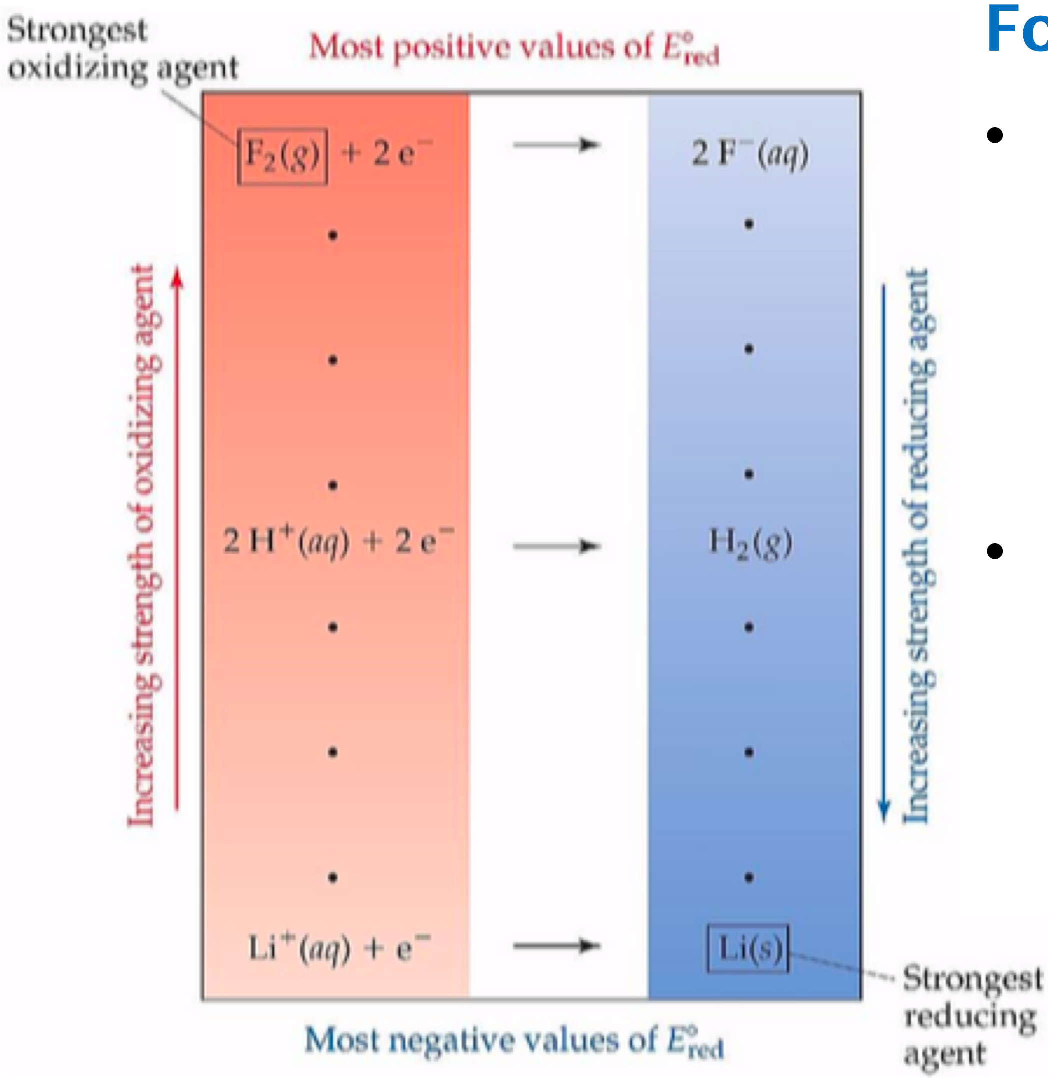
Cell Potential & Redox



For a reduction half-rxn:

- The more positive the value of E°, the easier it is to reduce the reactant – the reactant is a stronger oxidizing agent
- The more negative the value of E°, the easier it is to oxidize the reactant – the reactant is a stronger reducing agent

Cell Potential & Redox

1.) Which of the following pairs of substances is the stronger reducing agent?

A: (a) Mg(s)
(b) Cr(s)

(a) Fe(s) or Mg(s)

(b) Cr(s) or Co(s)

Thermodynamics of Redox Reactions

We have already seen the connection between cell potential and spontaneity:

$$E^\circ = E_{cathode} - E_{anode}$$

$$E^\circ = E_{red} - E_{ox}$$

$E > 0$ = spontaneous **$E < 0$ = nonspontaneous**

There must also be a relationship between Gibbs Free Energy and cell potential. Since the movement of electrons allows work to be done by the cell, ΔG for a redox reaction can be found from the equation:

$$\Delta G = -nFE$$

n = number of moles of electrons transferred
F = Faraday's constant (amount of electrical charge on 1 mole of electrons; 1F = 96,485C/mol = 96,485J/V-mol)
E = cell potential

Since n & F are positive, if $E > 0$, then $\Delta G < 0$ – spontaneous!

Thermodynamics of Redox Reactions

Since $\Delta G^\circ = -RT\ln K$, and under standard conditions $\Delta G^\circ = -nFE^\circ$, then

$$-RT\ln K = -nFE^\circ$$

$$E^\circ = (RT/nF)\ln K$$

For a Redox Reaction, Free Energy, Cell Potential, and the Equilibrium constant are all related!

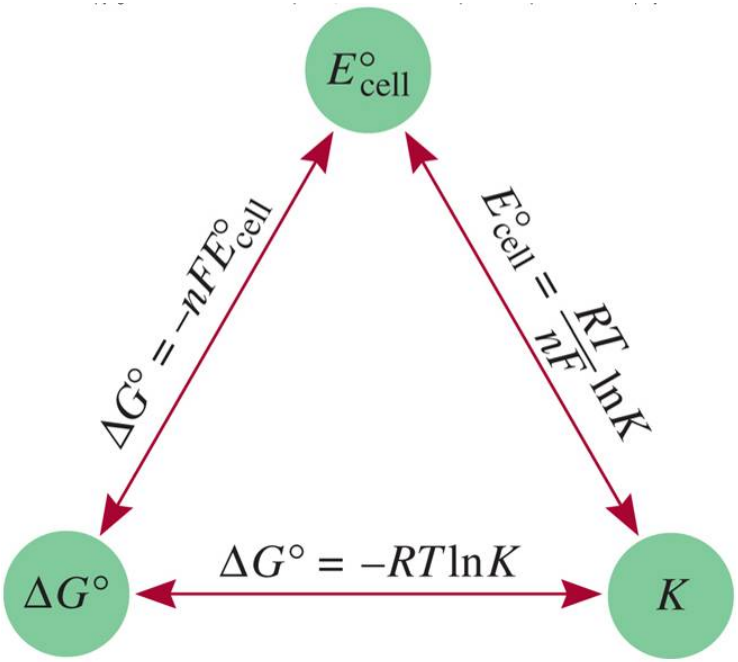


Table 19.2 Relationships Among ΔG°, K, and E°_{cell}

ΔG°	K	E°_{cell}	Reaction Under Standard-State Conditions
Negative	>1	Positive	Favors formation of products.
0	= 1	0	Reactants and products are equally favored.
Positive	<1	Negative	Favors formation of reactants.

Thermodynamics of Redox Reactions

1. What is the equilibrium constant at 25˚C for the reaction:

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

A: 6.4×10^{9}

Thermodynamics of Redox Reactions

2.) If the equilibrium constant for a two electron redox reaction at 298K is 1.5×10^{-4}, calculate the corresponding ΔG° and E°_{red}.

A: 2.2×10^{4} J/mol;-0.11V

Cell Potentials at Nonstandard Conditions: The Nernst Equation

Free Energy at nonstandard conditions:

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

Since $\Delta G = -nFE$, $\Delta G^\circ = -nFE^\circ$

Therefore:

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

Dividing by −nF gives the Nernst equation:

$$E = E^\circ_{cell} - (RT/nF)\ln Q$$

The Nernst can be used to evaluate the cell potential of systems that are not at 25˚C and/or do not contain 1M solutions

The Nernst Equation

1. A voltaic cell utilizes the following reaction:

$2Al(s) + 3I_2(s) \rightarrow 2Al^{3+}(aq) + 6I^{-}(aq)$

(a) What is the E_{cell} under standard conditions?

(b) What is the E_{cell} when $[Al^{3+}] = 4.0 \times 10^{-3}M$ & $[I^{-}] = 0.010M$ (still at 298K)

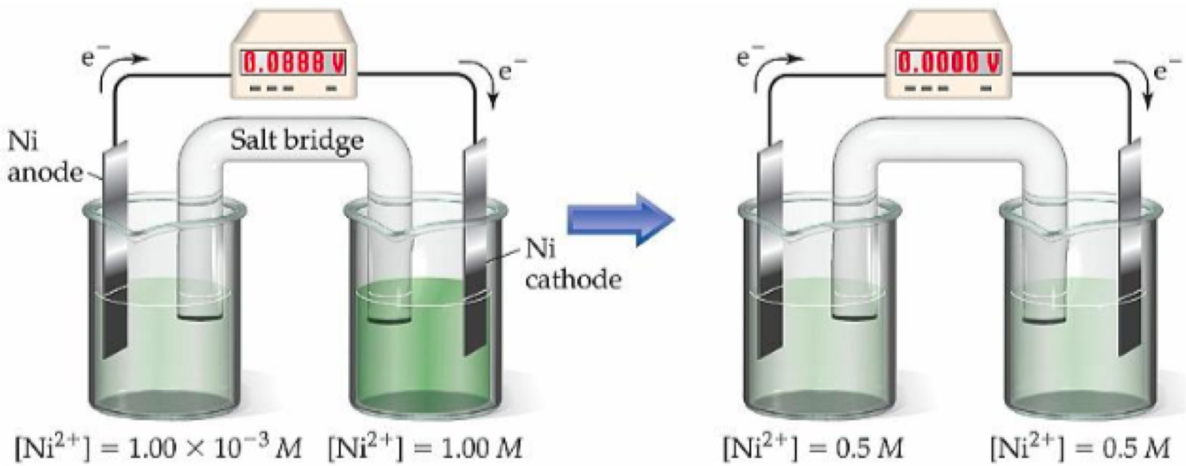
A:2.19V; 2.36V

Concentration Cells

Cells where the cell potential is generated entirely by a difference in concentration at the two electrodes (the ions present at the cathode and anode are the same)

Different Concentration:
Voltage
0.0888V

Same Concentration:
No voltage
(0.0000V)



$$\mathrm{Ni}(s)\,|\,\mathrm{Ni^{2+}}(0.001\ \mathrm{M})\,\|\,\mathrm{Ni^{2+}}(1.00\ \mathrm{M})\,|\,\mathrm{Ni}(s)$$

Anode: $\cancel{\mathrm{Ni}(s)} \rightarrow \mathrm{Ni^{2+}}(1.00 \times 10^{-3}\ \mathrm{M}) + \cancel{2e^-}$

Cathode: $\mathrm{Ni^{2+}}(1.00\ \mathrm{M}) + \cancel{2e^-} \rightarrow \cancel{\mathrm{Ni}(s)}$

$$\mathrm{Ni^{2+}}(1.00\ \mathrm{M}) \rightarrow \mathrm{Ni^{2+}}\ (1.00 \times 10^{-3}\ \mathrm{M})$$

Concentration Cells

How are concentration cells possible?

For the voltage producing cell in the previous slide, the two concentrations of Ni^{2+} were 1.00M and 1.00×10^{-3}M.

Diffusion occurs naturally from high concentration to low concentration, so the process ("reaction") is:

$$Ni^{2+}(1.00M) \rightarrow Ni^{2+}(1.00 \times 10^{-3}M)$$

Using the Nernst equation:

$$E = E^{\circ} - \frac{(8.314 J/molK)(298K)}{(2)(96{,}485 J/V\text{-}mol)} \ln \frac{[1.00 \times 10^{-3}]}{[1.00]}$$

$$E = 0V - [0.01284V \times (-6.908)] = 0.0887V$$

The voltage generated in this manner has physiological importance in systems such as the potassium ion system that controls nerve impulses.

Concentration Cells

1. A concentration cell is constructed at 298K with two $Zn(s)$-$Zn^{2+}(aq)$ half cells. One half-cell has a Zn^{2+} concentration of 1.35M, and the other has a Zn^{2+} concentration of 3.75×10^{-4}M. What is the cell potential?