Key Concepts

How FAR does a reaction proceed?

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$
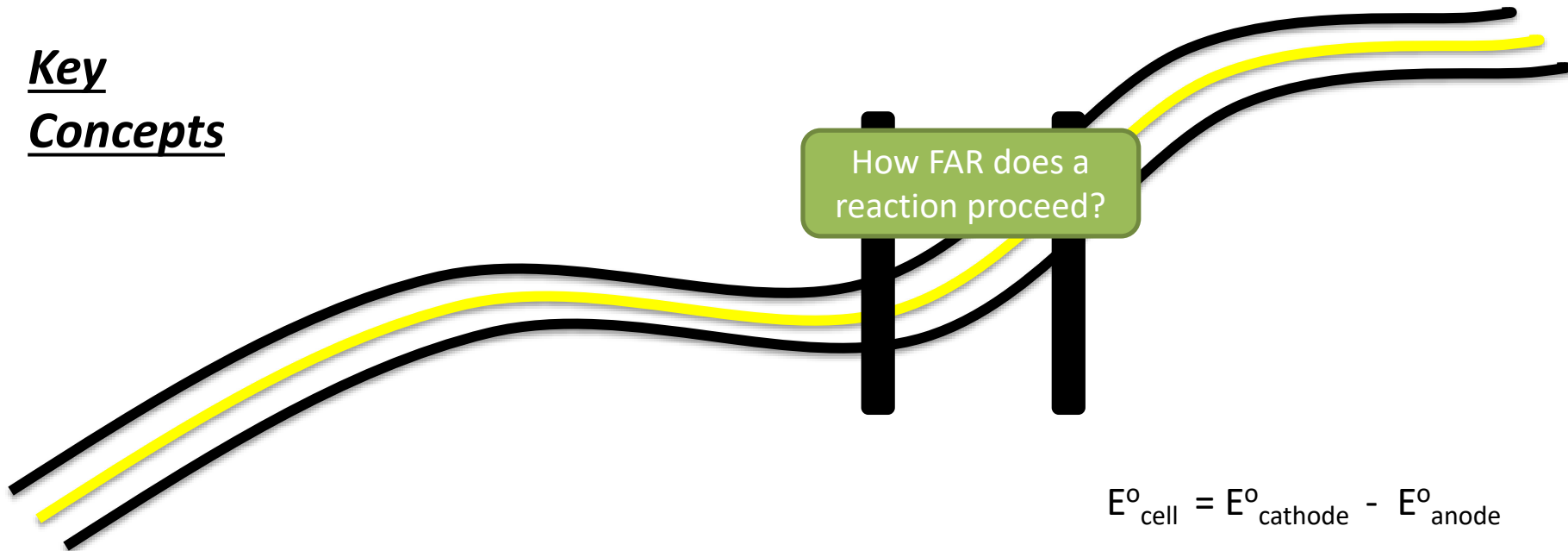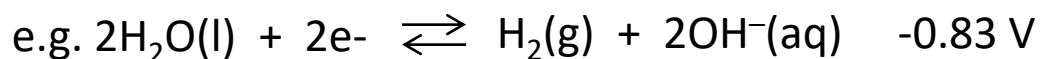
The key concepts of equilibria explain electrochemical processes (e.g. corrosion, batteries, fuel cells).

$$E_{cell} = E^o_{cell} + \frac{0.0592}{n_e} \log Q$$

e.g. $2H_2O(l) + 2e- \rightleftarrows H_2(g) + 2OH^-(aq)$ -0.83 V

$$E^o_{cell} = \frac{RT}{zF} \ln K$$

$$n_e F E^o_{cell} = R\, T\ln K$$

Learning Objectives

Draw a diagram for a voltaic cell including labels for essential details.

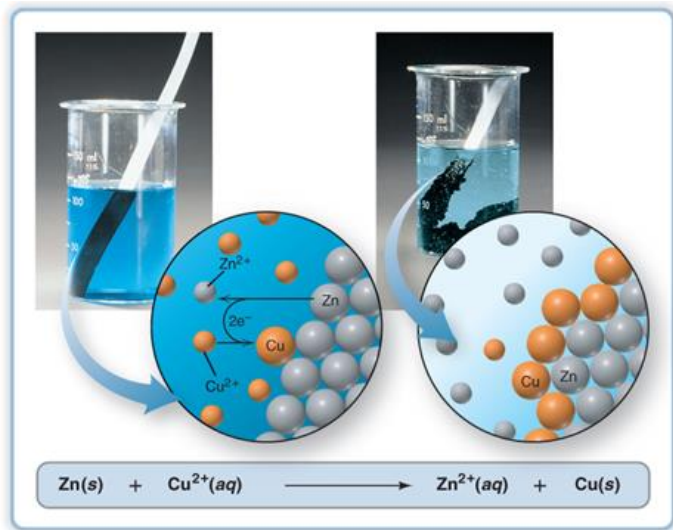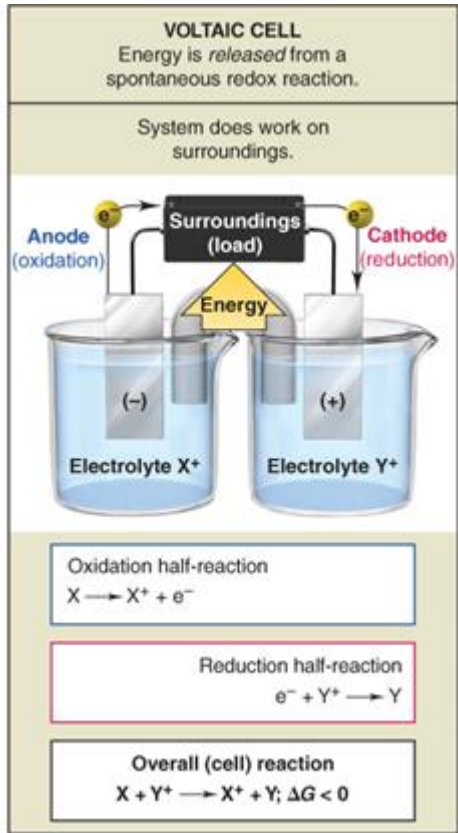*Calculate* E^o_{cell} for a given reaction using tabulated half-cell data.

Calculate E_{cell} using the Nernst equation.

For the process of electrolysis, *calculate* product amounts and currents required.
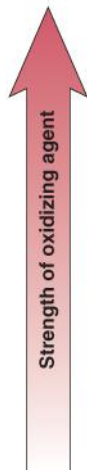
Identify corrosion conditions and sacrificial anodes.

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Draw a diagram for a voltaic cell including labels for essential details.

VOLTAIC CELL
Energy is *released* from a spontaneous redox reaction.

System does work on surroundings.

Anode (oxidation)
e⁻
Surroundings (load)
e⁻
Cathode (reduction)

Energy

(−)   (+)

Electrolyte X⁺   Electrolyte Y⁺

Oxidation half-reaction
$X \longrightarrow X^+ + e^-$

Reduction half-reaction
$e^- + Y^+ \longrightarrow Y$

Overall (cell) reaction
$X + Y^+ \longrightarrow X^+ + Y;\ \Delta G < 0$

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

Modified Figures 19.4 and 19.5

Calculate E^o_{cell} for a given reaction using tabulated half-cell data.

TABLE 19.3   Selected Standard Electrode Potentials (298 K)

Half-Reaction	$E^°_{half\text{-}cell}$ (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.05

Strength of oxidizing agent

Strength of reducing agent

Calculate E_cell using the Nernst equation.

For the process of electrolysis, *calculate* product amounts and currents required.
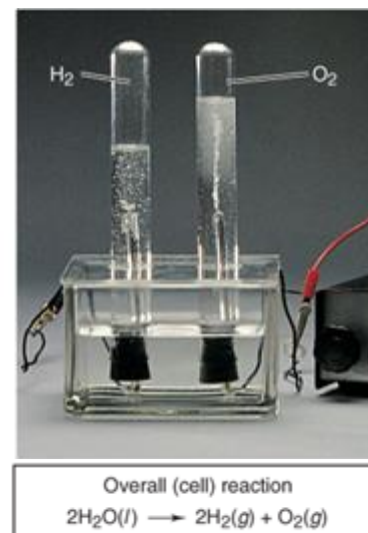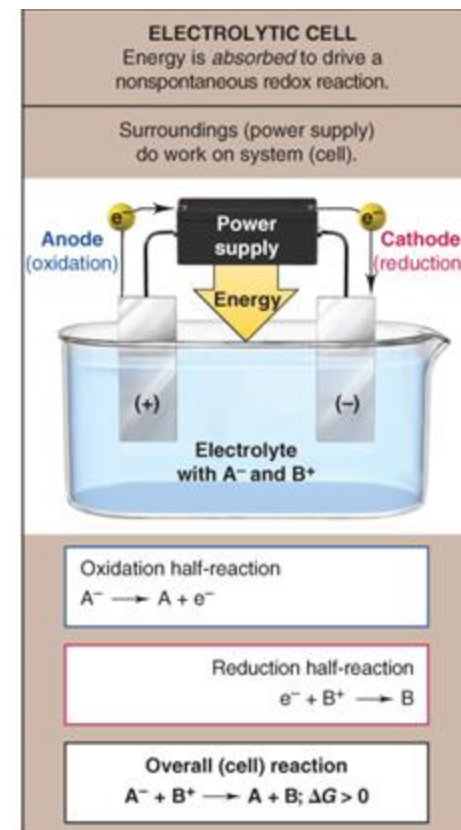

ELECTROLYTIC CELL
Energy is *absorbed* to drive a nonspontaneous redox reaction.

Surroundings (power supply) do work on system (cell).

Power supply

Anode (oxidation)

Cathode (reduction)

Energy

(+)

(−)

Electrolyte with A⁻ and B⁺

Oxidation half-reaction
$A^- \longrightarrow A + e^-$

Reduction half-reaction
$e^- + B^+ \longrightarrow B$

Overall (cell) reaction
$A^- + B^+ \longrightarrow A + B; \Delta G > 0$

H_2

O_2

Overall (cell) reaction
$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

Modifications of Figures 19.4 and 19.32

Identify corrosion conditions and sacrificial anodes.

$$2\text{Fe}(s) + \text{O}_2(g) + 4\text{H}^+(aq) \longrightarrow 2\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O}(l) \quad \text{(overall)}$$

③ The Fe^{2+} migrates through the drop and reacts with O$_2$ and H$_2$O to form rust.

② Electrons at the Fe (inactive) cathode reduce O$_2$ to H$_2$O.

Rust Fe$_2$O$_3$•nH$_2$O

2Fe ⟶ 2Fe^{2+} + 4e$^-$ (anodic region)

IRON BAR

① Oxidation of Fe forms a pit and yields electrons, which travel through the metal.

(cathodic region)

Electrons from Zn reduce O$_2$ to H$_2$O.

2Zn (anode)

Zn gives up electrons to Fe cathode.

Fe (inactive cathode)