Chapter 18: Electrochemistry

In an oxidation-reduction (redox) reaction, ____________ are transferred.

$Mg + 2\ AgNO_3 \rightarrow Mg(NO_3)_2 + 2\ Ag$

Oxidation: ______ of electrons
Reduction: _______ of electrons

Oxidizing agent:
Reducing agent:

Oxidation numbers:

- Elements: # = 0
- Ions: # = charge
- O: usually −2
- H: usually +1
- Halogens: usually −1

Balancing redox reactions

Balance this net ionic equation (spectator ions omitted)

$Fe^{2+}(aq) + MnO_4^{-}(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

1. Divide net ionic equation into 2 half-reactions

2. Balance each half-reaction
    - Elements (not O or H)
    - O (add H_2O)
    - H (add H^+)
    - Charge (add e^-)

3. Multiply half-reactions by integers so # e^- is equal

4. Add two half-reactions and cancel electrons fully.

Balancing in basic solution

5. If you're told the reaction is in **basic** solution:

   a. Add OH^- to both sides to cancel H^+

   b. Combine $H^+ + OH^- \rightarrow H_2O$

   c. Cancel excess H_2O

Practice balancing

$MnO_4^- + SO_3^{2-} \rightarrow MnO_2 + SO_4^{2-}$ in acidic, and basic solns

Voltaic cells

Electrochemical cells involve the use of electrical energy in the transfer of electrons between substances

1. **Voltaic cells** (galvanic cells) contain a **spontaneous** reaction that produces electrical energy (like a battery)
2. **Electrolytic cells** use electrical energy to drive a **nonspontaneous** reaction

Most cells have two **electrodes** (conductive metal strips) in an **electrolyte** solution (soluble ionic compound)

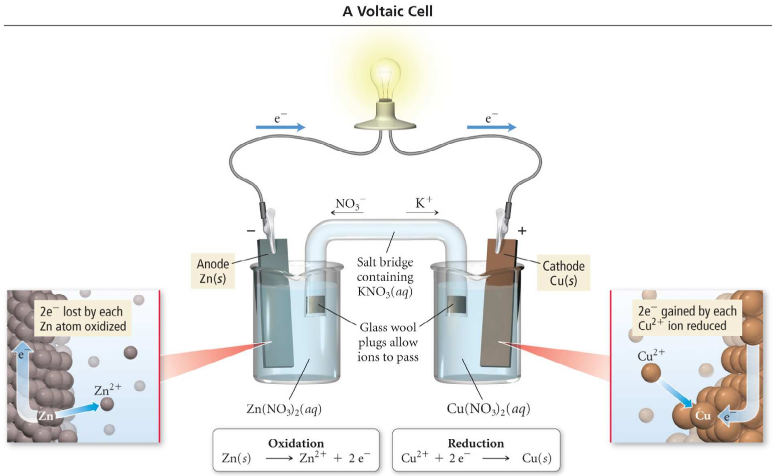
One **half-reaction** takes place at each electrode:

1. **Anode**: electrode where oxidation occurs (electrons are **lost** from the cell at the anode)
2. **Cathode**: electrode where reduction occurs (electrons **enter** the cell at the cathode)

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Oxidation half-reaction:
Reduction half-reaction:

Voltaic cells


A Voltaic Cell

The **anode** is the electrode of the oxidation half-rxn
The **cathode** is the electrode of the reduction half-rxn

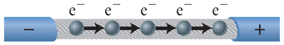
Salt bridge: completes circuit by keeping charges constant in each container

Active electrode: metal is part of redox reaction
Inactive electrode: metal conducts electricity but does not participate in redox reaction (graphite or Pt)

Cell notation: shows two half reactions with phases separated by | and half reactions separated by ||

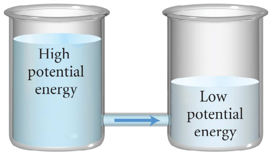
Reduction potentials

Electrical current: rate of electron flow (amperes, A) related to stoichiometry of redox reactions - not covered in this course



Electrical potential difference: the driving force for flow of electrons (volts, V)

- 1 V = 1 J/C (coulomb: unit of electrical charge)
- An energetic term, directly related to spontaneity and free energy
- **Cell potential** (E_{cell}): potential (in V) between two electrodes
- $E_{\text{cell}} > 0$ for a spontaneous process



Direction of spontaneous flow

Standard reduction potential ($E°$) potential for a reduction, relative to the standard hydrogen electrode

$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ $E°_{\text{red}} = 0.00$ V (by definition)

Reductions more spontaneous than this are **positive**, reductions less spontaneous than this are **negative**.

Standard reduction potentials

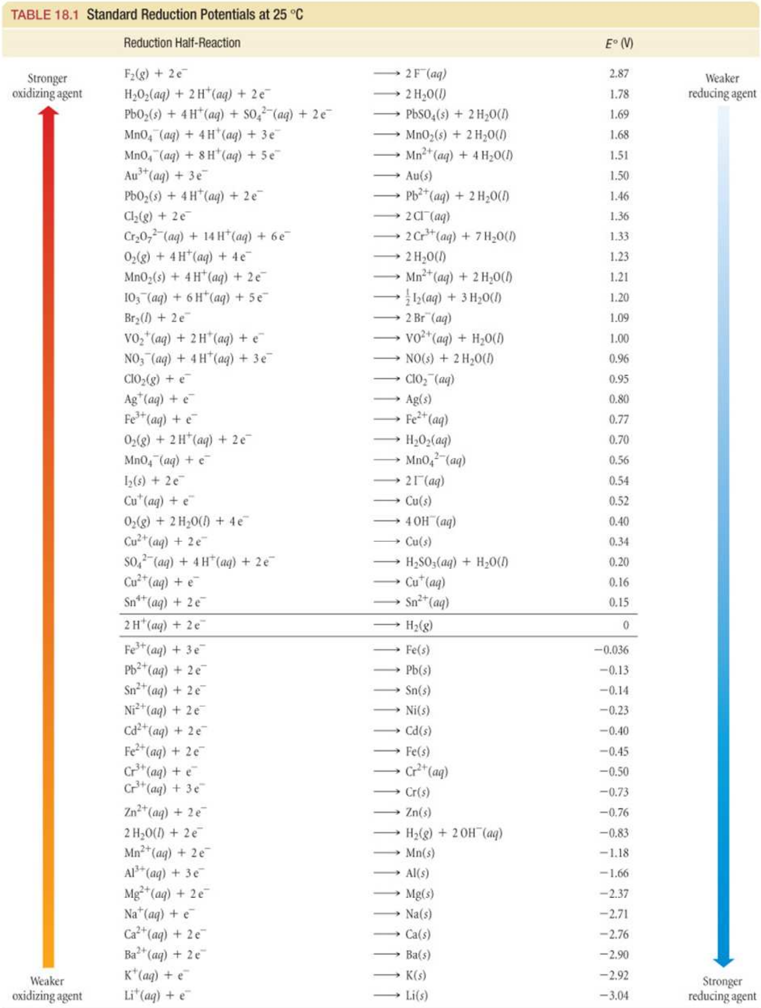


TABLE 18.1 Standard Reduction Potentials at 25 °C

Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$	$\longrightarrow PbSO_4(s) + 2H_2O(l)$	1.69
$MnO_4^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow MnO_2(s) + 2H_2O(l)$	1.68
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Au^{3+}(aq) + 3e^-$	$\longrightarrow Au(s)$	1.50
$PbO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	1.46
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.21
$IO_3^-(aq) + 6H^+(aq) + 5e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3H_2O(l)$	1.20
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$VO_2^+(aq) + 2H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\longrightarrow NO(s) + 2H_2O(l)$	0.96
$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20
$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Fe^{3+}(aq) + 3e^-$	$\longrightarrow Fe(s)$	−0.036
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^-$	$\longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.23
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50
$Cr^{3+}(aq) + 3e^-$	$\longrightarrow Cr(s)$	−0.73
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^-$	$\longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^-$	$\longrightarrow Ca(s)$	−2.76
$Ba^{2+}(aq) + 2e^-$	$\longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

Calculating standard cell potentials

For the zinc-copper cell,

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$ $E°$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E°$ ______________

$E°_{cell} =$

From the table of **reduction** potentials:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E°_{red} = 0.34$ V

$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$ $E°_{red} = -0.76$ V

Simply add the oxidation potential and the reduction potential. Don't forget to switch the sign of the oxidation.

Since cell potentials are **intensive** properties, you only need to add the values - they **do not** depend on number of electrons or any coefficients.

Write the balanced equation and calculate the standard cell potential ($E°_{cell}$) for $Cr(s)$ | $Cr^{3+}(aq)$ || $Cl_2(g)$ | $Cl^-(aq)$.

Predicting the direction of spontaneous change

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E°_{red} = 0.34$ V

$2\,H^+(aq) + 2\,e^- \rightarrow H_2(g)$ $E°_{red} = 0.00$ V

$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$ $E°_{red} = -0.76$ V

Which of the reactions above has the strongest tendency to occur in the forward direction as written?

That is the most favorable _____________ reaction.

So, _____ is the strongest ___________ agent.

The reaction with the **weakest** tendency to occur as written is the **most favorable** ____________ reaction.

So, _____ is the strongest ___________ agent.

What is the spontaneous reaction that will occur when a cell is constructed from $Cd(s)$, $Cd^{2+}(aq)$, $Pb(s)$, and $Pb^{2+}(aq)$

Cell potential, free energy, and the equilibrium constant

A spontaneous redox reaction has:

E_{cell}
ΔG_{rxn}
K

$$\boxed{\Delta G^\circ = -nFE^\circ_{\text{cell}}}$$

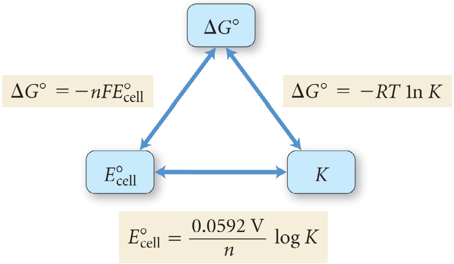
n = moles of electrons transferred in balanced eqn
F = 96,485 C / mol e^-

Calculate ΔG° (in kJ) for $2\,Ag^+ + Mg \rightarrow Mg^{2+} + 2\,Ag$.
Is the reaction spontaneous? What 2 ways can you tell?

Cell potential, free energy, and equilibrium constant

$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K$

$$\boxed{E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K = \frac{0.0592\text{ V}}{n}\log K}$$



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If E°_{cell} = 3.18 V and n = 2 mol e^-, what is K under standard conditions?

Nonstandard states in voltaic cells

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

Nernst equation: $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0592\ \text{V}}{n} \log Q$

The standard zinc-copper cell has a potential of 1.10 V.
Standard conditions are:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$

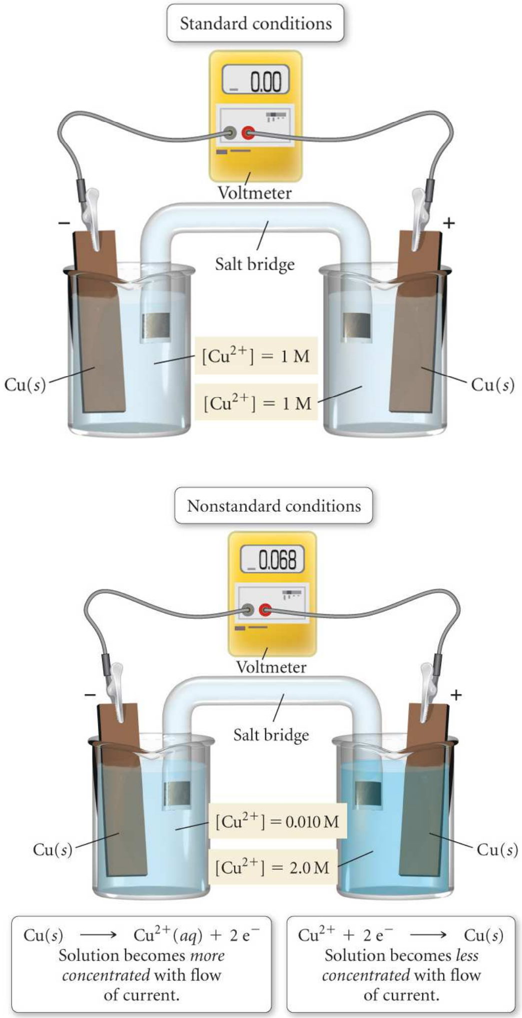
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

How will the cell potential change if we double the concentration of $Zn^{2+}(aq)$?

What if we double the concentration of $Cu^{2+}(aq)$?

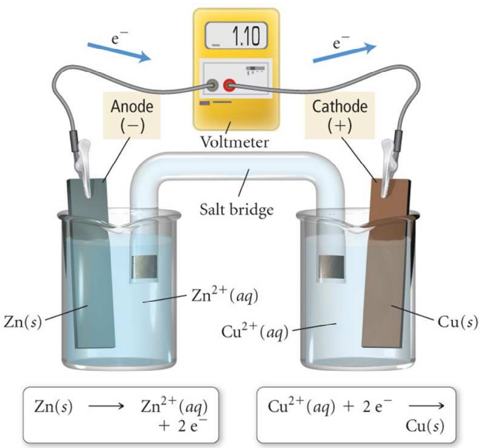
Concentration cells

A voltaic cell can be driven a difference in concentration between two otherwise identical half-cells.

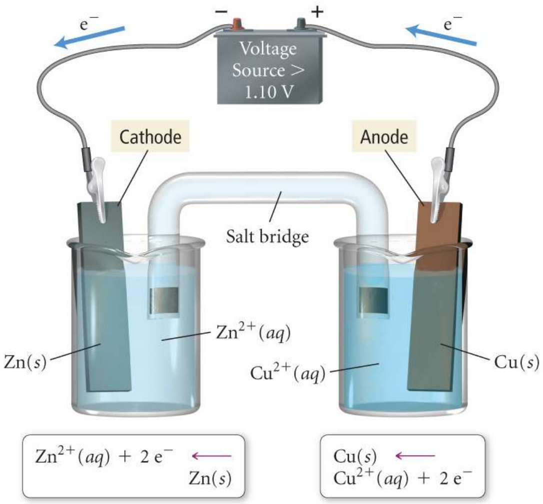


Voltaic vs electrolytic cells

Voltaic Cell



Electrolytic Cell



Electrolysis and electroplating