Chapter 19

Electrochemistry

Oxidation and Reduction (Redox)

- A reaction where electrons are transferred from one species to another.
  - OIL: Oxidation Is Loss (of electrons)
  - RIG: Reduction Is Gain (of electrons)
- You must be able to identify BOTH oxidation and reduction in a redox reaction. You can't have one without the other.

Oxidation Numbers

- A made up value that helps you keep track of how many electrons a particular atom "has" in the molecule.

- Gives us a way to watch how the electrons move in a Redox reaction.

Rules for Assigning Oxidation States

- Rules are in order of priority

1. free elements have an oxidation state = 0
   - Na = 0 and Cl_2 = 0 in 2 Na(s) + Cl_2(g)

2. monatomic ions have an oxidation state equal to their charge
   - Na = +1 and Cl = −1 in NaCl

3. (a) the sum of the oxidation states of all the atoms in a compound is 0
   - Na = +1 and Cl = −1 in NaCl, (+1) + (−1) = 0

Rules for Assigning Oxidation States

3. (b) the sum of the oxidation states of all the atoms in a polyatomic ion equals the charge on the ion

    - N = +5 and O = −2 in NO_3^-, (+5) + 3(−2) = −1

4. (a) Alkali metals have an oxidation state of +1 in all their compounds

    - Na = +1 in NaCl

4. (b) Alkaline Earth metals have an oxidation state of +2 in all their compounds

    - Mg = +2 in $MgCl_2$

Rules for Assigning Oxidation States

5. in their compounds, nonmetals have oxidation states according to the table below

    - nonmetals higher on the table take priority

Nonmetal	Oxidation State	Example
F	−1	CF_4
H	+1	CH_4
O	−2	CO_2
Group 7A	−1	CCl_4
Group 6A	−2	CS_2
Group 5A	−3	NH_3

Example: Determine the oxidation states of all the atoms in a propanoate ion, $C_3H_5O_2^-$

- There are no free elements or free ions in propanoate, so the first rule that applies is Rule 3b

$$(C_3) + (H_5) + (O_2) = -1$$

- Because all the atoms are nonmetals, the next rule we use is Rule 5, following the elements in order:
  - $H = +1$
  - $O = -2$

$$(C_3) + 5(+1) + 2(-2) = -1$$
$$(C_3) = -2$$
$$C = -\frac{2}{3}$$

Note: unlike charges, oxidation states can be fractions!

# Practice – Assign an oxidation state to each element in the following

- Br_2 Br = 0, (Rule 1)

- K^+ K = +1, (Rule 2)

- LiF   Li = +1, (Rule 4a) & F = −1, (Rule 5)

- CO_2 O = −2, (Rule 5) & C = +4, (Rule 3a)

- SO_4^{2-} O = −2, (Rule 5) & S = +6, (Rule 3b)

- Na_2O_2 Na = +1, (Rule 4a) & O = −1 , (Rule 3a)

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Oxidation and Reduction
Another Definition

- Oxidation occurs when an atom's oxidation state increases during a reaction. (Oxidation is LOSS of Electrons)

- Reduction occurs when an atom's oxidation state decreases during a reaction. (Reduction is GAIN of Electrons)

$$CH_4 \ + \ 2\,O_2 \rightarrow \ CO_2 + 2\,H_2O$$

-4 $+1$ $\qquad$ 0 $\qquad$ $+4$ -2 $\qquad$ $+1$ -2
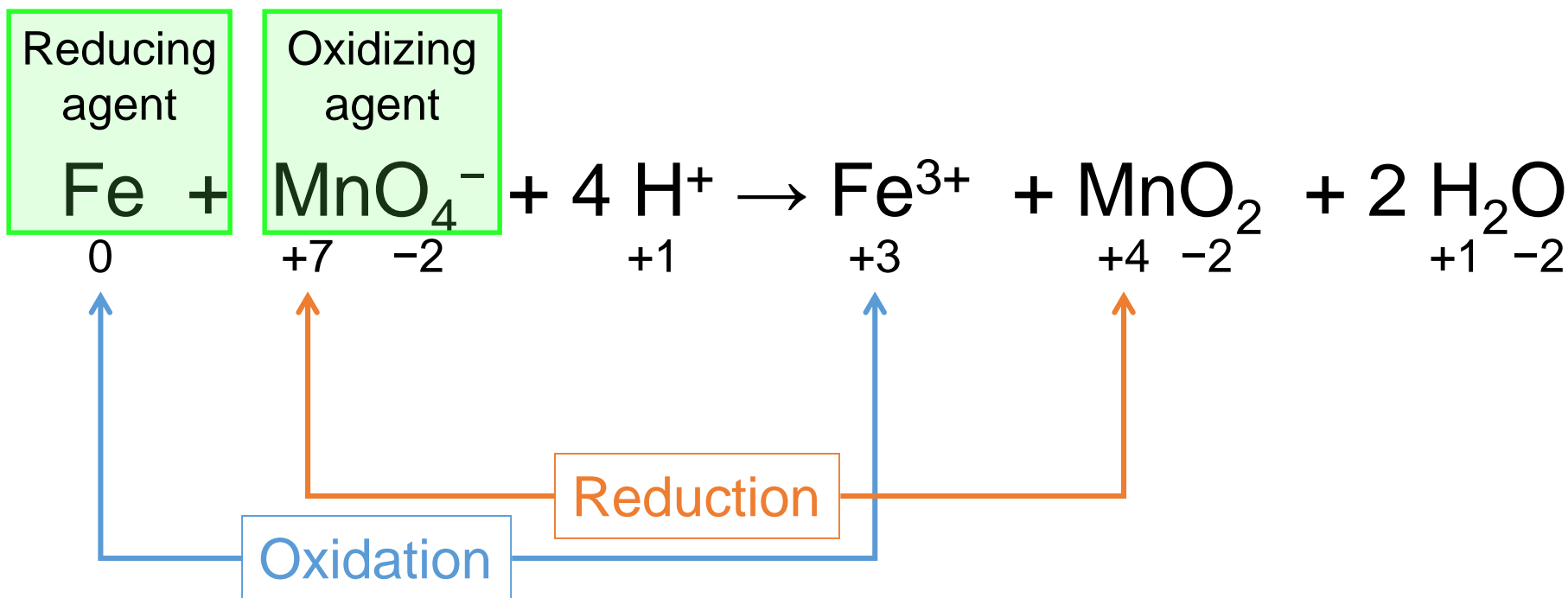
oxidation

reduction
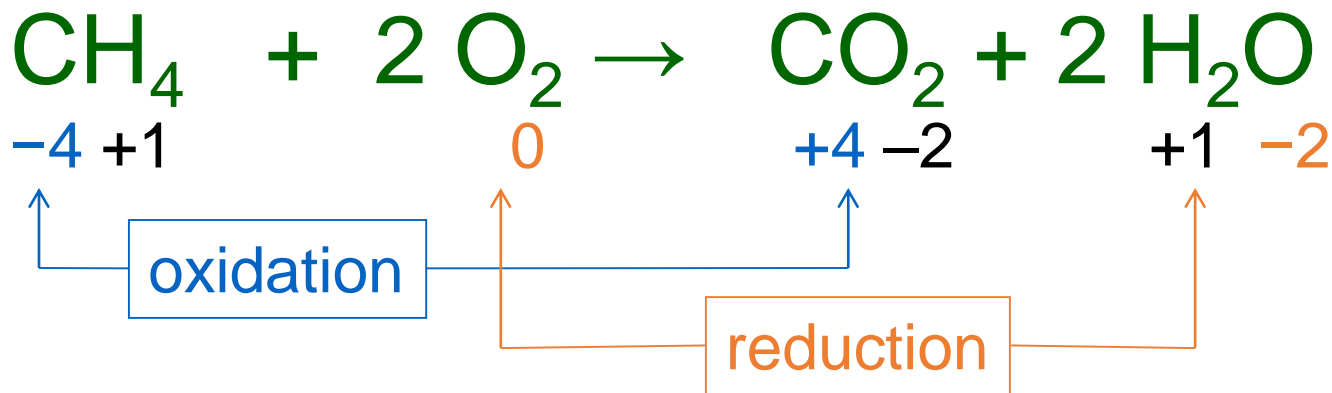
Agents:

- The reactant that reduces an element in another reactant is called the **reducing agent**
  - the reducing agent contains the element that is oxidized
- The reactant that oxidizes an element in another reactant is called the **oxidizing agent**
  - the oxidizing agent contains the element that is reduced

$$CH_4 \;+\; 2\,O_2 \rightarrow \; CO_2 + 2\,H_2O$$

−4 +1   0   +4 −2   +1 −2

oxidation
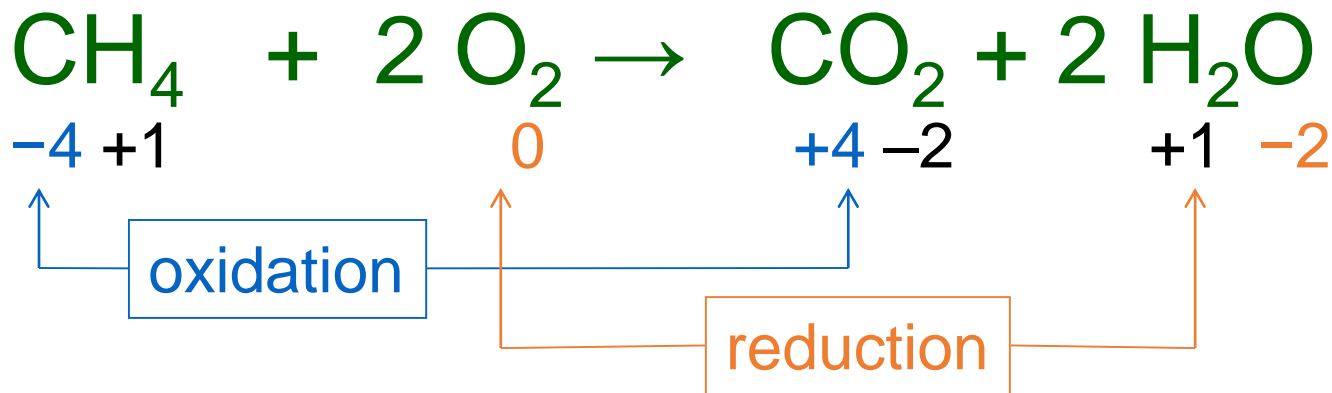
reduction

Example: Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reactions:

Reducing agent	Oxidizing agent
Fe	MnO_4^-

$$\text{Fe} + MnO_4^- + 4\ H^+ \rightarrow Fe^{3+} + MnO_2 + 2\ H_2O$$

0   +7 −2   +1   +3   +4 −2   +1 −2
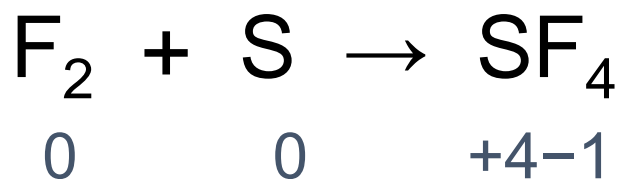
Reduction

Oxidation

Practice – Assign oxidation states, determine the element oxidized and reduced, and determine the oxidizing agent and reducing agent in the following reactions:

$$Sn^{4+} + Ca \rightarrow Sn^{2+} + Ca^{2+}$$

+4   0   +2   +2
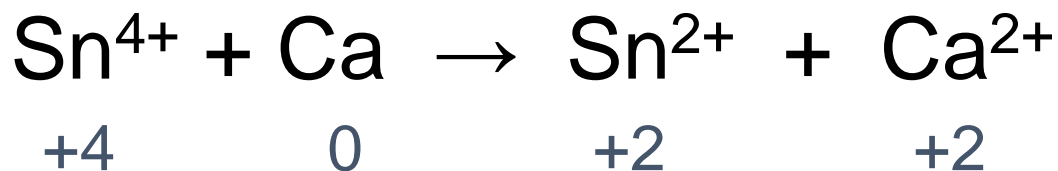
Ca is oxidized, Sn^{4+} is reduced

Ca is the reducing agent, Sn^{4+} is the oxidizing agent

$$F_2 + S \rightarrow SF_4$$

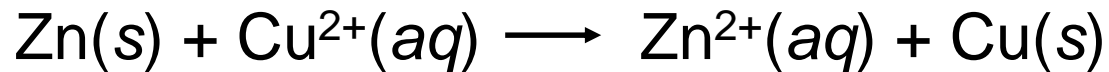0   0   +4 −1

S is oxidized, F is reduced

S is the reducing agent, F_2 is the oxidizing agent
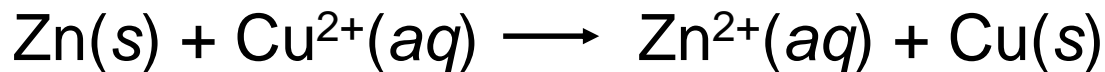
Galvanic vs Electrolytic Cells

- **Exploiting a redox reaction to convert chemical energy to electrical energy. You basically separate the reduction and oxidation so that the electrons must flow through a wire for the process to occur.**

  - **Galvanic (Voltaic) Cell**: A *spontaneous* chemical reaction which generates an electric current.

  - **Electrolytic Cell**: An electric current which drives a *nonspontaneous* reaction.

A galvanic cell IS a battery, and an electrolytic cell NEEDS a battery
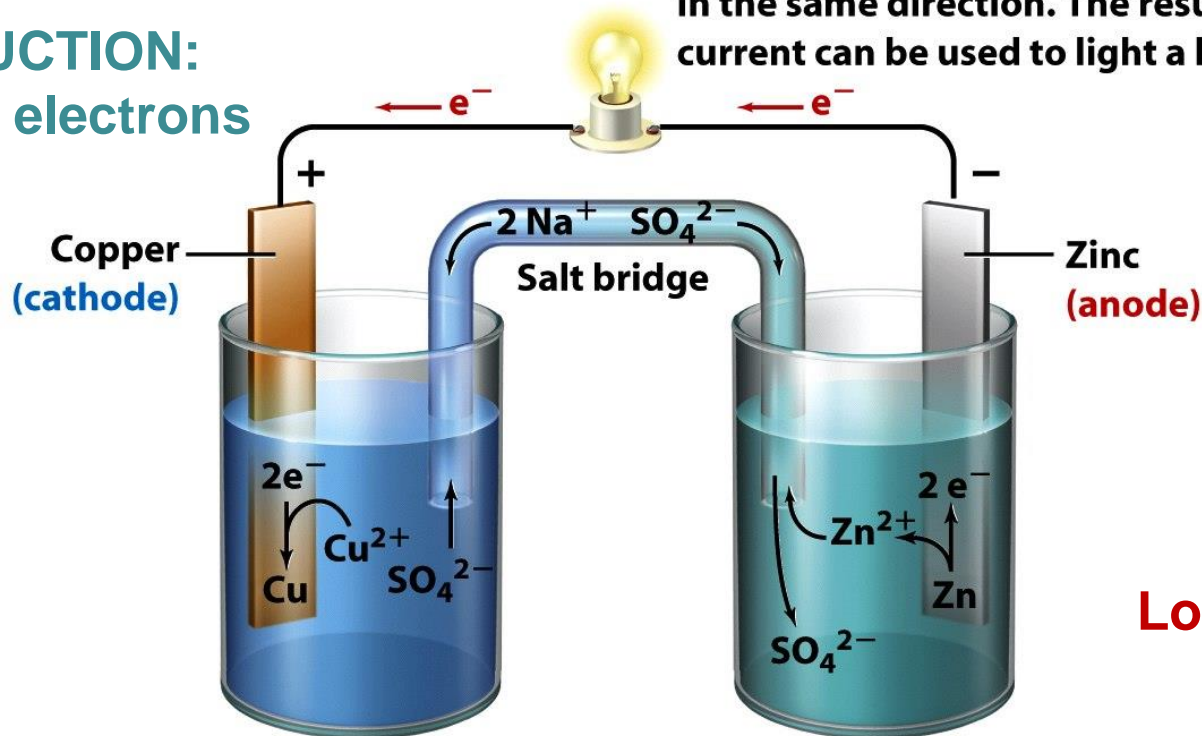
Galvanic Cells

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

Oxidation half-reaction: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$

Reduction half-reaction: $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

Galvanic Cells

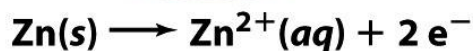$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The negative particles (electrons in the wire and anions in solution) travel around the circuit in the same direction. The resulting electric current can be used to light a lightbulb.

REDUCTION:
Gain of electrons

Copper (cathode)

2 Na$^+$ SO$_4{}^{2-}$
Salt bridge

Zinc (anode)

+   −

← e$^-$ ← e$^-$

FAT CAT:
From Anode
To CAThode

2e$^-$
Cu^{2+}
SO$_4{}^{2-}$
Cu

2 e$^-$
Zn^{2+}
Zn
SO$_4{}^{2-}$

OXIDATION:
Loss of electrons

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \qquad Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

Galvanic Cells

- **Anode**:
  - The electrode where oxidation occurs.
  - The electrode where electrons are produced.
  - Is what anions migrate toward.
  - Has a negative sign.

e^-

$SO_4^{2-} \longrightarrow Zn^{2+}$ — Zinc (anode)

$SO_4^{2-} \longrightarrow Zn^{2+}$

$SO_4^{2-} \longrightarrow Zn^{2+}$

Figure 17-3 Chemistry, 5/e
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Galvanic Cells

- **Anode**:
    - The electrode where oxidation occurs.
    - The electrode where electrons are produced.
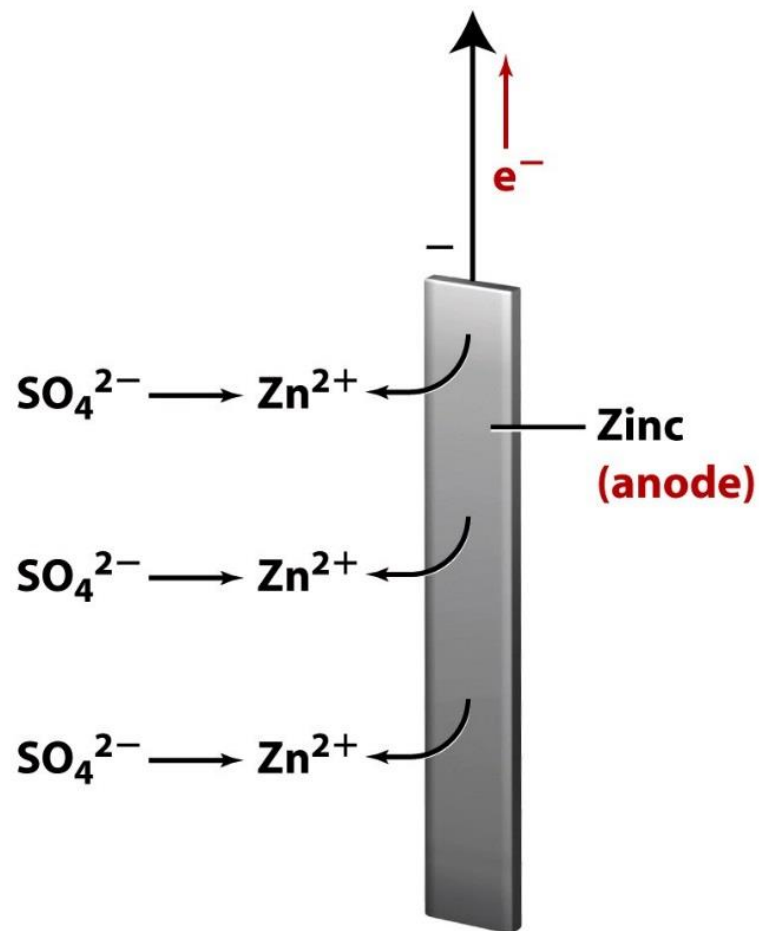   - Is what anions migrate toward.
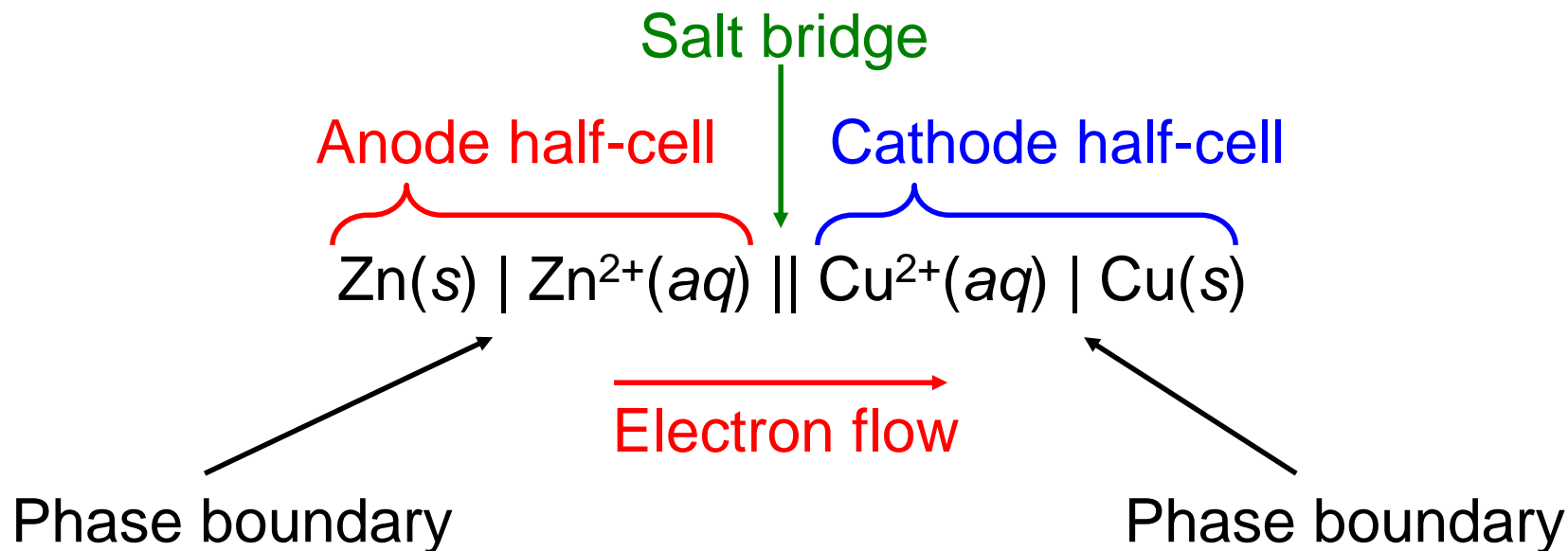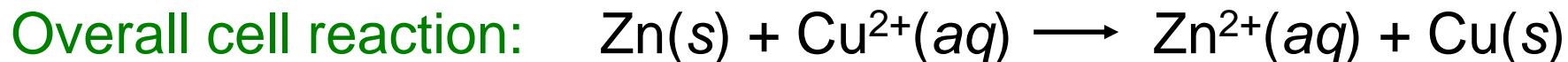   - Has a negative sign.

- **Cathode**:
    - The electrode where reduction occurs.
    - The electrode where electrons are consumed.
    - Is what cations migrate toward.
    - Has a positive sign.

Shorthand Notation for Galvanic Cells

Anode half-reaction: $\qquad\qquad$ $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode half-reaction: $\qquad$ $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $\qquad$ $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Salt bridge

Anode half-cell $\qquad$ Cathode half-cell

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

Electron flow

Phase boundary $\qquad\qquad\qquad\qquad$ Phase boundary
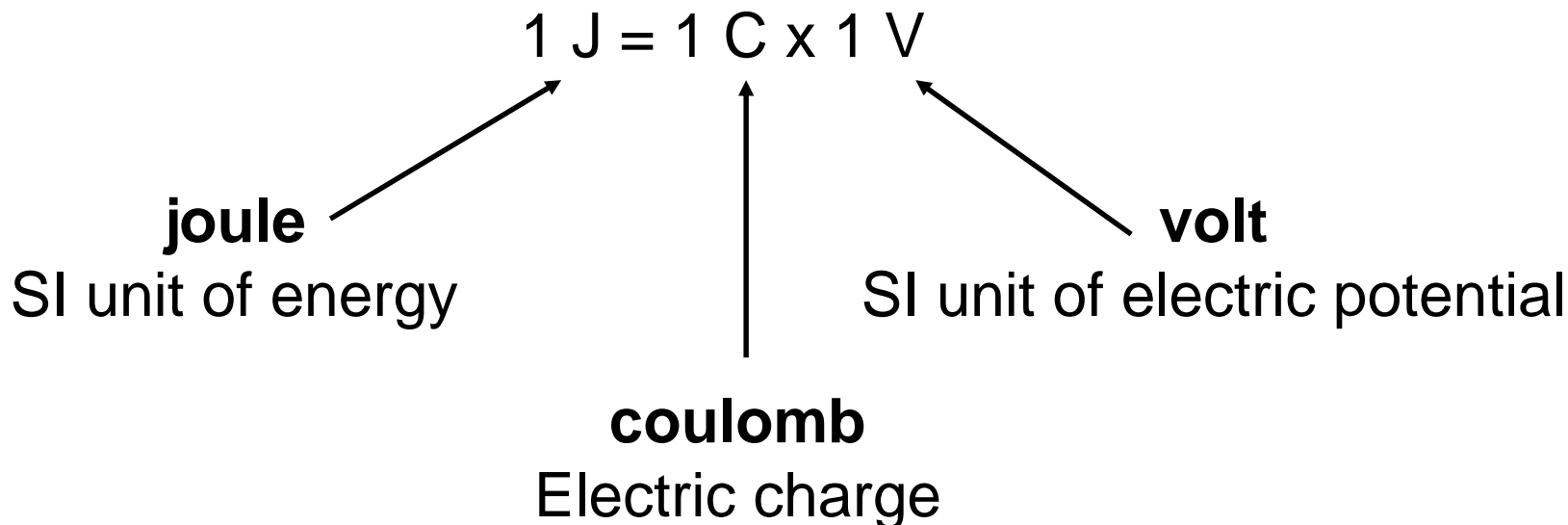
Cell Potentials and Free-Energy Changes for Cell Reactions

Electromotive Force (emf): The force or electrical potential that pushes the negatively charged electrons away from the anode (- electrode) and pulls them toward the cathode (+ electrode).

It is also called the **cell potential (E_{cell}).**

Cell Potentials and Free-Energy Changes for Cell Reactions

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

joule
SI unit of energy

volt
SI unit of electric potential

coulomb
Electric charge

1 coulomb is the amount of charge transferred
when a current of 1 ampere flows for 1 second.

WATERFALL!!

Cell Potentials and Free-Energy Changes for Cell Reactions

faraday or **Faraday constant**
the electric charge on 1 mol of electrons
96,5000 C/mol e⁻

$$\Delta G = -nFE \quad \text{or} \quad \Delta G° = -nFE°$$

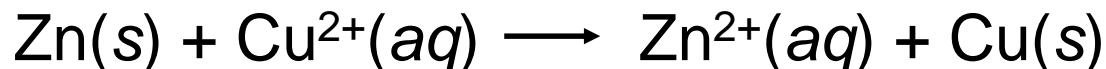**free-energy change**

cell potential

number of moles of electrons
transferred in the reaction

Cell Potentials and Free-Energy Changes for Cell Reactions

The standard cell potential at 25 °C is 0.10 V for the reaction:

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

Calculate the standard free-energy change for this reaction at 25 °C.

$\Delta G° = -nFE°$

$$= -(2 \text{ mol e}^-)\left(\frac{96,500 \text{ C}}{\text{mol e}^-}\right)(1.10 \text{ V})\left(\frac{1 \text{ J}}{1 \text{ C V}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$\Delta G° = \boxed{-212 \text{ kJ}}$

Standard Reduction Potentials

The **standard hydrogen electrode (S.H.E.)** has been chosen to be the reference electrode.
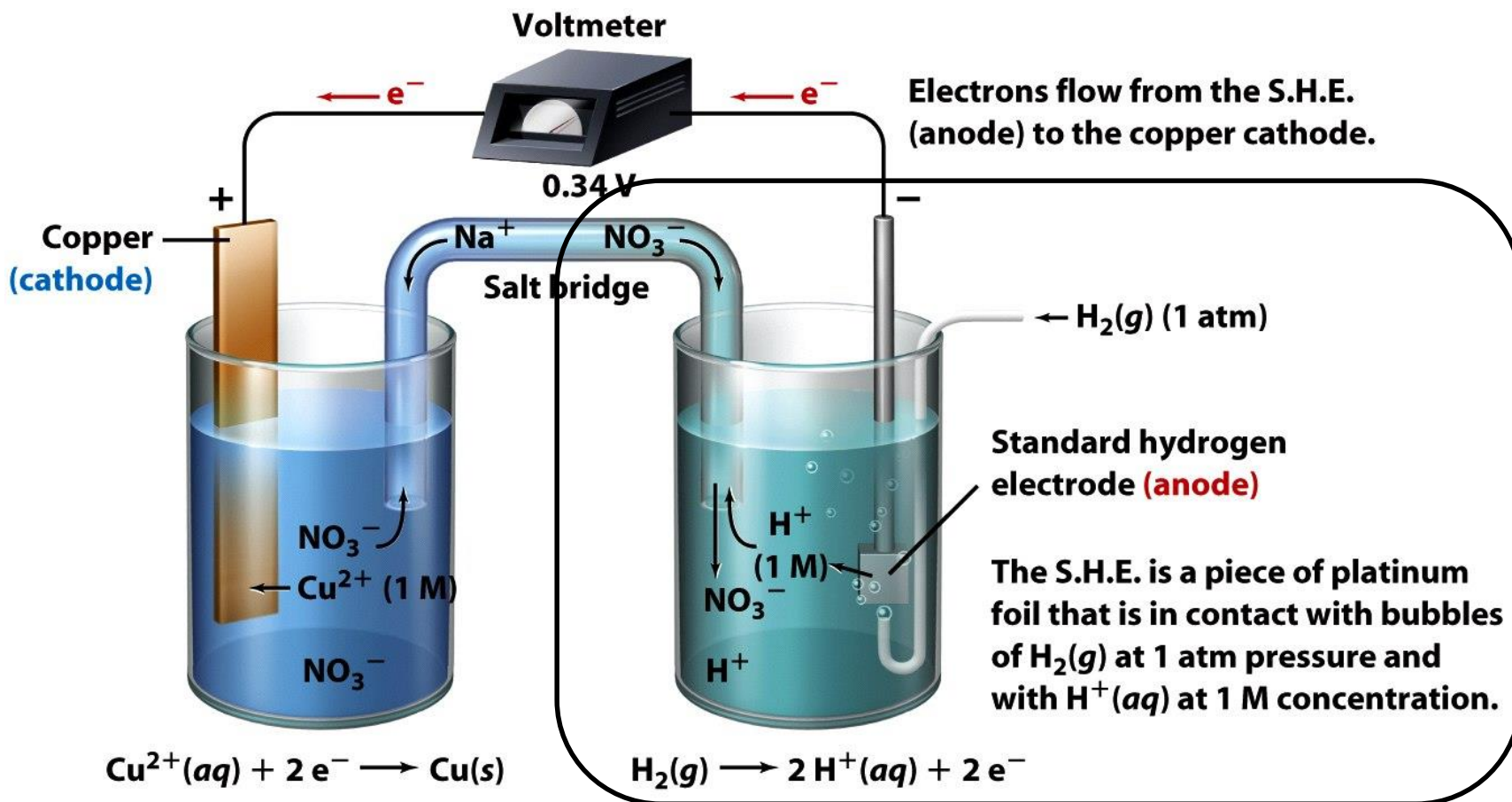

Voltmeter

$\longleftarrow$ e$^-$ $\longleftarrow$ e$^-$

Electrons flow from the S.H.E. (anode) to the copper cathode.

0.34 V

+   −

Copper (cathode)   Na$^+$ NO$_3$$^-$ $\leftarrow$ H$_2$(g) (1 atm)

Salt bridge

Standard hydrogen electrode (anode)

NO$_3$$^-$
$\leftarrow$ Cu^{2+} (1 M)

H$^+$ (1 M)$\leftarrow$
NO$_3$$^-$

The S.H.E. is a piece of platinum foil that is in contact with bubbles of H$_2$(g) at 1 atm pressure and with H$^+$(aq) at 1 M concentration.

NO$_3$$^-$ H$^+$

Cu^{2+}(aq) + 2 e$^-$ $\longrightarrow$ Cu(s)   H$_2$(g) $\longrightarrow$ 2 H$^+$(aq) + 2 e$^-$

Standard Reduction Potentials

Anode half-reaction: $H_2(g) \longrightarrow 2H^{1+}(aq) + 2e^-$

Cathode half-reaction: $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Overall cell reaction: $H_2(g) + Cu^{2+}(aq) \longrightarrow 2H^{1+}(aq) + Cu(s)$
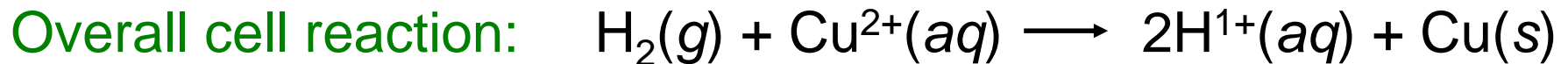
$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

$$0.34 \text{ V} = 0 \text{ V} + E^\circ_{red}$$

A standard reduction potential can be defined:

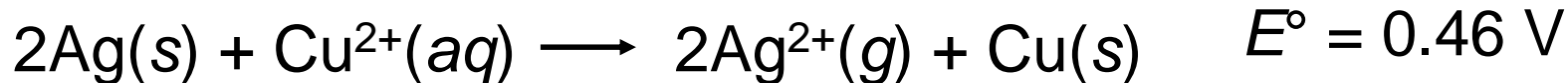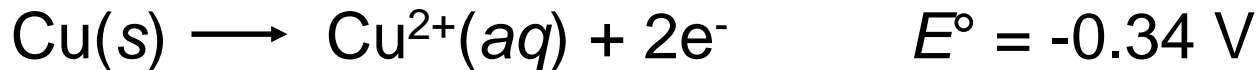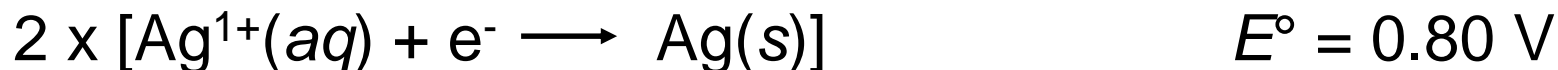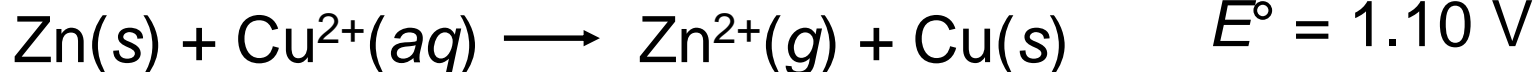$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad \textbf{\textit{E}°\, = 0.34 V}$$

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
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	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
$Br_2(aq) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	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
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	- 0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	- 0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	- 0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	- 0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	- 0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	- 0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	- 1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	- 2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	- 2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	- 3.04

Stronger oxidizing agent (up arrow, left)

Weaker oxidizing agent (bottom left)

Weaker reducing agent (top right)

Stronger reducing agent (down arrow, bottom right)

Table 17-1 Chemistry, 5/e

Using Standard Reduction Potentials

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$ $\qquad E° = -(-0.76 \text{ V})$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$ $\qquad E° = 0.34 \text{ V}$

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(g) + Cu(s)$$ $\qquad E° = 1.10 \text{ V}$

$$2 \times [Ag^{1+}(aq) + e^- \longrightarrow Ag(s)]$$ $\qquad E° = 0.80 \text{ V}$

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$ $\qquad E° = -0.34 \text{ V}$

$$2Ag(s) + Cu^{2+}(aq) \longrightarrow 2Ag^{2+}(g) + Cu(s)$$ $\qquad E° = 0.46 \text{ V}$
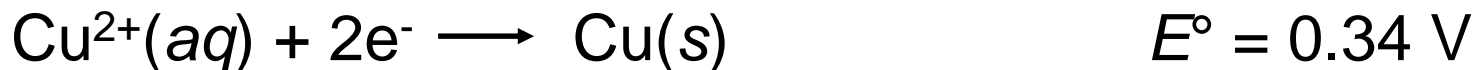
Half-cell potentials are **intensive** properties.

The Nernst Equation

$$\Delta G = \Delta G° + RT \ln Q$$

Using: $\Delta G = -nFE$ and $\Delta G° = -nFE°$

Nernst Equation: $E = E° - \dfrac{RT}{nF} \ln Q$

or

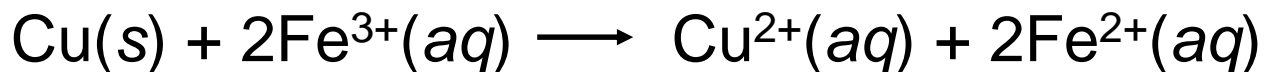$$E = E° - \dfrac{2.303RT}{n\boldsymbol{F}} \log Q$$

or

$$\boxed{E = E° - \dfrac{0.0592 \text{ V}}{n} \log Q} \quad \text{in volts, at 25°C}$$

The Nernst Equation

Consider a galvanic cell that uses the reaction:
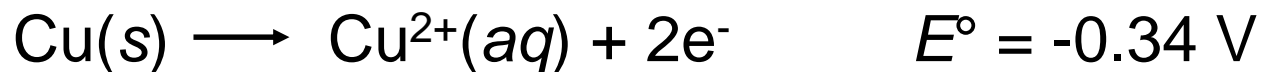
$$Cu(s) + 2Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$$

What is the potential of a cell at 25 °C that has the following ion concentrations?

$[Fe^{3+}] = 1.0 \times 10^{-4}$ M $[Cu^{2+}] = 0.25$ M $[Fe^{2+}] = 0.20$ M

The Nernst Equation

$$E = E° - \frac{0.0592 \text{ V}}{n} \log Q$$

Calculate $E°$:

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad E° = -0.34 \text{ V}$$

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \qquad E° = 0.77 \text{ V}$$

$$E°_{cell} = -0.34 \text{ V} + 0.77 \text{ V} = 0.43 \text{ V}$$

The Nernst Equation

$$E = E° - \frac{0.0592 \text{ V}}{n} \log Q$$

Calculate E:

$$E = E° - \left(\frac{0.0592 \text{ V}}{n}\right) \log \frac{[Cu^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$$

$$= 0.43 \text{ V} - \left(\frac{0.0592 \text{ V}}{2}\right) \log \left(\frac{(0.25)(0.20)^2}{(1.0 \times 10^{-4})^2}\right)$$

$$E = \boxed{0.25 \text{ V}}$$

Standard Cell Potentials and Equilibrium Constants
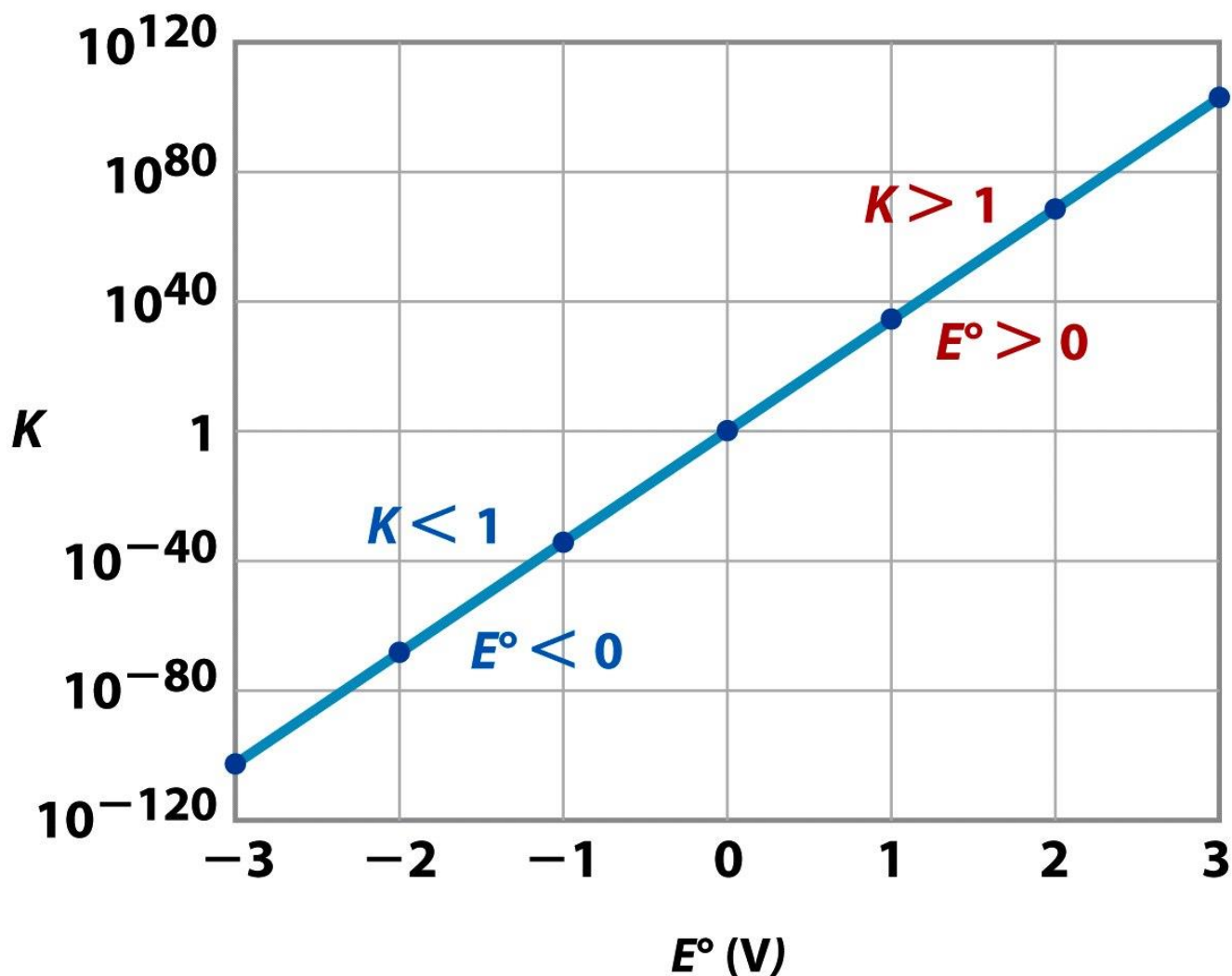
Using $\Delta G° = -nFE°$ and $\Delta G° = -RT \ln K$

$$-nFE° = -RT \ln K$$

$$E° = \frac{RT}{nF} \ln K = \frac{2.303 \, RT}{nF} \log K$$

$$E° = \frac{0.0592 \text{ V}}{n} \log K \qquad \text{in volts, at 25°C}$$

Standard Cell Potentials and Equilibrium Constants

Figure 17-7 Chemistry, 5/e
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Standard Cell Potentials and Equilibrium Constants

Three methods to determine equilibrium constants:

1. K from concentration data: $\quad K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

2. K from thermochemical data: $\quad \ln K = \dfrac{-\Delta G^\circ}{RT}$

3. K from electrochemical data: $\quad E^\circ = \dfrac{RT}{nF} \ln K$

   or

   $\ln K = \dfrac{nFE^\circ}{RT}$

Electrolysis and Electrolytic Cells

Electrolysis: The process of using an electric current to bring about chemical change.

TABLE 17.2 Relationship between Cell Potentials E and Free-Energy Changes ΔG

Reaction Type	E	ΔG	Cell Type
Spontaneous	+	−	Galvanic
Nonspontaneous	−	+	Electrolytic
Equilibrium	0	0	Dead battery

Table 17-2 Chemistry, 5/e
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Electrolysis and Electrolytic Cells

Electrolysis of Molten Sodium Chloride

Anode: $$2Cl^{1-}(l) \longrightarrow Cl_2(g) + 2e^-$$

Cathode: $$2Na^{1+}(l) + 2e^- \longrightarrow 2Na(l)$$

Overall: $$2Na^{1+}(l) + 2Cl^{1-}(l) \longrightarrow 2Na(l) + Cl_2(g)$$

The battery pulls electrons from the anode and pushes them into the cathode.

Anode   Battery   Cathode

Inert electrodes

$\leftarrow Cl^-$ $Na^+ \rightarrow$

$2\,Cl^-(l) \longrightarrow Cl_2(g) + 2\,e^-$ $2\,Na^+(l) + 2\,e^- \longrightarrow 2\,Na(l)$