Electron-Transfer Reactions

Oxidation/Reduction Reactions: Involve transfer of electrons between species.

- Reduction:
- Oxidation:

NOTE: Oxidation and reduction must occur together!

Electron-transfer rxns can be used:

- to prepare new materials (electrolysis and electrosynthesis) or
- to provide energy in the form of electrical current (galvanic and voltaic cells).

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Balancing Redox Reactions:

To successfully balance a redox reaction you MUST be able to identify what is being oxidized and what is being reduced!

Example: Balance the equation for the reaction between nitric acid and cobalt metal to give cobalt(III) and NO_2 gas.

$$Co(s) + NO_3^-(aq) \rightarrow Co^{3+}(aq) + NO_2(g)$$

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Systematic Method for Balancing Redox Reactions in Acid Solution

1. Break the overall reaction into individual oxidation and reduction **half-reactions.**
2. Balance each half reaction for **mass** (atoms).
   – Add H_2O to balance oxygen, H^+ to balance hydrogen
3. Balance each reaction for **charge**.
   – Add electrons (e^-) to equalize charge on both sides of the reaction.
4. Multiply the balanced half reactions by the appropriate factors so that the **number of electrons transferred** in each reaction are the same.
5. **Add** the resulting reactions, **cancelling** any components that appear on both sides of the equation.
6. **DOUBLE CHECK** your result for mass and charge balance!

What about *basic* solution??

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Predicting Tendencies of Redox Rxns

THERMODYNAMICS

DEMO: Zinc metal immersed in a Cu^{2+} solution.

Observations?

Overall Reaction:

Half-Reactions:

What do your observations tell you about the relative strengths of Zn and Cu as oxidizing agents?

What if we separate the half cells?

Cell notation

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Quantifying the Tendency for Something to be Reduced (Oxidized).

Potential: "electron pressure"

- Positive potential → Favorable process

Standard Potential (E^o):

$$\Delta G^o = -nFE^o$$

- Assumes standard conditions (T = 298K, []=1 M, p = 1 bar)

  $H^+ + e^- \rightleftarrows \frac{1}{2}H_2$ is defined as zero (E^o = 0.000 V).
- As reduction potential becomes more positive, the tendency for the reduction reaction to occur increases.
- Values for *Standard Reduction Potentials* are tabulated.
  - Quantifies the tendency for a material to be reduced (act as an oxidizing agent)
- E^o for the reverse reaction (oxidation) is the same size, but opposite sign of the E^o for reduction.

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Standard Potentials

TABLE 20.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C

Reduction Half-Reaction	E°, V
Acidic solution	
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	+2.01
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	+1.763
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	+1.455
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.358
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$2IO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow I_2(s) + 6H_2O(l)$	+1.20
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.065
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	+0.956
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.800
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.695
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.340
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow 2H_2O(l) + SO_2(g)$	+0.17
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.154
$S(s) + 2H^+(aq) + 2e^- \longrightarrow H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.125
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.137
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.440

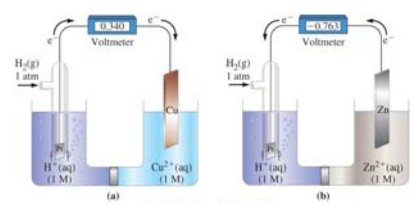

TABLE 20.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C (Continued)

Reduction Half-Reaction	E°, V
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.763
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.676
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.356
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.713
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.84
$K^+(aq) + e^- \longrightarrow K(s)$	−2.924
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.040
Basic solution	
$O_3(g) + H_2O(l) + 2e^- \longrightarrow O_2(g) + 2OH^-(aq)$	+1.246
$OCl^-(aq) + H_2O(l) + 2e^- \longrightarrow Cl^-(aq) + 2OH^-(aq)$	+0.890
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.401
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.828

Calculating E^o_{cell} from $E^o_{1/2}$ for the Component Reactions.

Comparison of the tendencies for each reaction to occur. The reaction will proceed in the direction where ΔG is more favorable.

$$Zn^0 + Cu^{2+} \rightleftarrows Zn^{2+} + Cu^0$$

Look at half reactions:

	E^o	ΔG^o
Anode:		
Cathode:		
Overall:		

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Calculating E^o_{cell} from $E^o_{1/2}$ for the Component Reactions.

So, by convention:

- If the cathode reaction is written as a reduction and the anode reaction is written as an oxidation:

$$E^o_{cell} = E^o_{cathode} + E^o_{anode}$$

- Many texts suggest to leave both reactions written as reductions, then

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Example: Is the following reaction product-favored under standard conditions? What is the value of E^o_{cell}?

$$H_2O_2 + 2H^+ + 2Br^- \rightleftarrows Br_2 + 2H_2O$$

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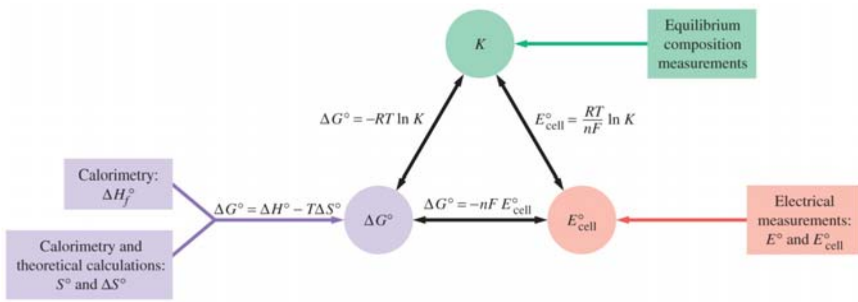
Three Related Parameters



What About Nonstandard Conditions?

Remember, since potentials are thermodynamic quantities, we can use thermodynamic relationships!

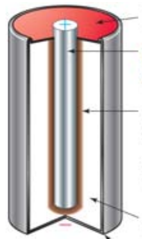
$$\Delta G = \Delta G^o + RT\ln Q$$

Example: Given the reaction in the previous example, what is E_{cell} when $[H_2O_2]$ = 1.00M, $[Br_2]$ = 1.00 M, $[Br^-]$ = 0.000100M and pH = 4.00?

Batteries and Fuel Cells

Energy storage devices:

Redox rxn → electrons we can use!



Primary Batteries:

Dry Cell Battery:

Anode: $Zn(s) \rightleftarrows Zn^{2+}(aq) + 2e^-$

Cathode: $2\ MnO_2(s) + H_2O\ (\ell) + 2e^- \rightleftarrows Mn_2O_3(s) + 2OH^-(aq)$

Additional Reactions:

$NH_4^+ + OH^- \rightleftarrows NH_3(g) + H_2O(\ell)$

$Zn^{2+} + 2NH_3 + Cl^- \rightleftarrows [Zn(NH_3)_2]Cl_2(s)$

- Problems?

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Dry Cell Batteries

Other anode/cathode combinations tackle these problems:

- Alkaline batteries
- Mercury batteries
- Lithium batteries

Alkaline Batteries

- NaOH (or KOH) replaces ammonium chloride electrolyte

Anode: $Zn(s)\ \ 2OH^-(aq) \rightleftarrows Zn(OH)_2(s) + 2e^-$

Cathode: $2\ MnO_2(s) + H_2O\ (\ell) + 2e^- \rightleftarrows Mn_2O_3(g) + 2OH^-(aq)$

- Decreases gas production, slows dissolution of zinc.

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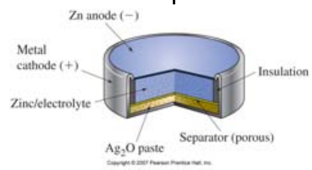
Secondary Batteries (rechargeable)

Primary batteries: eventually all the reactants are used up!

Silver-Zinc Batteries:

$Zn(s) + Ag_2O(s) = ZnO(s) + 2Ag(s)$



Secondary batteries: can be regenerated by driving the cell reaction in reverse.

- Requires an applied external potential (aka a charger!)

Car Battery:

$Pb(s) + PbO_2(s) + 2\ H_2SO_4(aq) \rightleftharpoons 2PbSO_4(s) + 2H_2O(\ell)$

Ni-Cad Batteries

$Cd(s) + 2NiO(OH)(s) + 2H_2O(l) = 2Ni(OH)_2(s) + Cd(OH)_2(s)$

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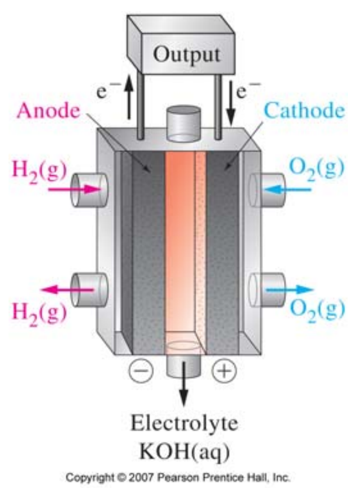
Fuel Cells

- Continuous supply of fuel is oxidized
  fuel + oxidant $\rightarrow$ products
- Fuel Cell Animation: http://auto.howstuffworks.com/fuel-cell2.htm
- Anode and cathode typically separated by a solid electrolyte "membrane"
- Catalyst at the electrode/electrolyte interface helps speed reaction
  - Increase efficiency
- Fuel cell challenges



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Corrosion

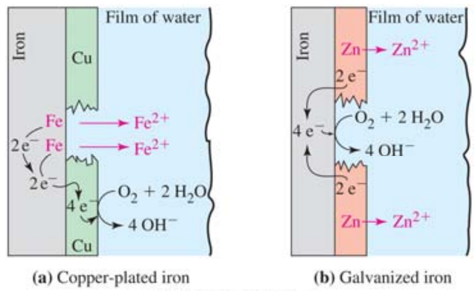
Result of a favorable redox reaction.

In base: $Fe + O_2 + 2H_2O \rightleftarrows 2Fe^{2+} + OH^-$ $E^o = 0.841$ V

In acid: $Fe + O_2 + 4H^+ \rightleftarrows 2Fe^{2+} + 2H_2O$ $E^o = 0.841$ V

Preventing Corrosion:

- Anodic inhibition:
- Cathodic protection:



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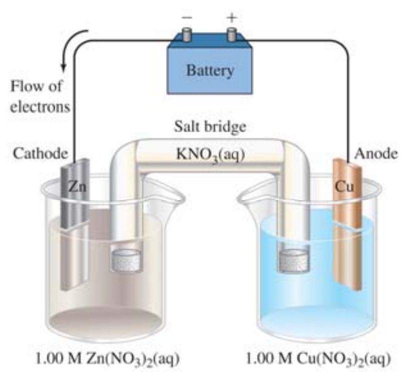
Electrolysis: Driving redox reactions

- We can adjust the potential of an electrode to drive either an oxidation or a reduction reaction.
- If we keep track of how many electrons have transferred over time, we can quantitatively determine the extent of reaction.

Challenges

1. Slow kinetics – overpotential
2. Competing reactions
3. Concentration-dependent potentials
4. Electrode surface chemistry



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Electrolysis: Electron Bookkeeping

$$\text{Ampere (A)} = \frac{\text{Charge}}{\text{Time}} =$$

96485 Coulombs = 1 mole of electrons

F = 96485 C/mol e-

Example: In the commercial production of sodium by electrolysis, the cell operates at 7.0 V and a current of 25×10^3 A. How many grams of sodium can be produced in one hour?

$$Na^+ + e^- \rightarrow Na$$

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