

Electrochemistry

BALANCING REDOX REACTIONS

- The oxidation number of any element, in its elemental form, is zero.
- The sum of the oxidation numbers in a compound must add up to be equal to the overall charge on the compound (if there is no charge on the compound, they add up to zero)
- The oxidation state of fluorine is -1
- Any Group 1A metal is +1 and any Group 2A metal is +2
- Hydrogen is +1
- Oxygen is -2
- Any Group 7A element (except F) is -1

TO BALANCE A REDOX REACTION, FIRST ASSIGN OXIDATION STATES TO ALL ATOMS ON BOTH SIDES OF THE ARROW.

BALANCING REDOX REACTIONS

RECALL THAT A REDOX REACTION IS ONE WHERE THE OXIDATION STATE OF ONE OR ELEMENTS CHANGES AS THE REACTION PROCEEDS.



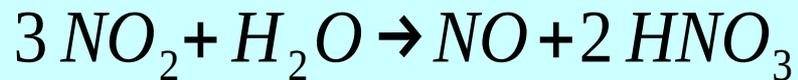
Here Cl = + 5 on the left and -1 on the right.

O = -2 on the left and 0 on the right.

What is the reducing agent?

Oxidizing agent?

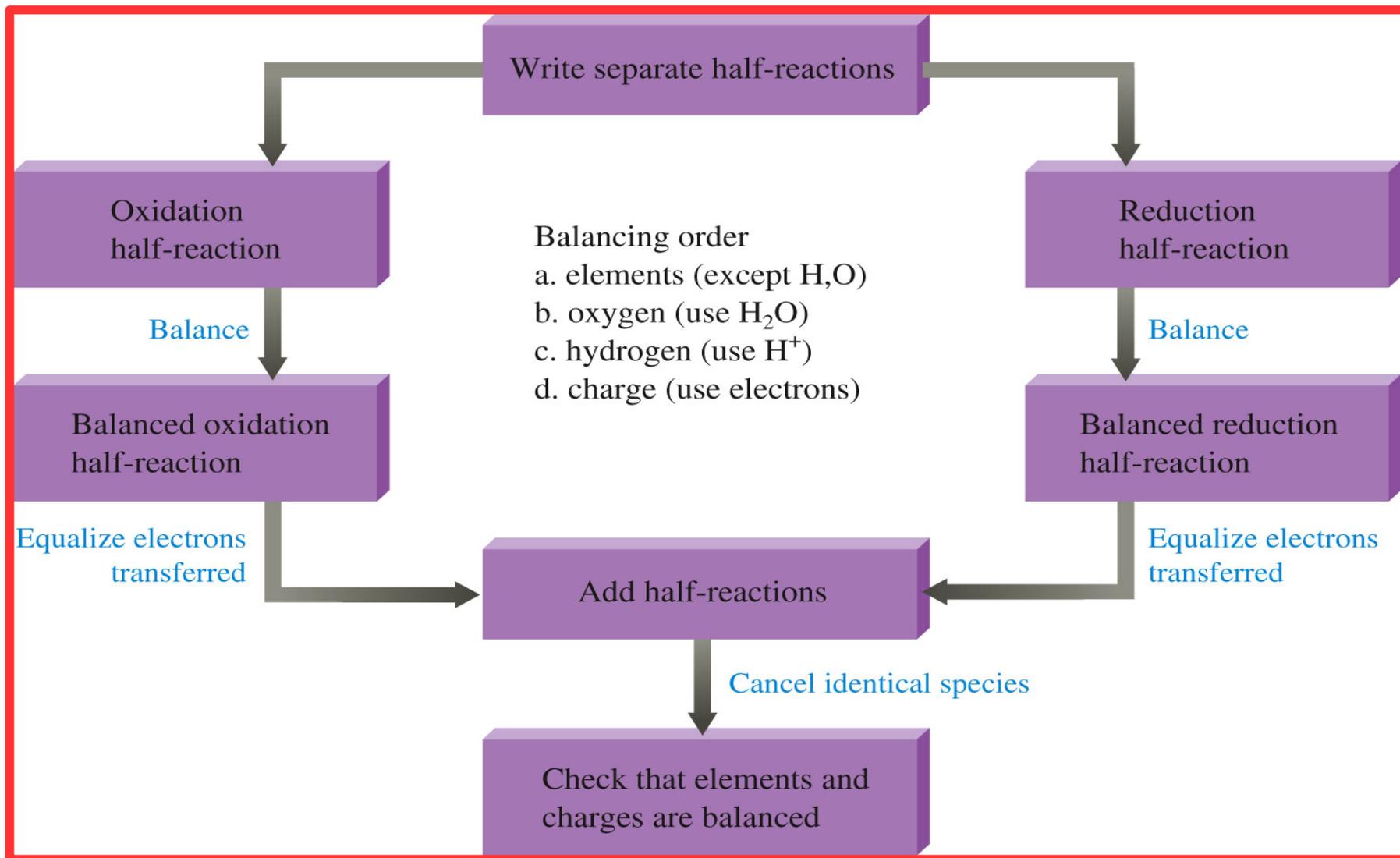
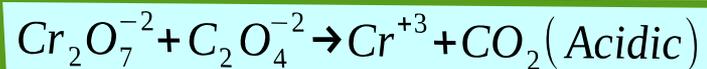
Is the following a redox reaction? If so, what is the oxidizing agent? Reducing agent?



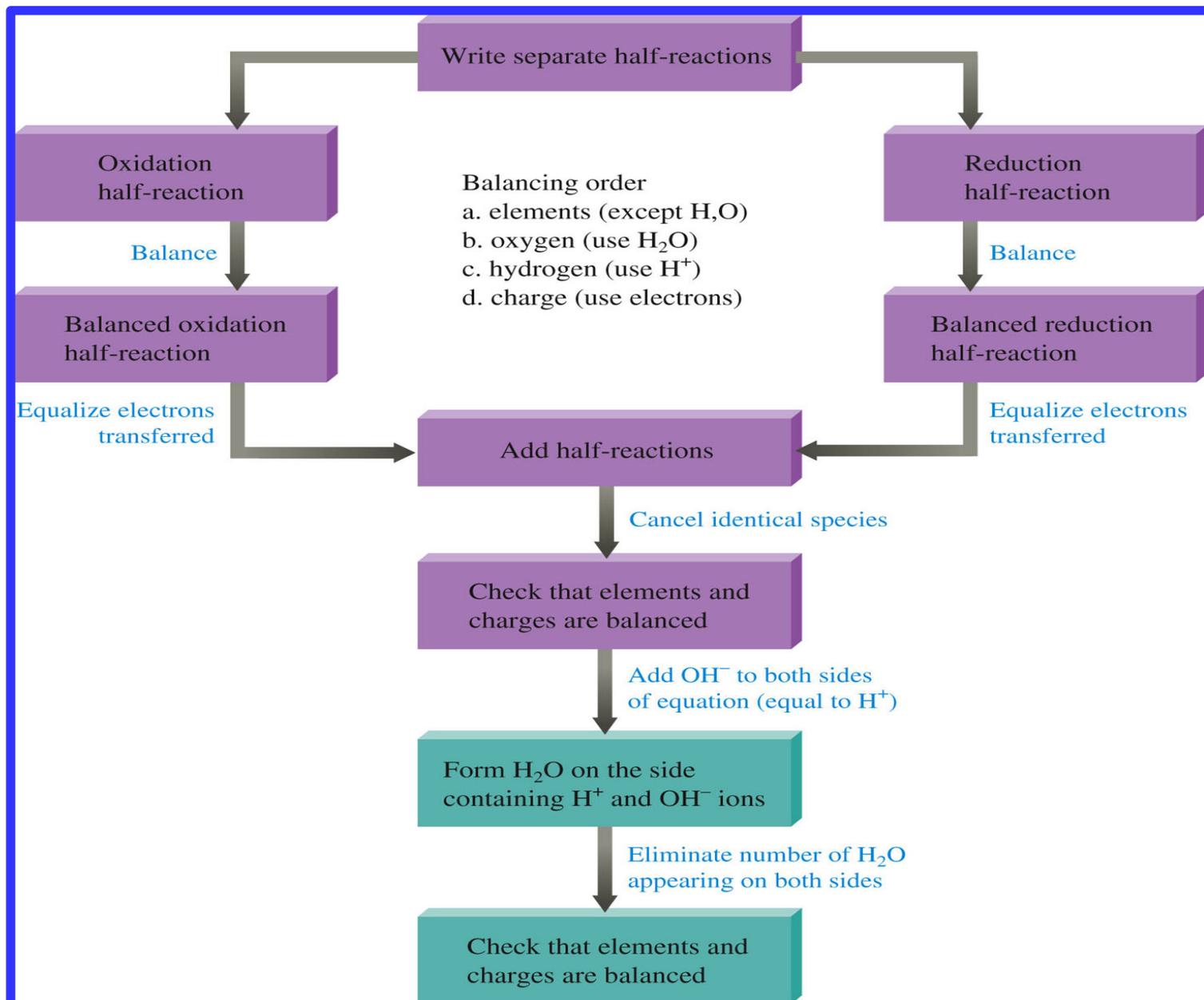
BALANCING REDOX REACTIONS

1. Write the oxidation half reaction and reduction half reaction separately.
2. Balance the atoms except O and H in both half reactions.
3. Balance both half reactions for O by adding 1 H₂O for every O you need.
4. Balance both half reactions for H by adding 1 H⁺ for each H you need.
5. Balance the charge in both half reactions with electrons.
6. Make the number of electrons in both half reactions the same by multiplying (if necessary).
7. Add the two half reactions to get the overall balanced equation.
8. IFF the reaction occurs in basic solution add one OH⁻ on both sides of the arrow for each H⁺.
9. Cancel any H₂O's that appear on both sides of the arrow.

Acidic Solutions



Basic Solutions

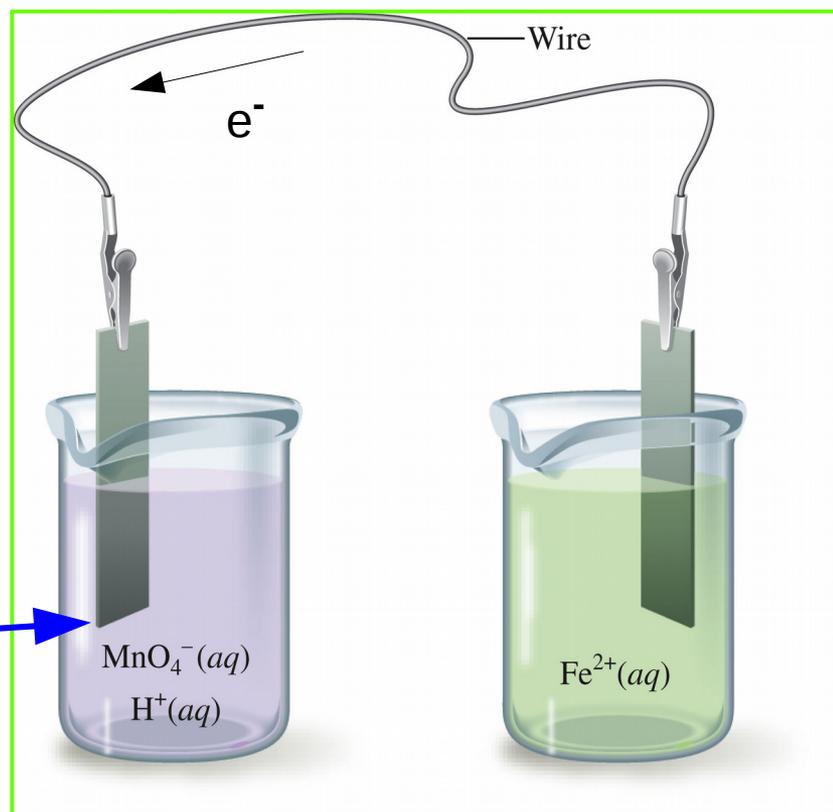
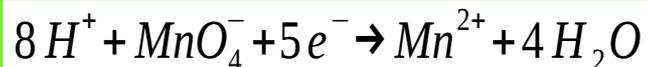
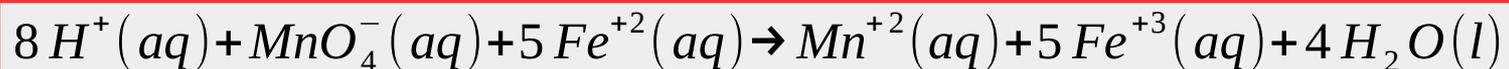


Galvanic Cells

A galvanic cell is a device where chemical energy is converted into electrical energy.

This is done by separating the oxidation and reduction half reactions of a redox reaction into separate cells.

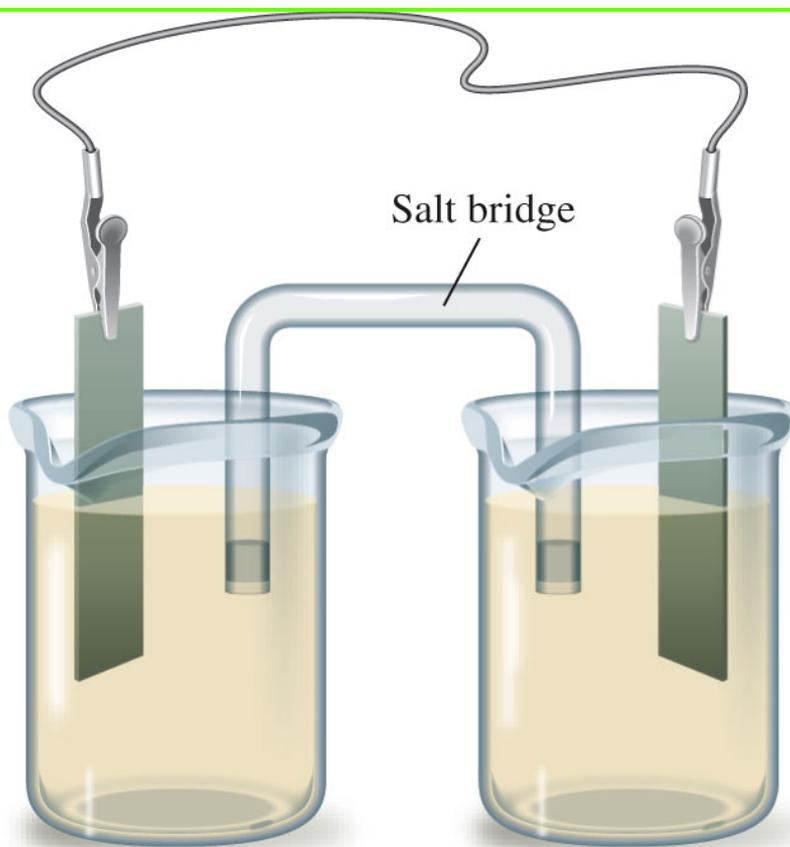
For example, the reaction between the permanganate ion and the iron(II) ion in acidic solution:



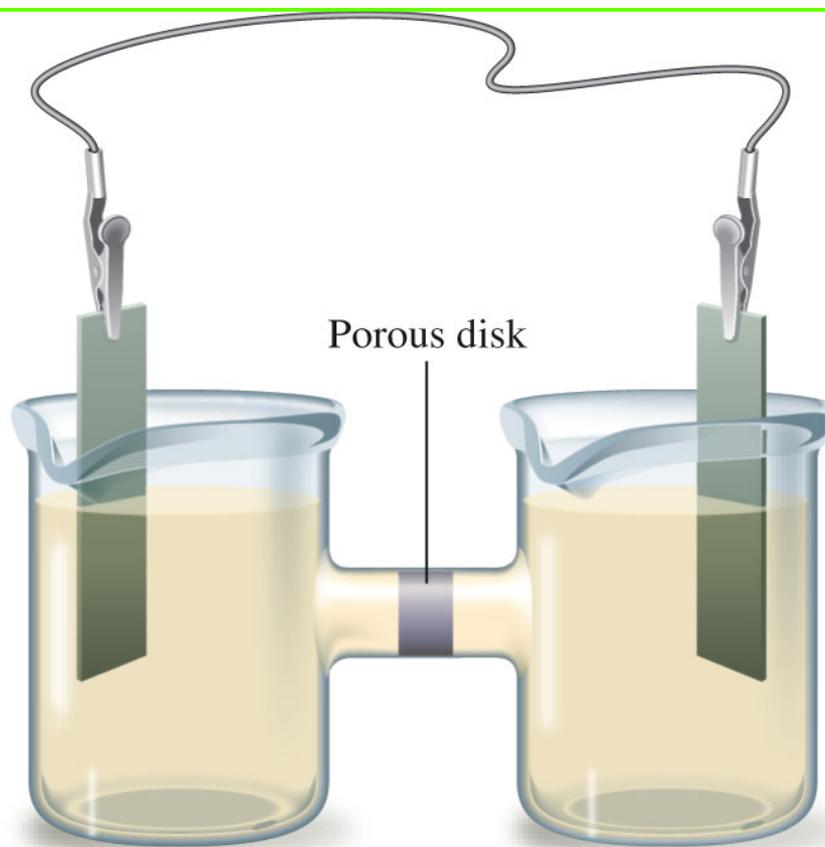
The reaction will stop quickly due to the build up of positive charge in the Fe cell and negative charge in the MnO_4^- cell.

Galvanic Cells

The solution to this is to provide a means for the charge to re-balance. We do this with a salt bridge (a U-shaped tube with an electrolyte in it that does not react with anything in our reaction), or a porous disk in a tube that connects the two solutions.



(a)

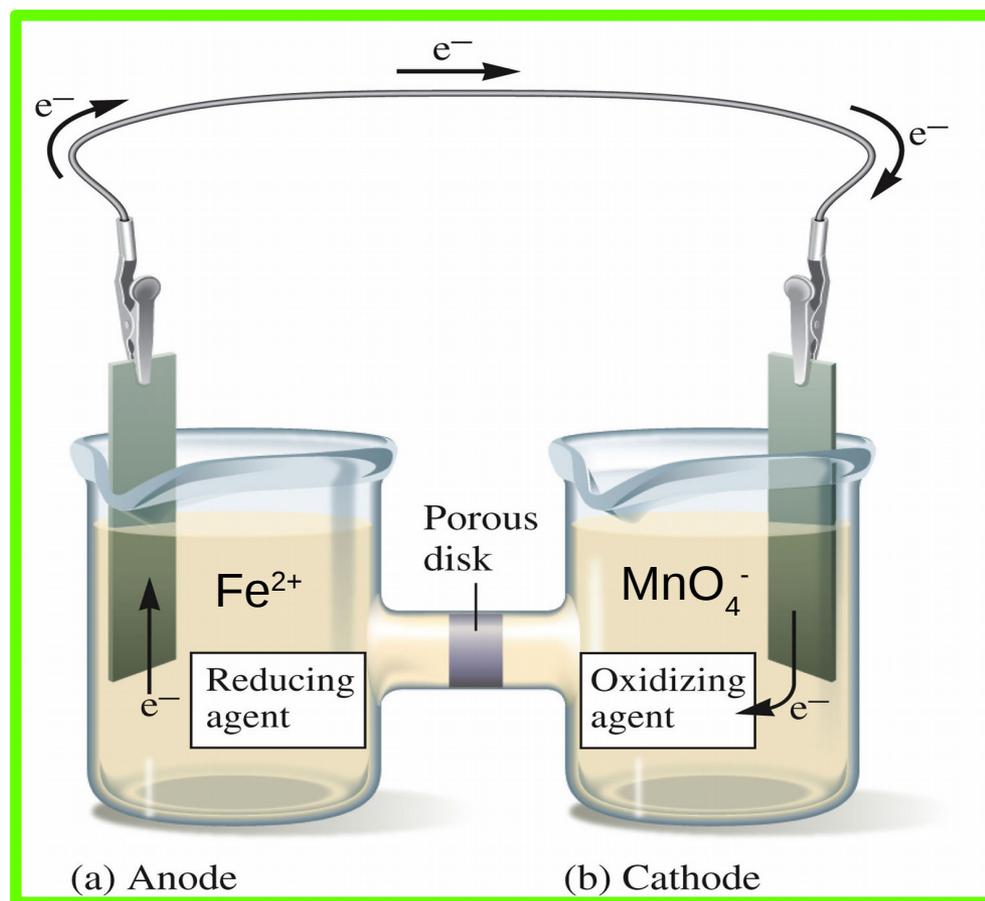


(b)

Cathodes and Anodes

The electrode where oxidation occurs is called the anode (anions flow towards it).

The electrode where reduction occurs is called the cathode (cations flow towards it).



Cell Potential

In a galvanic cell the oxidizing agent in one cell “pulls” electrons through a wire from a reducing agent in another cell. The strength of this “pull” is called the cell potential, E_{cell} , or electromotive force (emf) of the cell.

The unit of cell potential is the volt, V, which is defined as the amount of work, in joules, per amount of charge transferred, in coulombs.

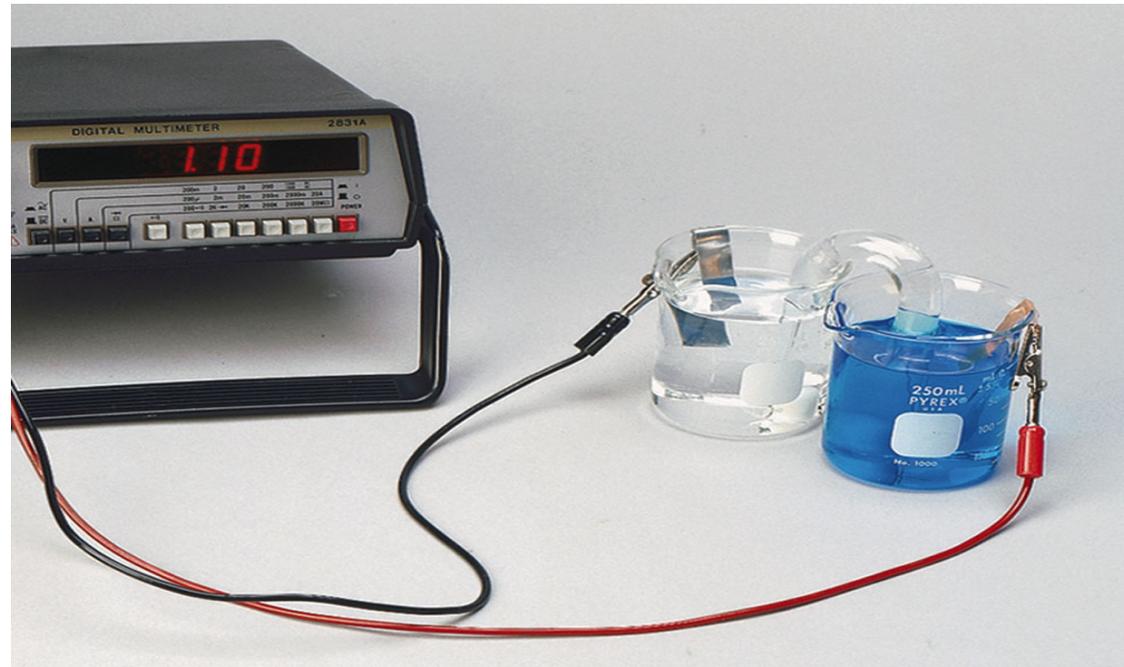
$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}}$$

Measuring Cell Potential

A voltmeter will measure the potential by drawing a current through a wire of known resistance.

When current flows through a wire there is resistance, which causes loss of energy through heat. This wastes some of the energy being used from the cell.

This means that the voltmeter measures a potential which is less than the maximum cell potential.

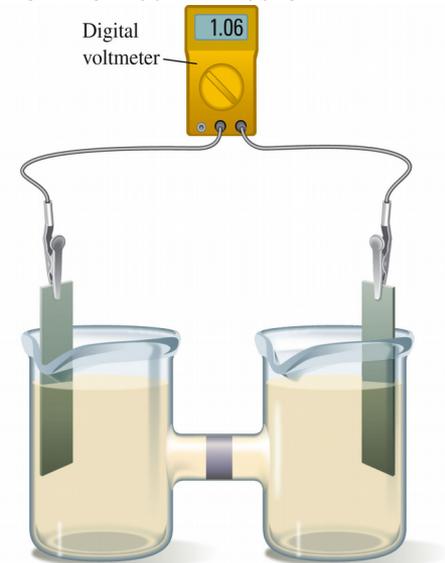


Measuring Cell Potential

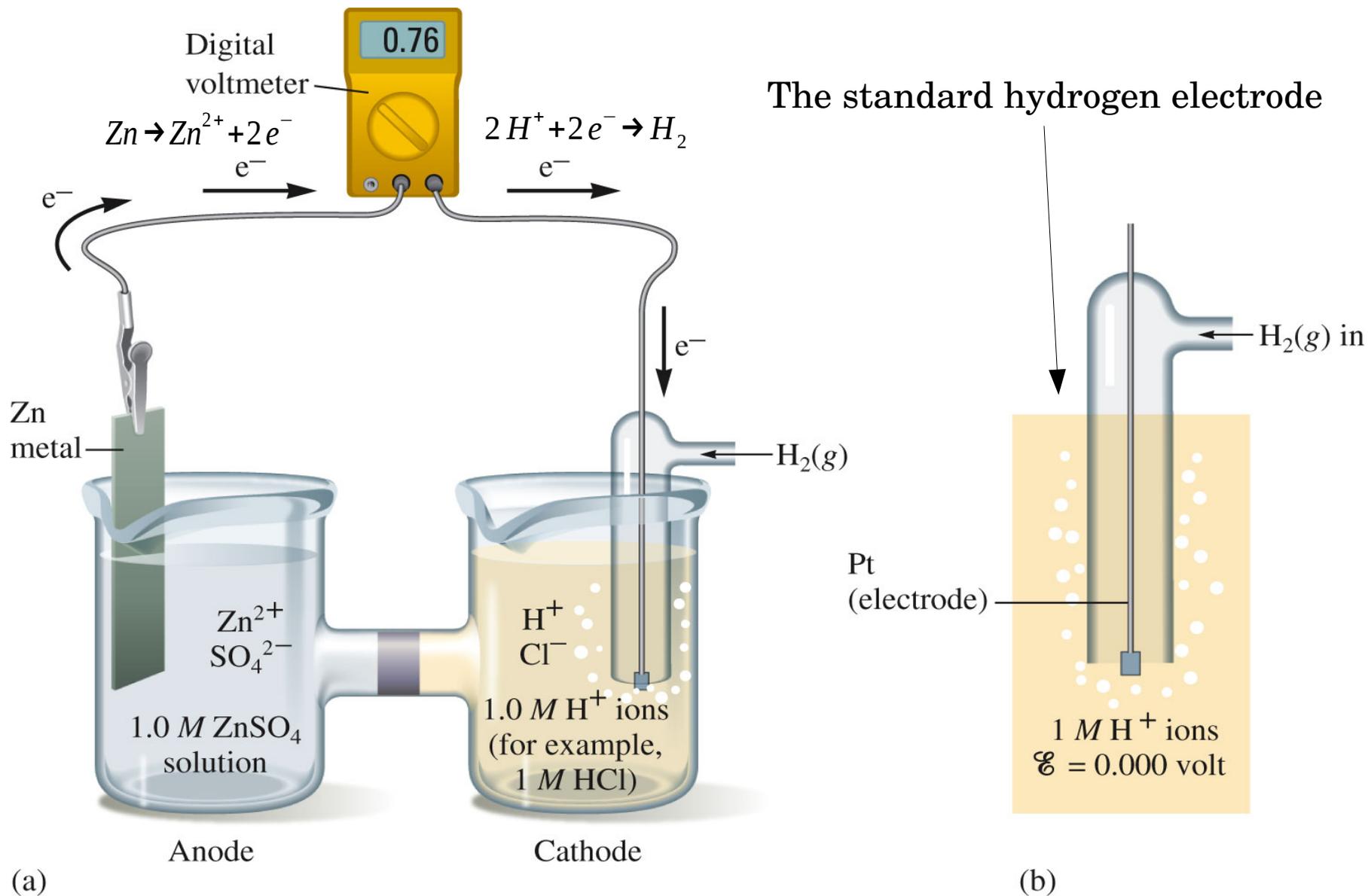
We can measure the maximum cell potential by setting up a variable voltage instrument (a potentiometer) which has an external power supply.

We set this up so that the instrument is in opposition to the cell potential and tune it so that no current flows. The voltage of the potentiometer that just balances the cell potential is equal in magnitude but opposite in sign to the cell potential.

Alternatively, digital voltmeters draw very little current and will work to measure the cell potential too.



Standard Reduction Potentials



Standard Reduction Potentials

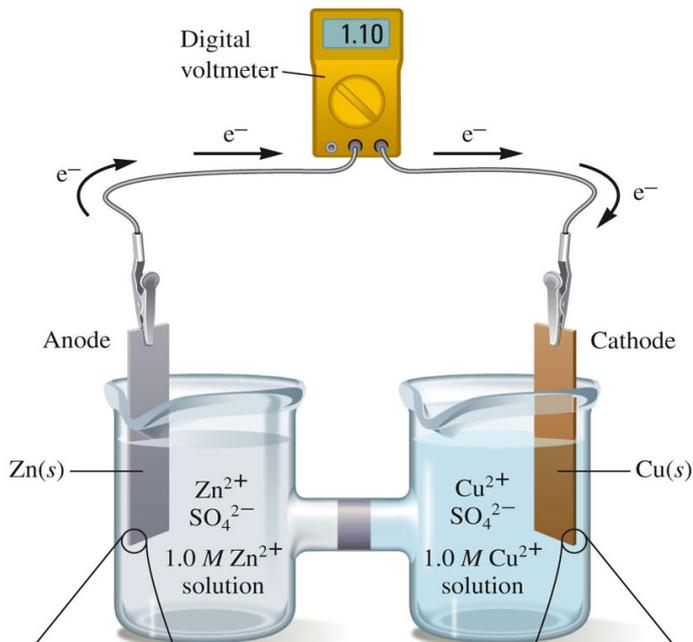
While we can measure the total potential of this cell, we can't measure the potential of an individual electrode.

So we (somewhat) arbitrarily set the potential of the standard hydrogen electrode under standard conditions (1 atm P_{H_2} and 1 M H^+) to 0.00 V.

$$E_{\text{cell}}^{\circ} = E_{\text{H}^+ \rightarrow \text{H}_2}^{\circ} + E_{\text{Zn} \rightarrow \text{Zn}^{2+}}^{\circ}$$

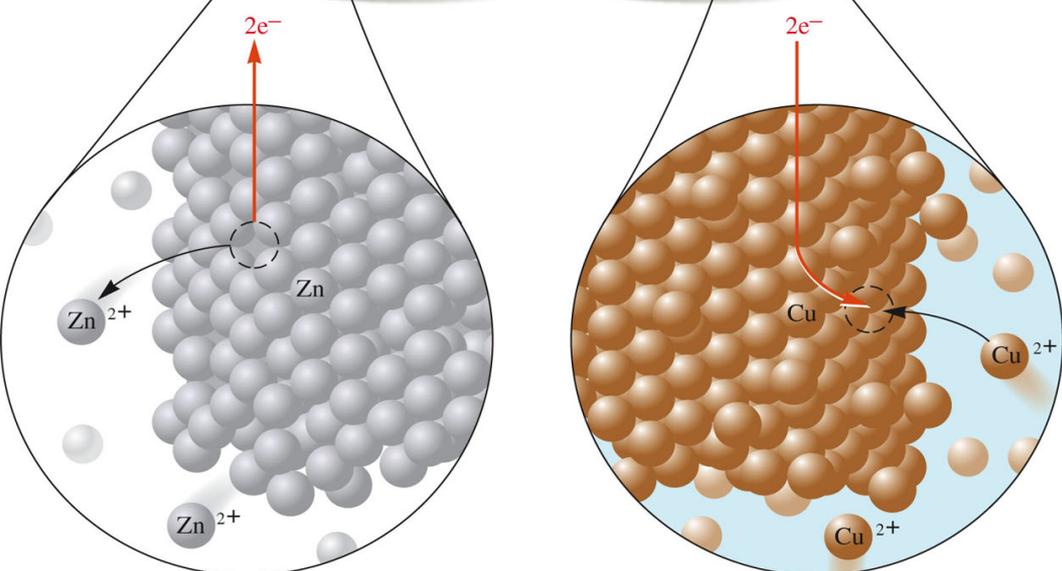
0.76 V 0.00 V 0.76 V

Standard Reduction Potentials



$$E_{cell}^{\circ} = E_{Zn \rightarrow Zn^{2+}}^{\circ} + E_{Cu^{2+} \rightarrow Cu}^{\circ}$$

1.10 V 0.76 V ? V



By knowing the potential of the Zn half reaction and measuring the potential of the cell, we find the potential of the Cu half reaction (under standard conditions) : 0.34 V

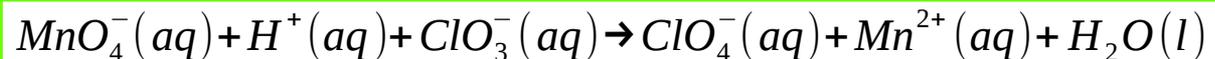
Standard Reduction Potentials

Half-Reaction	\mathcal{E}° (V)	Half-Reaction	\mathcal{E}° (V)
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	1.99	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.27
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$2\text{e}^- + 2\text{H}^+ + \text{IO}_4^- \rightarrow \text{IO}_3^- + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.09	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.23
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.80	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52		

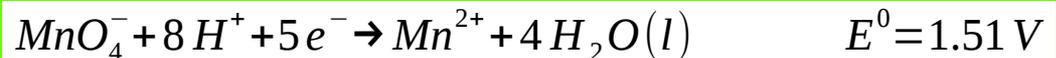
Combining Half-Reactions

1. Reverse the half reaction with the lowest potential (least positive potential). Change the sign of this half reaction. It is now written as the oxidation half reaction.
2. Multiply each half reaction by an integer so that they each have the same number of electrons (the least common multiple of the original numbers of electrons).
3. Add the two half reactions (the electrons must cancel) and the potentials to get the balanced equation and the cell potential.

For example, write the balanced equation and find the cell potential for the following reaction:

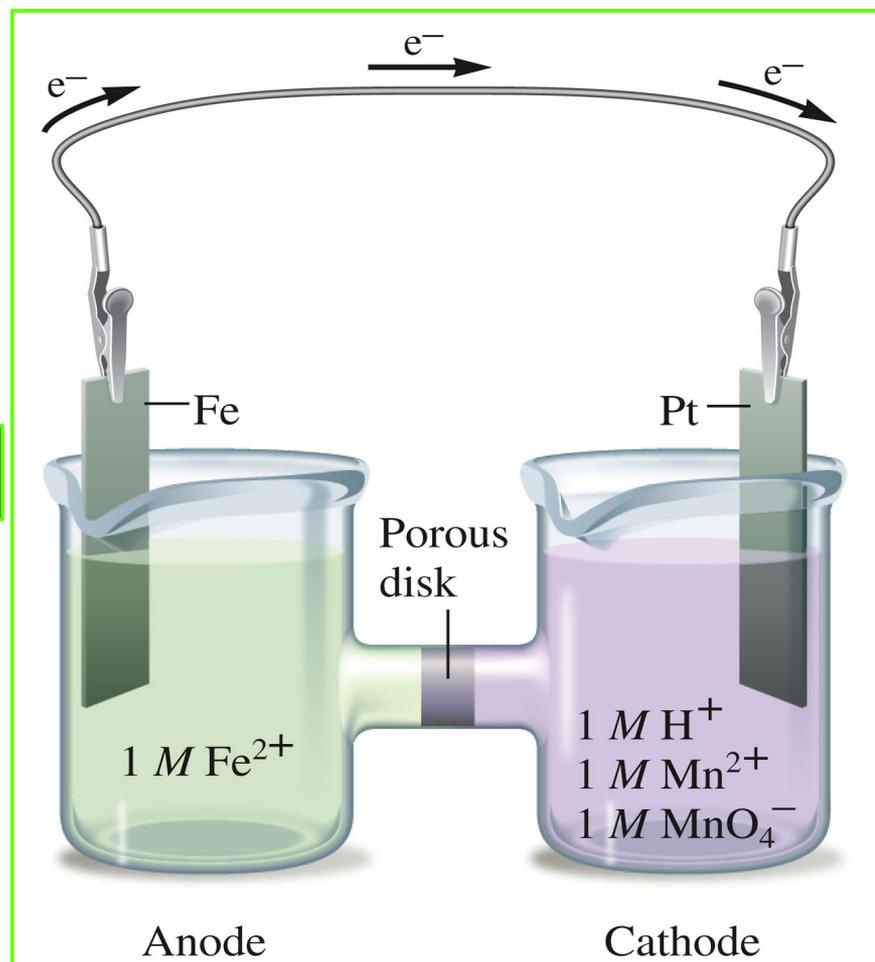


The half reactions are:



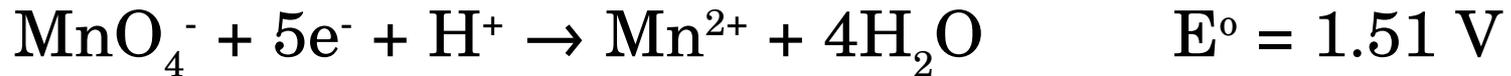
Line Notation

1. The anode is on the left and the cathode on the right.
2. A double vertical line separates them and represents the salt bridge or porous plug.
3. A single line represents a phase boundary.
4. The far left component represents the anode electrode material and the far right represents the cathode electrode material.



A Description of a Galvanic Cell

Consider a galvanic cell based on the following half reactions:

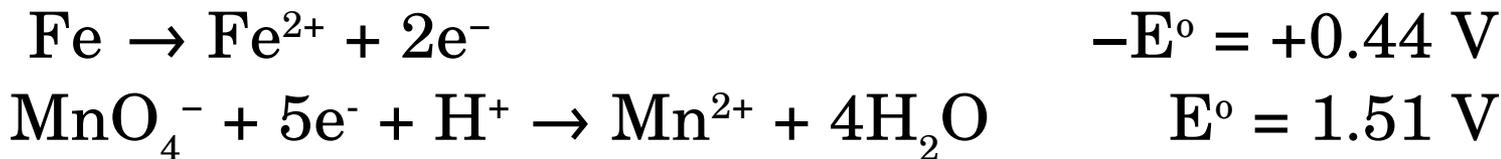


These are both reductions, in a galvanic cell one must run in reverse (undergo oxidation). Which one?

A galvanic will run spontaneously in the direction that has a positive cell potential.

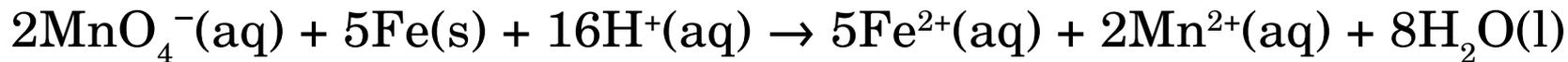
This means Fe will be oxidized in this cell.

A Description of a Galvanic Cell

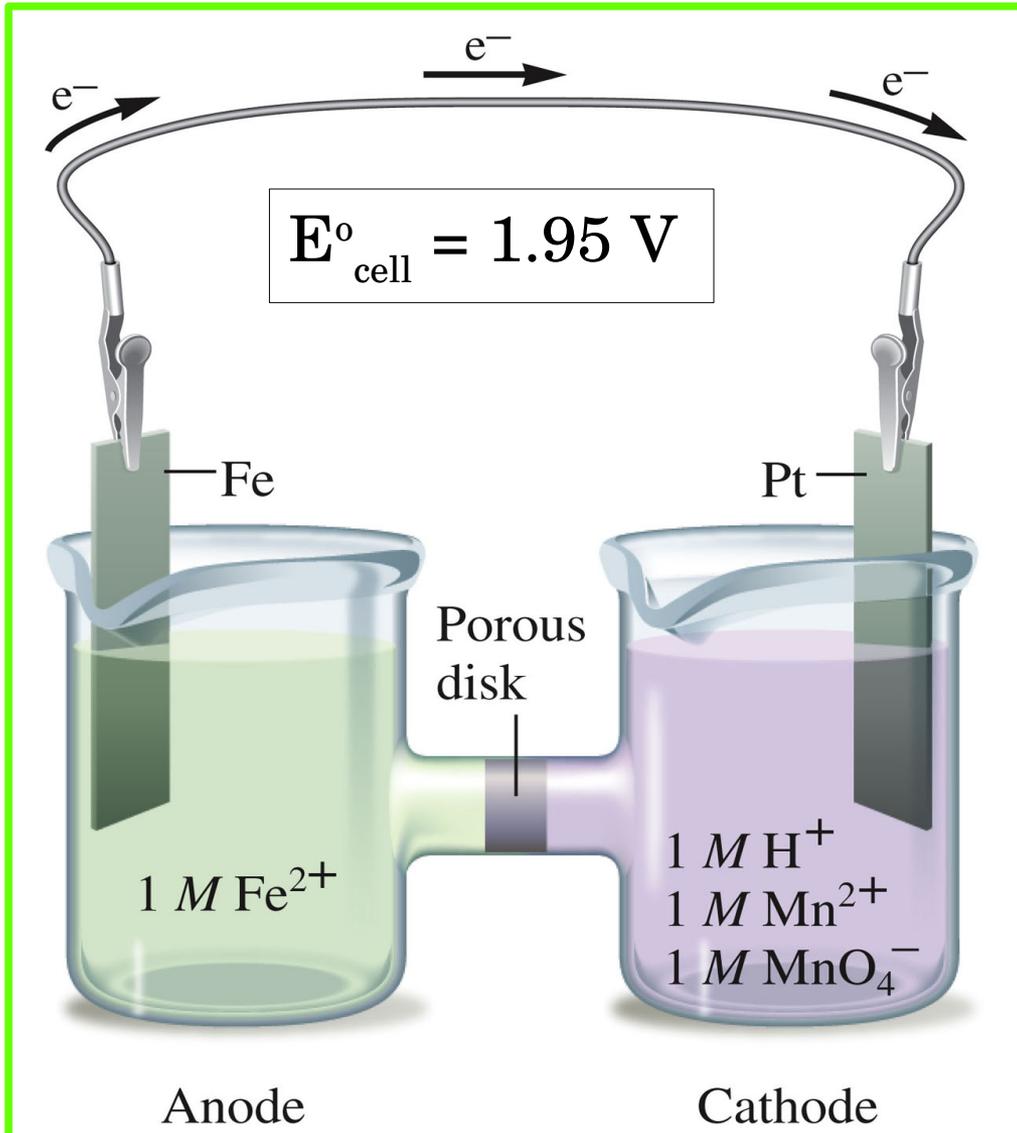
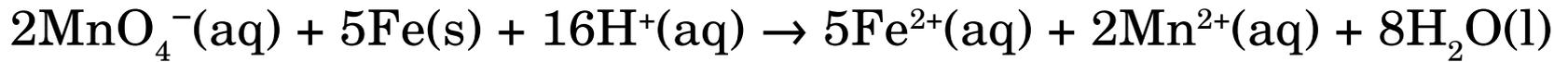


Now we see that iron is the anode and that permanganate is at the cathode (the actual cathode will be an inert metal, likely platinum).

The cell potential is $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 1.51 \text{ V} + 0.44 \text{ V} = 1.95 \text{ V}$
and the balanced reaction is



A Description of a Galvanic Cell



Everything is in standard states (1 M etc.)

Description of a Galvanic Cell

A complete description of a galvanic cell includes:

1. The cell potential and the balanced cell reaction.
2. The direction of electron flow (positive E°_{cell})
3. Labels for the cathode and anode.
4. The make-up of each electrode (Pt, etc.) and the ions present in each compartment.

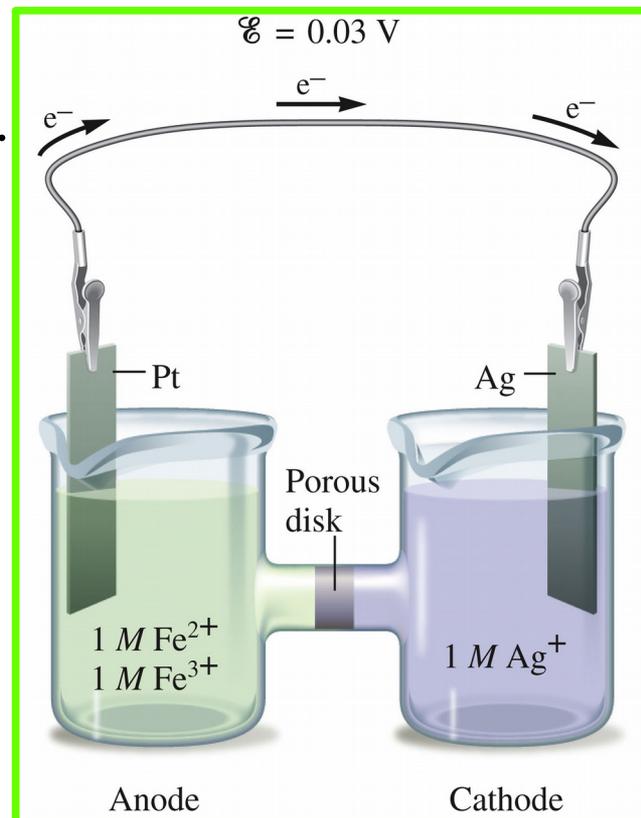
Example: Give a complete description of the galvanic cell based on the following half reactions.



$$E^{\circ} = 0.77 \text{ V}$$



$$E^{\circ} = 0.80 \text{ V}$$



Cell Potential, Work, and Free Energy

The work that can be done by moving electrons through a wire depends on the electromotive force (emf). The emf is defined by the potential difference between 2 points in the circuit.

$$emf = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

$$E = \frac{-w}{q}$$

Positive E means work done by the cell, which is defined as being negative. To do electrical work current must flow. There is always frictional loss. In any real process the work obtained is less than the calculated maximum. This is a demonstration of the 2nd law of thermodynamics (for a process to be spontaneous the entropy of the universe must increase).

Cell Potential, Work, and Free Energy

The total charge is determined by the total moles of electrons (n) that pass through the circuit:

$$\text{Total charge} = nF$$

Here F is the Faraday constant which is the charge in coulombs on 1 mole of electrons:

$$F = 96,485.3 \text{ C/mol } e^- = 96,485.3 \text{ J/Vmol}\cdot e^-$$

The measured cell potential is the maximum voltage the cell can produce, which gives us the maximum electrical work we can get from the reaction:

$$w_{max} = -nFE_{cell}$$

The maximum amount of work that can be done comes from the free energy. $\Delta G = w_{max} = -nFE_{cell}$

Cell Potential, Work, and Free Energy

The maximum amount of work that can be done comes from the free energy. $\Delta G = w_{\max} = -nFE_{\text{cell}}$. Because ΔG must be < 0 for a process to be spontaneous, E_{cell} must be positive. For reactants and products in their standard states:

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

But we also know

$$\Delta G^{\circ} = -RT \ln K$$

or

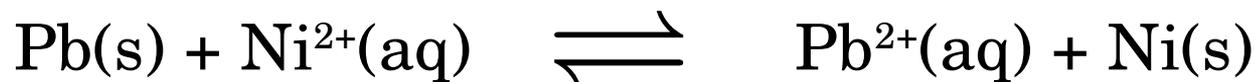
$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$$

at 25°C, putting the values in for R, T, and F we get

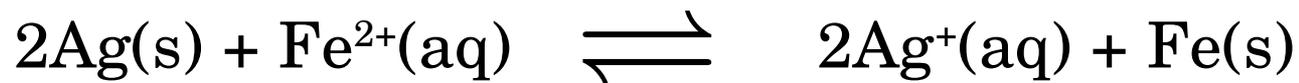
$$E_{\text{cell}}^{\circ} = \frac{0.02569}{n} \ln K = \frac{0.05916}{n} \log K$$

Cell Potential, Work, and Free Energy

Calculate the standard free energy change for the following reaction at 25 °C:



Calculate the equilibrium constant for the following reaction at 25 °C and at 75 °C:



The Nernst Equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$-nFE = -nFE^\circ + RT \ln Q$$

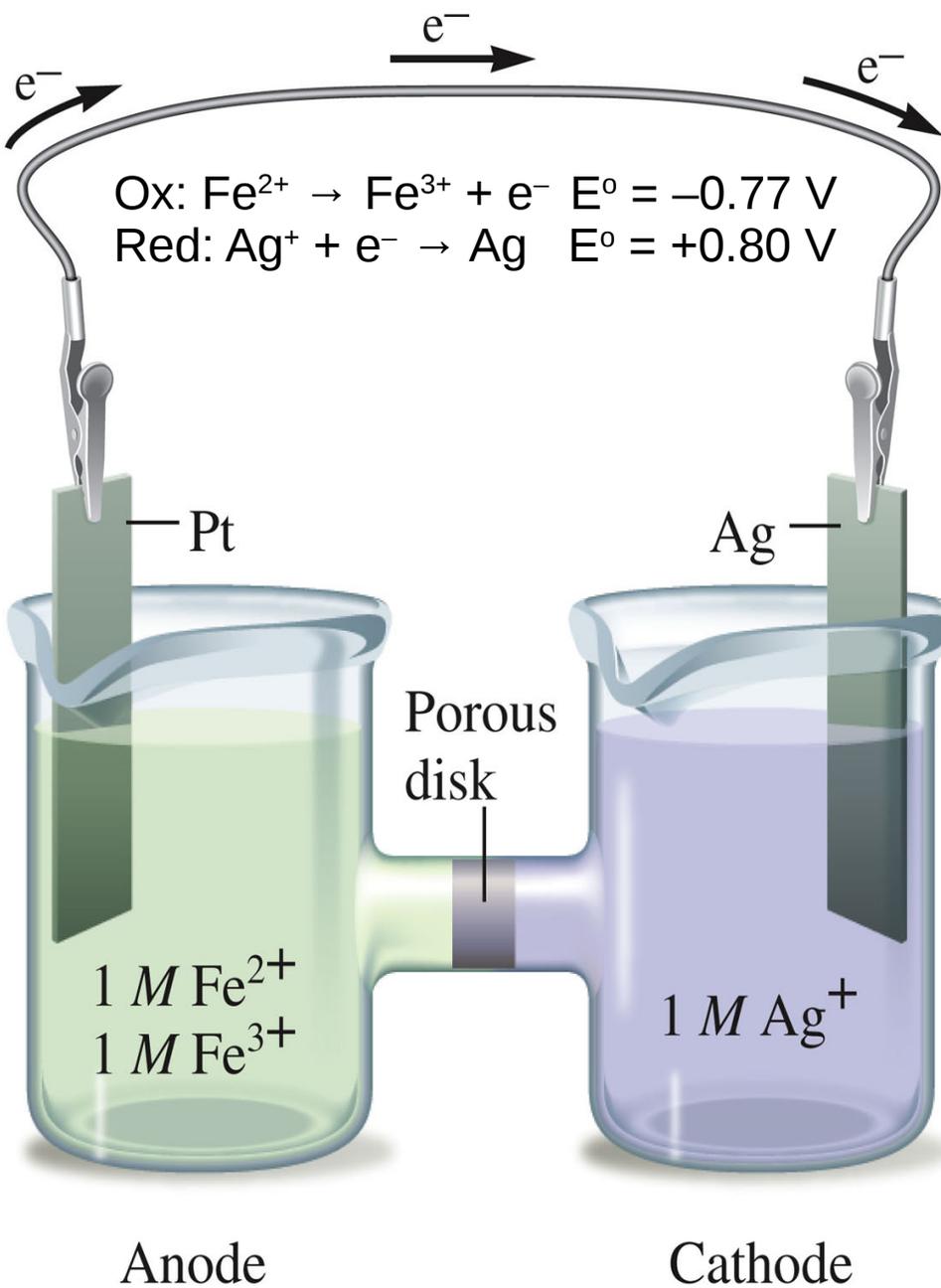
$$E = E^\circ - \frac{RT}{nF} \ln [Q]$$

The Nernst Equation

or at 298 K

$$E = E^\circ - \frac{0.05916 \text{ V}}{n} \log [Q]$$

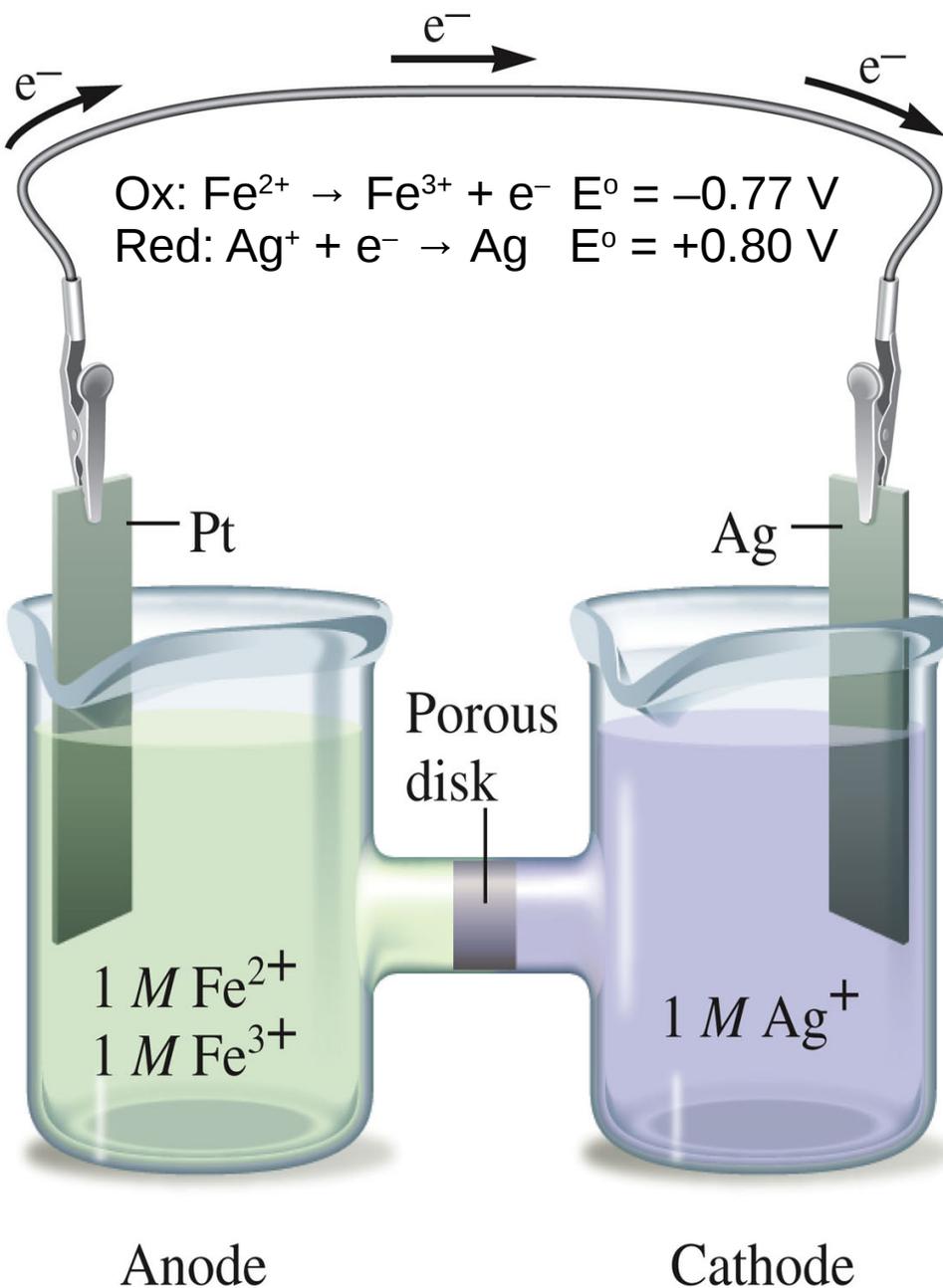
$$E^{\circ} = 0.03 \text{ V}$$



$$E = E^{\circ} - \frac{0.05916 \text{ V}}{1} \log \frac{[Fe^{3+}]}{[Ag^{+}]}$$

As the reaction proceeds the $[Fe^{3+}]$ increases and $[Ag^{+}]$ decreases causing E to decrease until $E = 0$ (the cell is at equilibrium) and $Q = K$.

$$E^{\circ} = 0.03 \text{ V}$$



$$E = E^{\circ} - \frac{0.05916 \text{ V}}{1} \log \frac{[Fe^{3+}]}{[Ag^{+}]}$$

At equilibrium:

$$E^{\circ} = 0.05916 \text{ V} \log \frac{[Fe^{3+}]}{[Ag^{+}]} = 0.03 \text{ V}$$

or the ratio of [Fe³⁺] to [Ag⁺] = 3.2. When the ratio is greater than this the cell will not run in this direction, but it will in the reverse direction.

Concentration Cells

Because the cell potential depends on the concentrations of ions in the compartments, it is possible to construct a cell with the same ion, but different concentrations in each compartment. For example: $\text{Cu(s)} \mid \text{Cu}^{2+}(0.05 \text{ M}) \parallel \text{Cu}^{2+}(2.00 \text{ M}) \mid \text{Cu(s)}$

Here $E^\circ_{\text{cell}} = 0$ because $E^\circ_{\text{cathode}} = E^\circ_{\text{anode}}$ so:

$$E = \frac{-0.05916}{2} \log \frac{[\text{Cu}^{2+}]_{\text{dilute}}}{[\text{Cu}^{2+}]_{\text{concentrated}}} = 0.047 \text{ V}$$

Using Concentration Cells to Determine K_{sp}

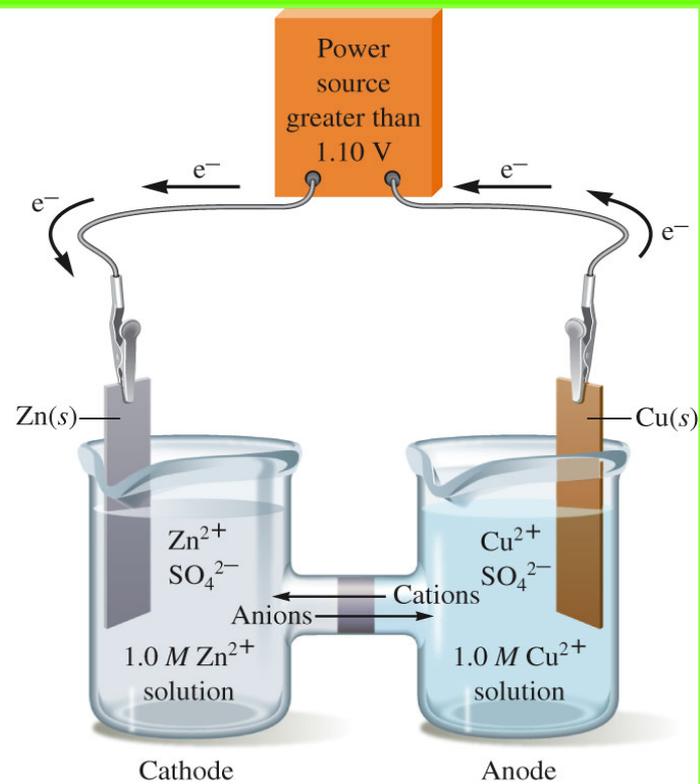
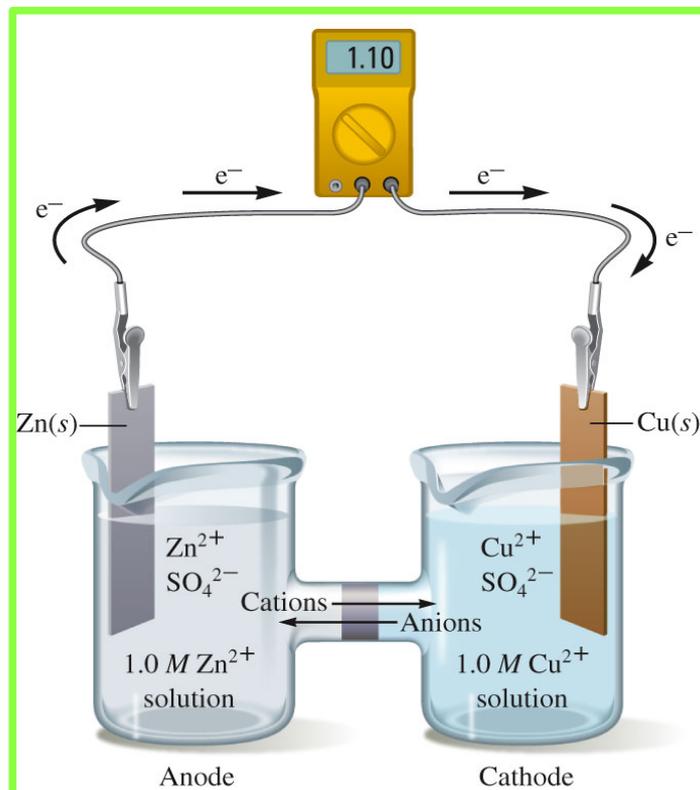
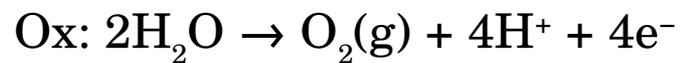
The following cell was used to determine the K_{sp} of CuCl:



The measured cell potential is 0.177 V. What is the $[\text{Cu}^+]$ in the CuCl compartment and the value of K_{sp} for CuCl?

$$\begin{aligned} E &= \frac{-0.05916}{1} \log \frac{[\text{Cu}^+]_{\text{dilute}}}{1.00 \text{ M}} = 0.177 \text{ V} \\ \Rightarrow [\text{Cu}^+] &= 0.00102 \text{ M} \\ \Rightarrow K_{sp} &= 1.04 \times 10^{-6} \end{aligned}$$

Electrolysis



Quantitative Applications of Electrolysis

An unknown metal, M, is electrolyzed. It took 74.1 seconds for a current of 2.00 A to plate out 0.107 g of the metal from a solution containing $M(\text{NO}_3)_3$. What is the metal?

Bi (209 g/mol)

