

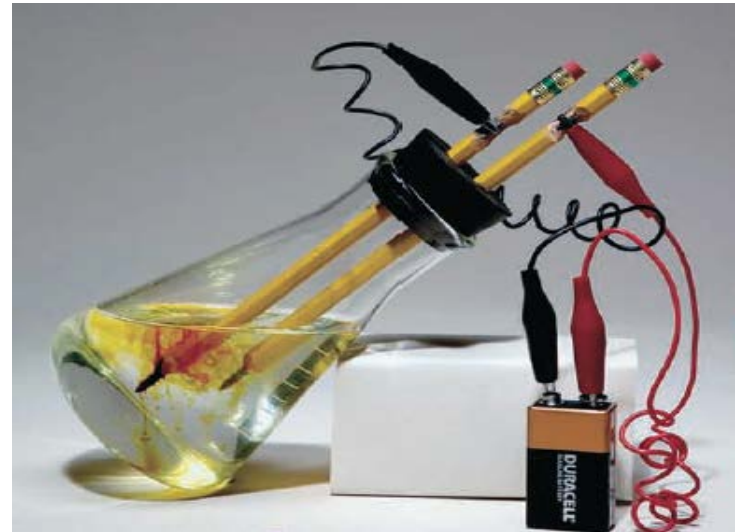
GENERAL CHEMISTRY

A decorative graphic consisting of a solid teal horizontal bar that spans the width of the slide. Below this bar, on the right side, there are several horizontal lines of varying lengths and colors, including teal and white, creating a stepped, modern look.

ELECTROCHEMISTRY

Lemon battery

Zinc and copper strips in a lemon generate a voltage.



Half-Reactions

Balancing Oxidation – Reduction Reactions in Acidic and Basic Solutions

Skeleton Oxidation–Reduction Equations

To set up the skeleton equation and then balance it, we should answer to the following questions:

- What species is being oxidized (or, what is the reducing agent)? What species is being reduced (or, what is the oxidizing agent)?
- What species result from the oxidation and reduction?
- Does the reaction occur in acidic or basic solution?

Example



acidic solution

Half-Reaction Method in Acidic and Basic Solutions

Although the preceding skeleton equation is not complete, it does give the essential information about the oxidation–reduction reaction. Moreover, given the skeleton equation, you can complete and balance the equation using the half-reaction method.

Steps in Balancing Oxidation–Reduction Equations in Acidic Solution

Step 1: Assign oxidation numbers to each atom so you know what is oxidized and what is reduced.

Step 2: Split the skeleton equation into two half-reactions, proceeding as follows. Note the species containing the element that increases in oxidation number, and write those species to give the oxidation half-reaction. Similarly, note the species containing the element that decreases in oxidation number, and write the reduction half-reaction.

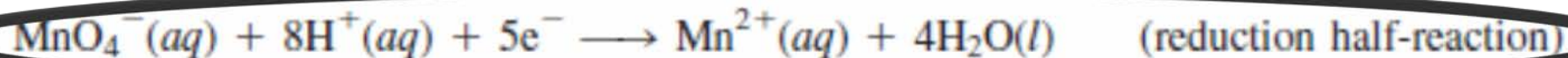
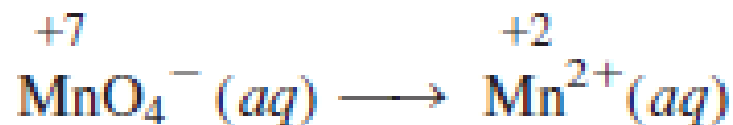
Step 3: Complete and balance each half-reaction.

- a. Balance all atoms except O and H.
- b. Balance O atoms by adding H₂O's to one side of the equation.
- c. Balance H atoms by adding H ions to one side of the equation.
- d. Balance electric charge by adding electrons (e) to the more positive side

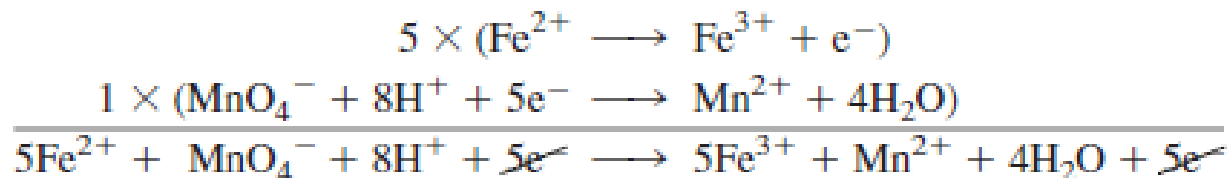
Step 4: Combine the two half-reactions to obtain the final balanced oxidation–reduction equation.

- a. Multiply each half-reaction by a factor such that when the half-reactions are added, the electrons cancel. (Electrons cannot appear in the final equation.)
- b. Simplify the balanced equation by canceling species that occur on both sides, and reduce the coefficients to smallest whole numbers. Check that the equation is indeed balanced.

Let us see how we would apply this **method** to the skeleton equation we wrote for the oxidation of iron(II) ion by permanganate ion in acidic solution.



Check that this half-reaction is balanced in the different kinds of atoms and in electric charge. Note that electrons are gained, as you expect for reduction.



After canceling electrons, the equation is in simplest form (Step 4b). The final balanced equation is



You can write this equation in terms of the hydronium-ion notation, $\text{H}_3\text{O}(\text{aq})$, if you wish, by changing $8\text{H}(\text{aq})$ to $8\text{H}_3\text{O}(\text{aq})$ and adding $8\text{H}_2\text{O}(\text{l})$ to the other side of the equation to give a total of $12\text{H}_2\text{O}(\text{l})$.

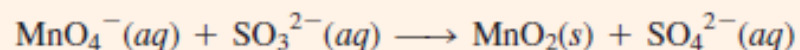
Additional Steps for Balancing Oxidation–Reduction Equations in Basic Solution

Step 5: Note the number of H ions in the equation. Add this number of OH ions to both sides of the equation.

Step 6: Simplify the equation by noting that H reacts with OH to give H₂O. Cancel any H₂O's that occur on both sides of the equation and reduce the equation to simplest terms.

Balancing Equations by the Half-Reaction Method (Basic Solution)

Permanganate ion oxidizes sulfite ion in basic solution according to the following skeleton equation:

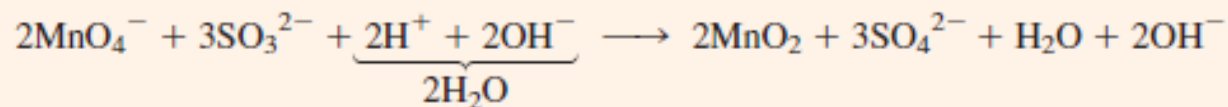


Use the half-reaction method to complete and balance this equation

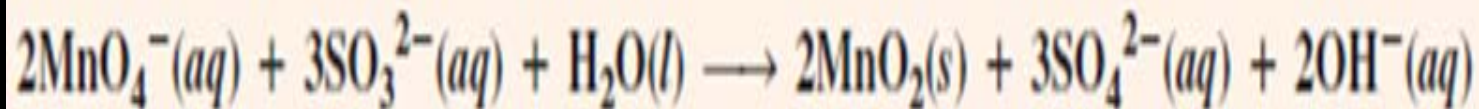
Solution: After balancing the equation as if it were in acid solution, you obtain the following:



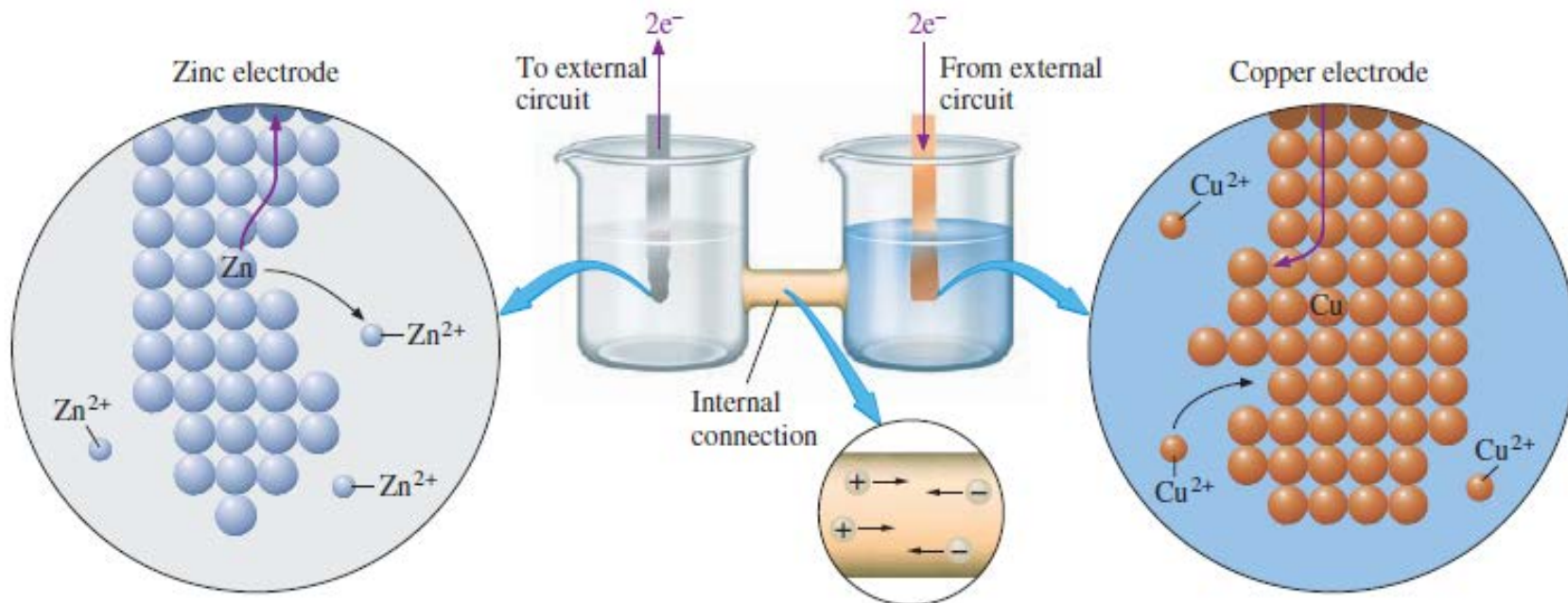
Following **Step 5**, you add 2OH to both sides of the equation.



You replace $2\text{H} + 2\text{OH}$ by $2\text{H}_2\text{O}$ on the left side, then cancel one of these with the H_2O on the right side. The balanced equation for the reaction in basic solution is



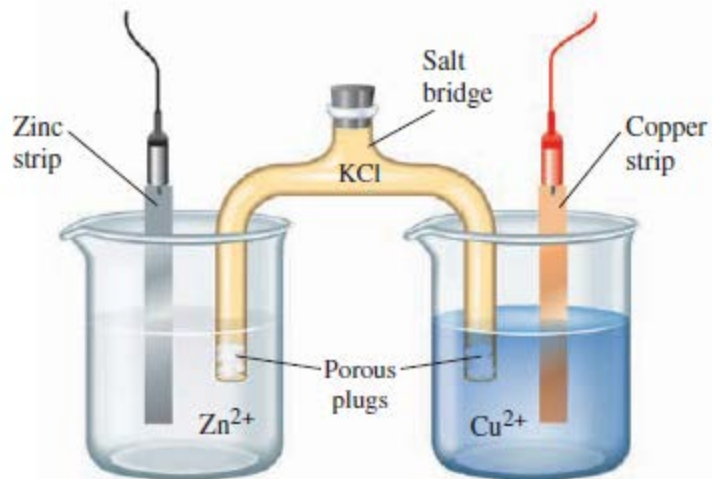
Construction of Voltaic Cells



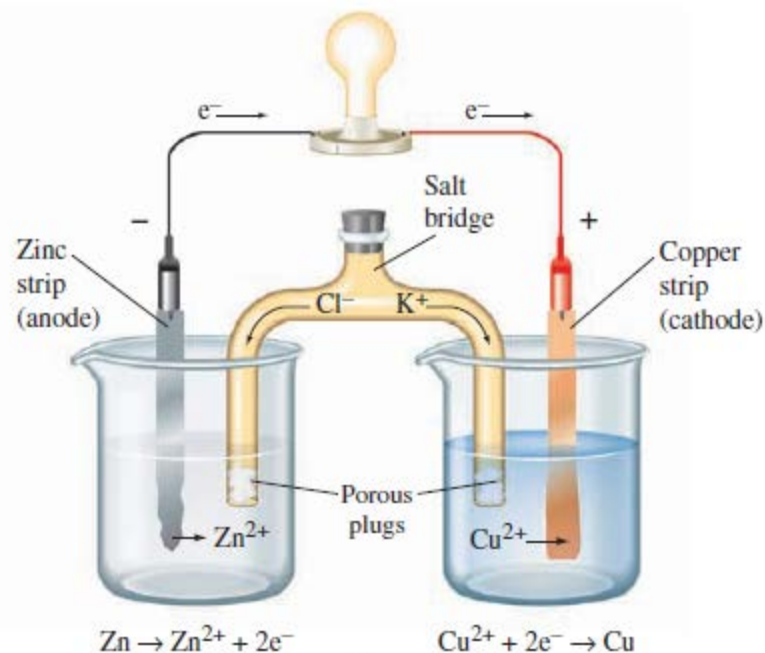
Atomic view of a voltaic cell

In the half-cell on the left, a zinc metal atom loses two electrons. These flow through the zinc electrode to the external circuit, then to the copper electrode in the half-cell on the right. Negative charge on the copper electrode (from the electrons) attracts a copper ion, which reacts with the electrons on the electrode to form a copper metal atom. The internal connection, discussed later in the text, allows ions to flow between the two half-cells; it is required to maintain charge balance.

A zinc-copper voltaic cell



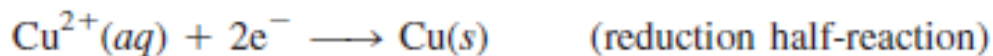
A



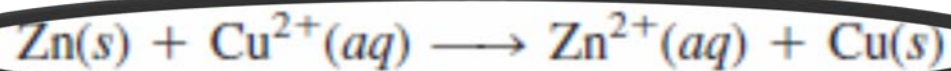
B



C

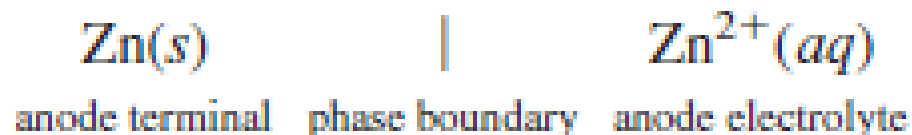
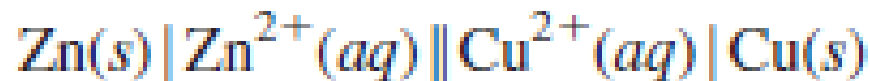


Note that the sum of the two half-reactions



Notation for Voltaic Cells

The cell described earlier, consisting of a zinc metal–zinc ion half-cell and a copper metal–copper ion half-cell, is written



A hydrogen electrode

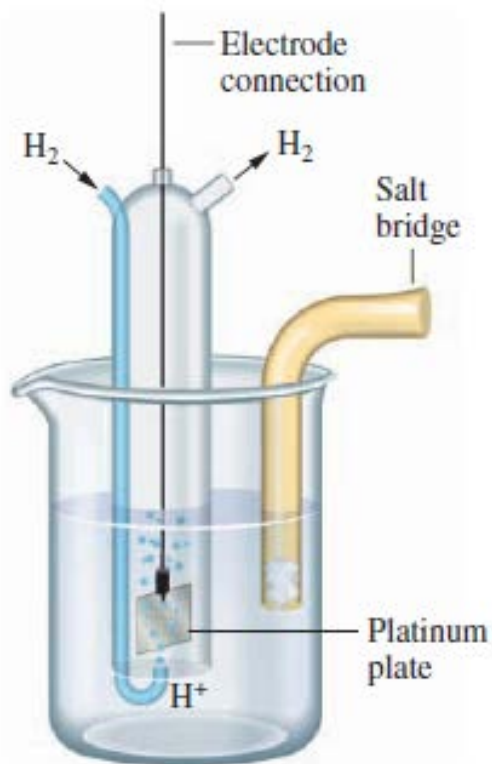
The cathode half-reaction is



The notation for the hydrogen electrode, written as a cathode, is



To write such an electrode as an anode, you simply reverse the notation:



Here are several additional examples of this notation for electrodes

Cathode



Cathode Reaction

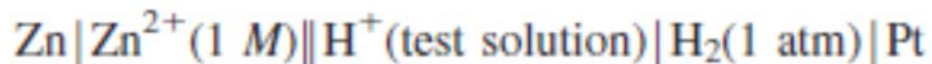


Standard Electrode (Reduction) Potentials in Aqueous Solution at 25C*

Cathode (Reduction) Half-Reaction	Standard Potential, E° (V)
$\text{Li}^+(aq) + e^- \rightleftharpoons \text{Li}(s)$	-3.04
$\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(s)$	-2.71
$\text{Mg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Mg}(s)$	-2.38
$\text{Al}^{3+}(aq) + 3e^- \rightleftharpoons \text{Al}(s)$	-1.66
$2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Zn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Zn}(s)$	-0.76
$\text{Cr}^{3+}(aq) + 3e^- \rightleftharpoons \text{Cr}(s)$	-0.74
$\text{Fe}^{2+}(aq) + 2e^- \rightleftharpoons \text{Fe}(s)$	-0.41
$\text{Cd}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cd}(s)$	-0.40
$\text{Ni}^{2+}(aq) + 2e^- \rightleftharpoons \text{Ni}(s)$	-0.23
$\text{Sn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Sn}(s)$	-0.14
$\text{Pb}^{2+}(aq) + 2e^- \rightleftharpoons \text{Pb}(s)$	-0.13
$\text{Fe}^{3+}(aq) + 3e^- \rightleftharpoons \text{Fe}(s)$	-0.04

$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	0.15
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}^+(\text{aq})$	0.16
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	0.34
$\text{IO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{I}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.49
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	0.52
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	0.54
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	0.77
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l})$	0.80
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	0.80
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Hg}(\text{l})$	0.85
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.90
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Hg}_2^{2+}(\text{aq})$	0.90
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	1.07
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	1.36
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.49
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	1.78
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}(\text{aq})$	2.01
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	2.87

Determination of pH



The cell reaction is



The cell potential depends on the hydrogen-ion concentration of the test solution, according to the Nernst equation. The standard cell potential of the cell equals 0.76V, and

$$Q = \frac{[\text{Zn}^{2+}]P_{\text{H}_2}}{[\text{H}^+]^2} = \frac{1}{[\text{H}^+]^2}$$

Substituting into the Nernst equation, you obtain

$$E_{\text{cell}} = 0.76 - \frac{0.0592}{2} \log \frac{1}{[\text{H}^+]^2} = 0.76 + 0.0592 \log [\text{H}^+]$$

Where [H] is the hydrogen-ion concentration of the test solution. To obtain the relationship between the cell potential (E_{cell}) and pH, you substitute the following into the preceding equation:

$$\text{pH} = -\log [\text{H}^+]$$

The result is

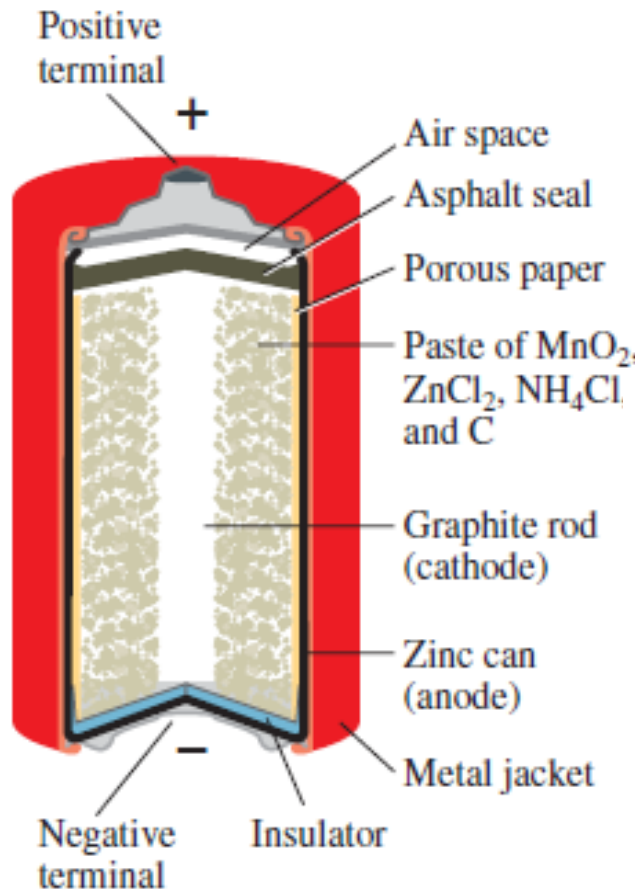
$$E_{\text{cell}} = 0.76 - 0.0592 \text{ pH}$$

Which you can rearrange to give the pH directly in terms of the cell potential:

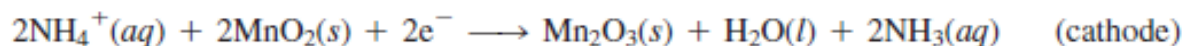
$$\text{pH} = \frac{0.76 - E_{\text{cell}}}{0.0592}$$

Some Commercial Voltaic Cells

Leclanché dry cell



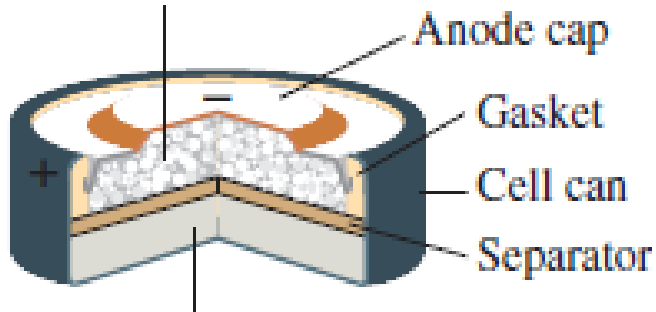
The electrode reactions are complicated but are approximately these:



The voltage of this dry cell is initially about 1.5 V, but it decreases as current is drawn off. The voltage also deteriorates rapidly in cold weather.

A small alkaline dry cell

Anode (negative):
Zn powder +
KOH electrolyte

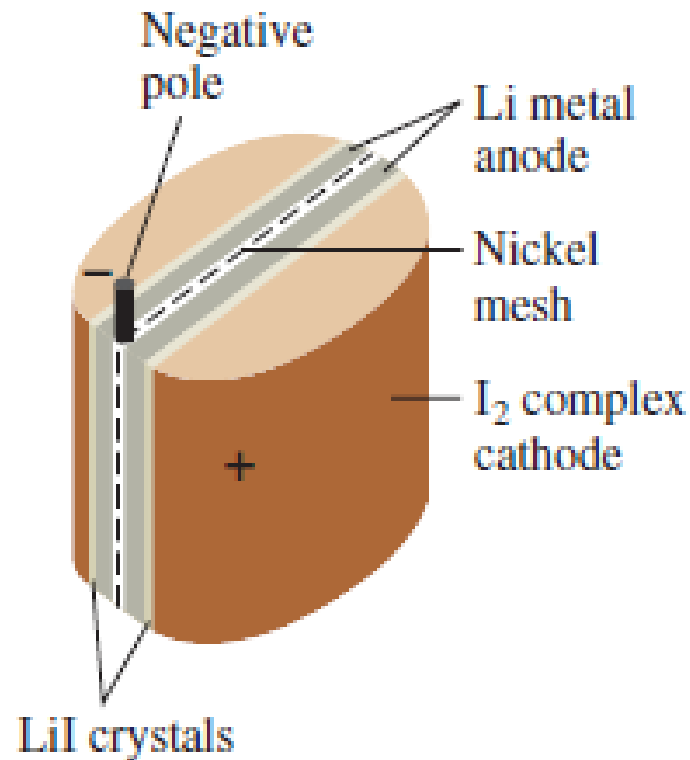


Cathode (positive):
MnO₂ + KOH electrolyte

An **alkaline dry cell** (at the figure) is similar to the Leclanché cell, but it has potassium hydroxide in place of ammonium chloride. This cell performs better under current drain and in cold weather. The half-reactions are:



A solid-state lithium-iodine battery

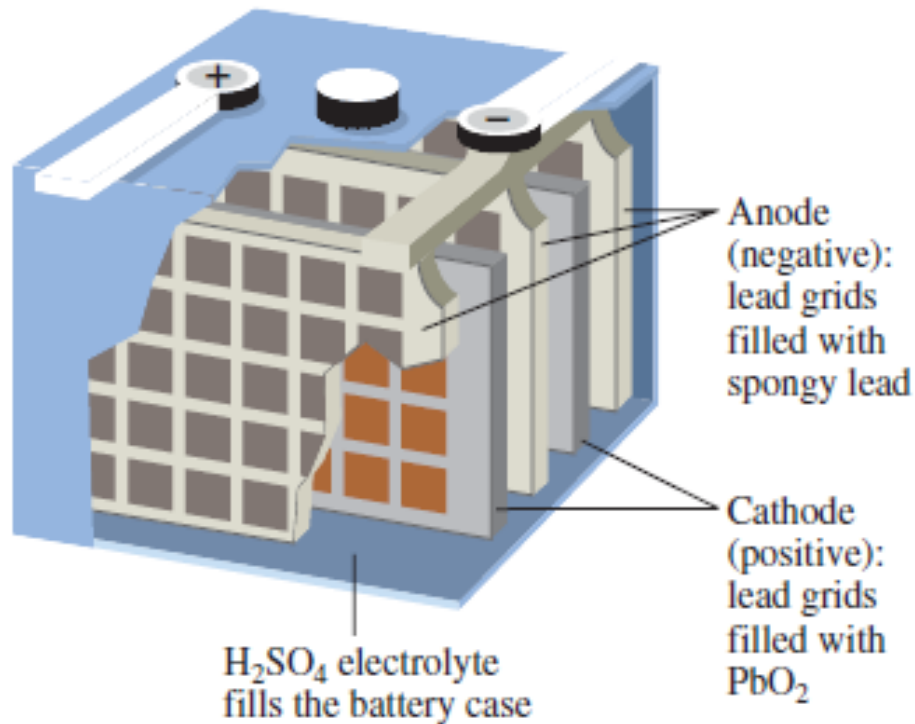


The anode is lithium metal and the cathode is a complex of iodine, I₂; the electrodes are separated by a thin crystalline layer of lithium iodide. The battery consists of two cells enclosed in a titanium shell.

A lead storage battery

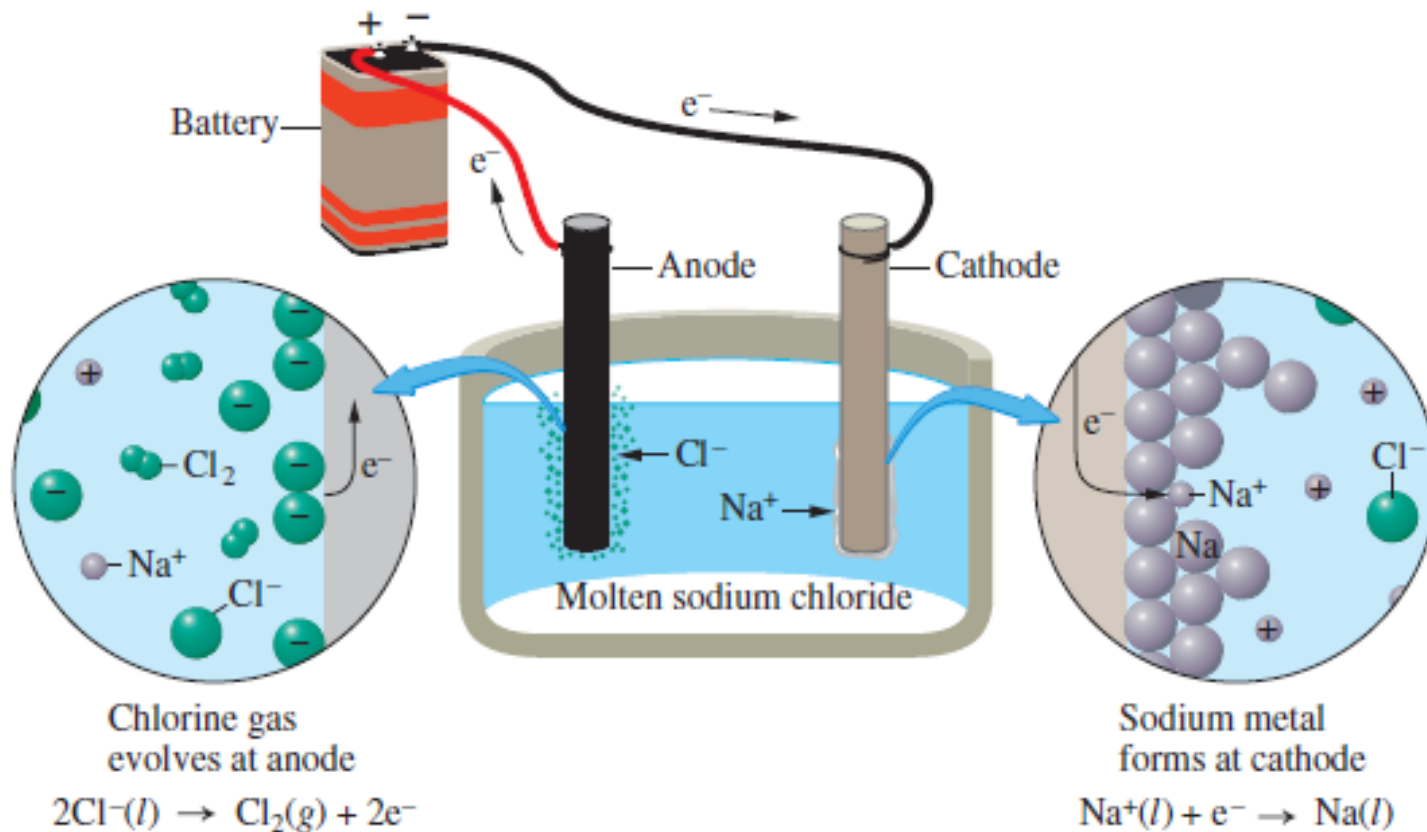
Both are bathed in an aqueous solution of sulfuric acid,

The half-cell reactions during discharge are:



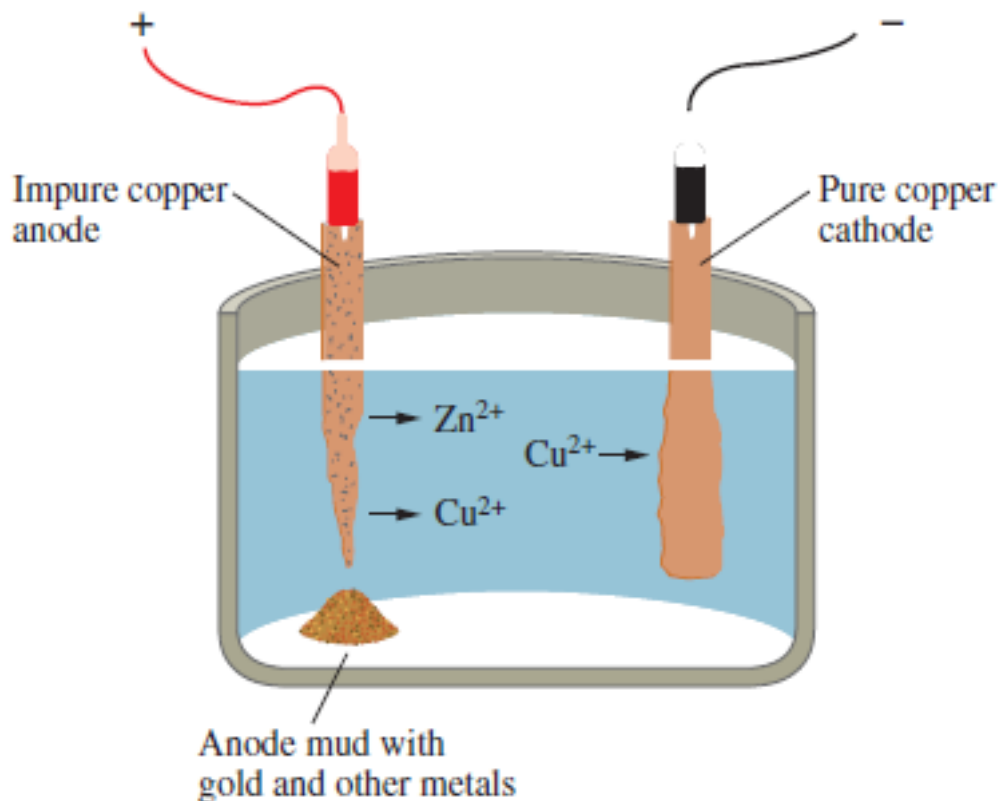
Each cell delivers about 2 V, and a battery consisting of six cells in series gives about 12 V.

Electrolysis of Molten Salts



Sodium metal forms at the cathode from the reduction of Na ion; chlorine gas forms at the anode from the oxidation of Cl ion. Sodium metal is produced commercially this way, although the commercial cell must be designed to collect the products and to keep them away from one another.

Electroplating of Metals



Left: Copper(II) ion leaves the anode and plates out on the cathode.

Reactive ions, such as Zn^{2+} , remain in solution, and unreactive substances (including gold) collect as a mud under the anode. Right:

Very pure copper sheets alternate with impure copper slabs in this electrolytic tank. The pure copper sheets grow in size and are removed in about a month.

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