$, so $Q = 2.50 \times 2400 = 6000 \text{ C}$. Moles of $\text{e}^- = 6000 / 96\,485 = 0.0622 \text{ mol}$. $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, so moles of $\text{Cu} = 0.0311 \text{ mol}$. Mass = $0.0311 \times 63.55 = \mathbf{1.98 \text{ g}}$.

Key points to remember

- Oxidation is at the anode and reduction is at the cathode, in every cell.
- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, in volts; a positive value means spontaneous.
- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, with $F = 96\,485 \text{ C/mol}$; $\log K = nE^\circ/0.0592$ at 25°C .
- Nernst: $E = E^\circ - (0.0592/n) \log Q$; $E = 0$ when $Q = K$.
- Faraday: $Q = It$, $n(\text{e}^-) = Q/F$, then use the mole ratio to find the mass.

Cells, cell potential and electrolysis: frequently asked questions

What is the difference between a galvanic cell and an electrolytic cell?

A galvanic cell turns a spontaneous reaction into electrical energy, with a negative anode and

a positive cathode. An electrolytic cell uses electrical energy to drive a non-spontaneous reaction, with a positive anode and a negative cathode. Oxidation is at the anode in both.

How do you decide which electrode is the cathode?

Compare the standard reduction potentials. The half-reaction with the higher (more positive) E° is reduced, so it is the cathode in a galvanic cell. The other half-cell is the anode and runs as an oxidation.

Why is E° not multiplied when a half-reaction is doubled?

Potential is energy per unit of charge, so it does not depend on how many moles react. Only n , the electrons in the balanced equation, changes. It matters in $\Delta G^\circ = -nFE^\circ$ but not in E°_{cell} .

How is cell potential related to the equilibrium constant?

Combining $\Delta G^\circ = -nFE^\circ$ with $\Delta G^\circ = -RT \ln K$ gives $\log K = nE^\circ/0.0592$ at 25 °C. A large positive E° means a very large K , and $E^\circ_{\text{cell}} = 0$ means $K = 1$.

How do you use Faraday's law to find a mass deposited?

Find the charge with $Q = It$, divide by 96 485 C/mol to get moles of electrons, divide by the electrons per ion to get moles of metal, then multiply by the molar mass.