Wednesday March 12, 2014

Objective: The student will be able to (1) balance REDOX reactions using the half-cell method, (2) describe the components of a voltaic cell, (3) determine the electrical output of a voltaic cell.

Homework: Electrochemistry Intro. PS and E-chem PS #2

Warm - Up: (5 minutes)

56.3 grams of silver nitrate are reacted with 52.1 grams of sodium phosphate. How many grams of the precipitate cation are formed?

Introduction to Redox Terms

REDOX: tandem reactions of oxidation and reduction.

$F_{2(g)} + 2e^- \rightarrow 2F^-$

$F^- \rightarrow F_{2(g)} + 2e^-$

SOP
SRP] $E°$

OXIDATION • One reactant loses electrons. • Reducing agent is oxidized. • Oxidation number increases.	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized**. The oxidation number of Zn **increases** from 0 to +2.
REDUCTION • Other reactant gains electrons. • Oxidizing agent is reduced. • Oxidation number decreases.	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced**. The oxidation number of H **decreases** from +1 to 0.

(OA / RA, OILRIG, show reactions)

Balancing Redox Reactions

Let's try to balance this bad boy!

$$KOH_{(aq)} + KMnO_{4(aq)} + KI_{(aq)} \rightarrow K_2MnO_{4(aq)} + KIO_{3(aq)} + H_2O_{(l)}$$

Balancing Redox Reactions
Half-Cell Method

Steps:

1. Divide the skeleton reaction into two half reactions.

2. Balance the atoms and charges:

- **X ➔ O ➔ H**
- **add electrons**

3. multiple the e^{-}_{s} so they are equal

4. add the half reactions and include SOM

[4b.] add OH^{-} (basic solution only)

5. Check

Ex. 1 $Cr_2O_7^{2-}{}_{(aq)} + I^-{}_{(aq)} \rightarrow Cr^{+3}{}_{(aq)} + I_{2\,(s)}$

[acidic solution]

$Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

$2Cr + 7(-2) = -2$

$Cr = +6 \rightarrow +3$ red

$14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

$+12 \quad +6$

$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$

$3(2I^- \rightarrow I_2 + 2e^-)$ ox

$6I^- \rightarrow 3I_2 + 6e^-$

$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$

$14H^+ + 6I^- + Cr_2O_7^{2-} \rightarrow 3I_2 + 2Cr^{+3} + 7H_2O$

$$MnO_4^-{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \rightarrow MnO_{2(s)} + CO_3^{2-}{}_{(aq)}$$

[basic solution]

$4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$

$\times 2$

$3e^- + 4H^+ + MnO_4^- \rightarrow MnO_2 + 2H_2O$

$+2H_2O$

$C_2O_4^{2-} \rightarrow 2CO_3^{2-} + 4H^+ + 2e^-$

$\times 3$

$6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O$

$+ 2H_2O + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + 4H^+ + 6e^-$

$4H_2O$

$4OH^- + 2H_2O + 3C_2O_4^{2-} + 2MnO_4^- \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+ + 4OH^-$

$+2H_2O$

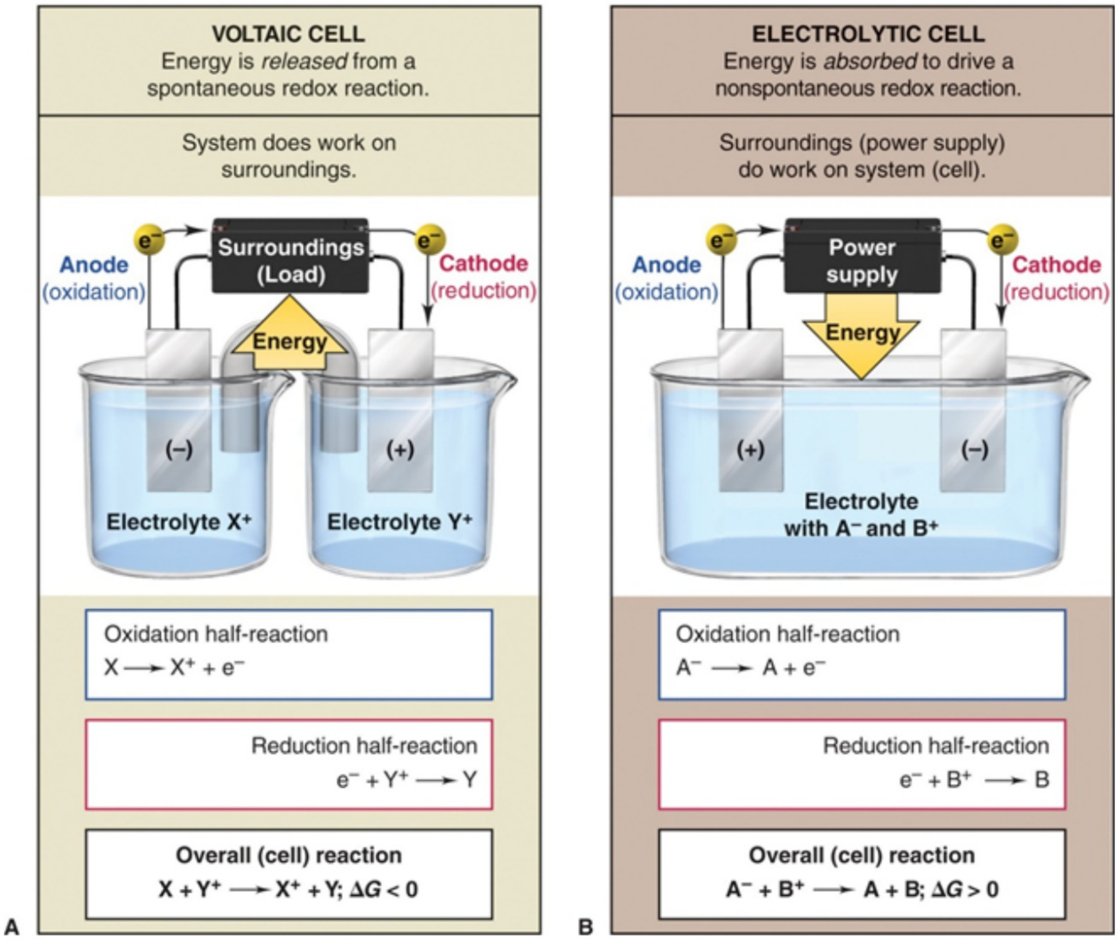
Practice 1

$MnO_4^-{}_{(aq)} + I^-{}_{(aq)} \rightarrow MnO_4^{2-}{}_{(aq)} + IO_3^-{}_{(aq)}$

[basic solution]

Ans: $6OH^- + 6MnO_4^-{}_{(aq)} + I^-{}_{(aq)} \rightarrow 6MnO_4^{2-}{}_{(aq)} + IO_3^-{}_{(aq)} + 3H_2O_{(l)}$

Overview of Electrochemical Cells



Notation for a Voltaic Cell

The components of each half-cell are written in the same order as in their half-reactions.

The anode components are written on the ***left***.

The cathode components are written on the ***right***.

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,(1M)\,|\,\mathrm{Cu}(s)$$

The single line shows a phase boundary between the components of a half-cell.

The double line shows that the half-cells are physically separated.

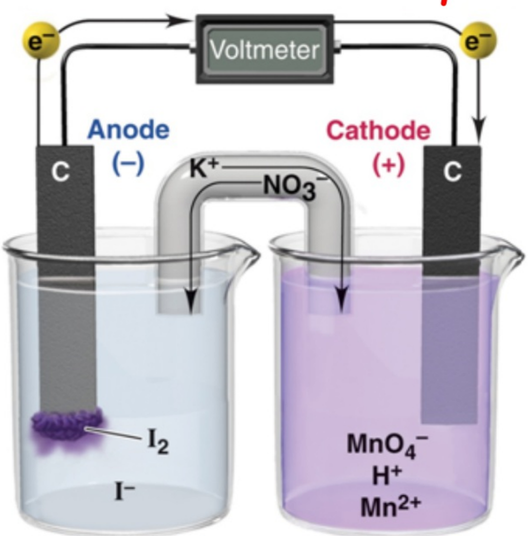
If needed, concentrations of dissolved components are given in parentheses. (If not stated, it is assumed that they are 1 *M*.)

Notation for a Voltaic Cell

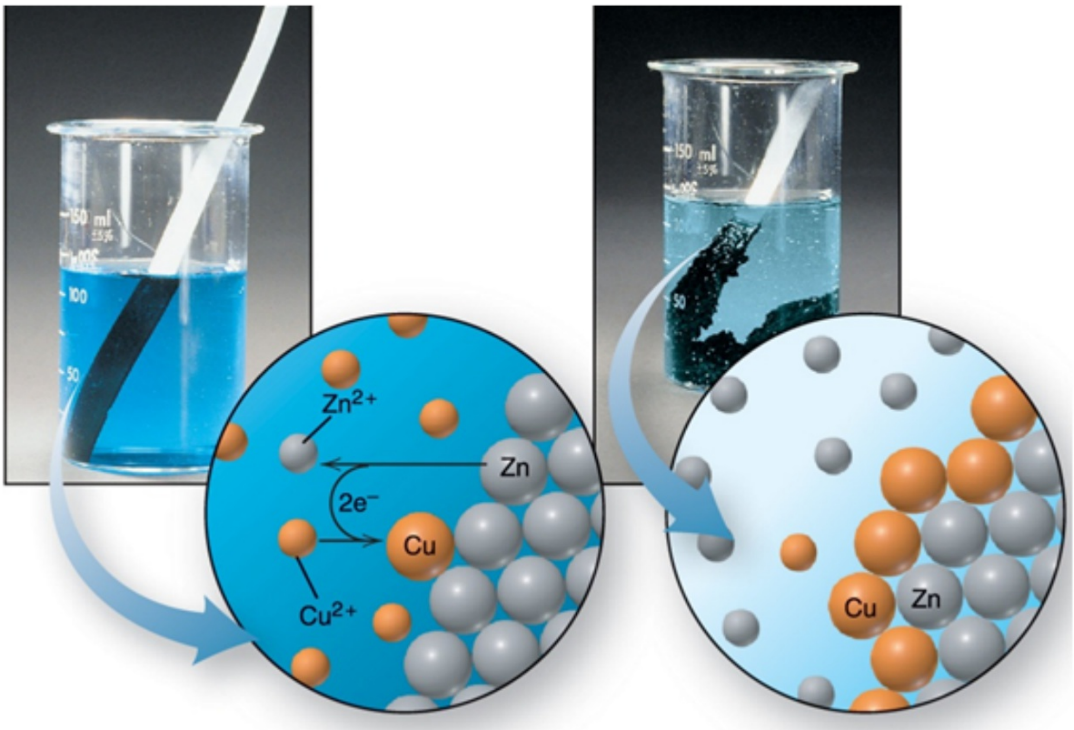
graphite | $I^-(aq)$ | $I_2(s)$ || $MnO_4^-(aq)$, $H^+(aq)$, $Mn^{2+}(aq)$ | graphite

The inert electrode is specified.

A comma is used to show components that are in the same phase.



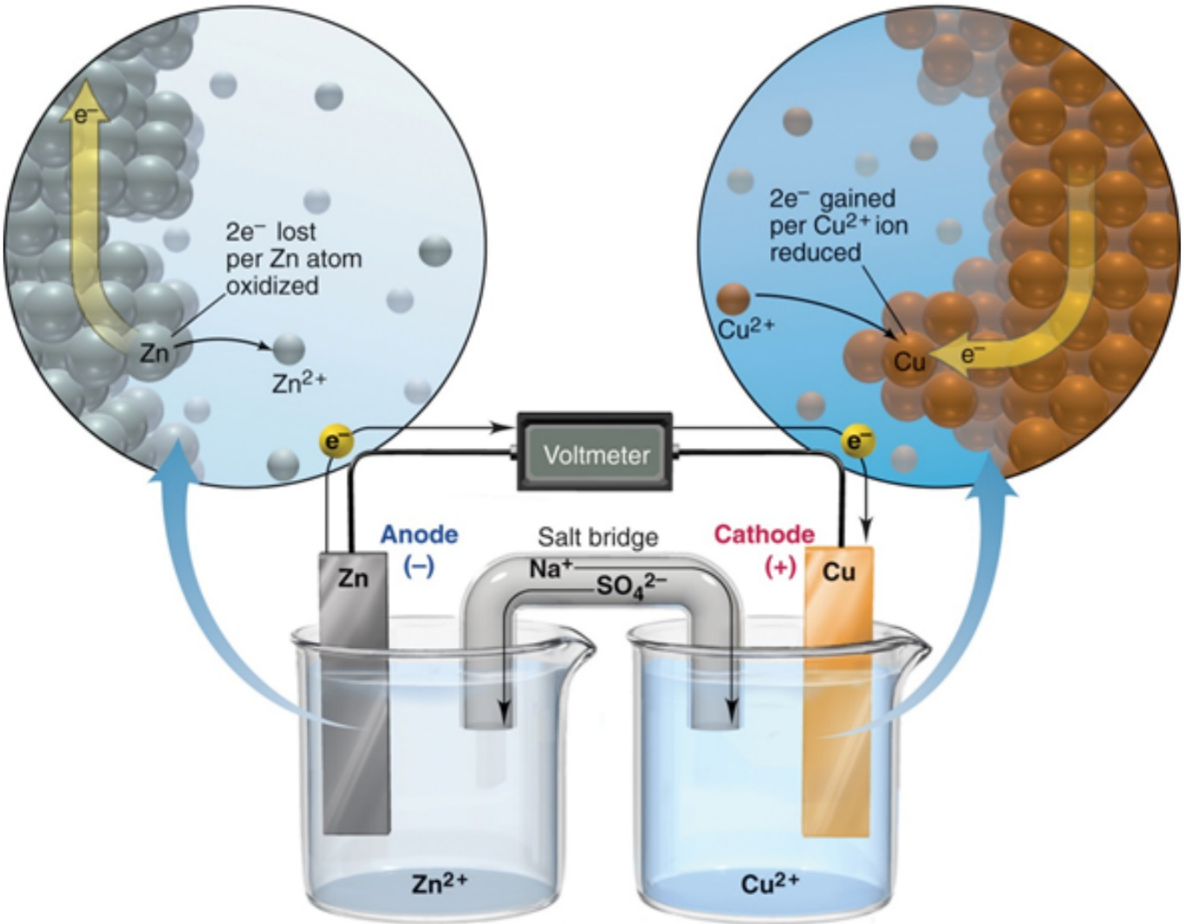
Standard State of Redox Reactions



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

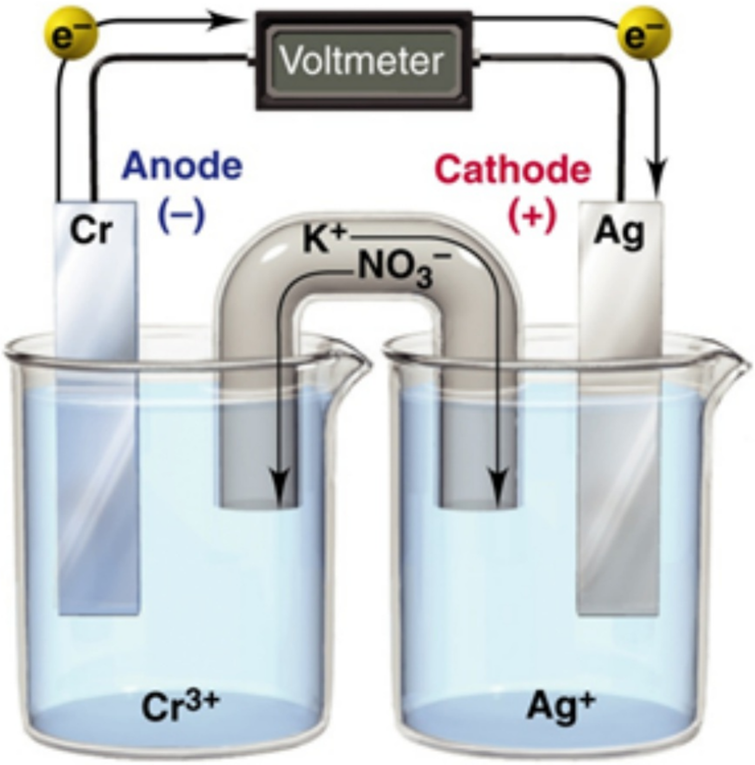
seperation of the half reactions

Components of a Voltaic Cell



Draw a diagram, show balanced equations, and write the notation for a voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge. Measurement indicates that the Cr electrode is negative relative to the Ag electrode.

Sample Problem Solution



Cell Potential: Output of a Voltaic Cell

cell potential (E_{cell}, voltage, or emf): the difference in electrical potential between the two electrodes.

In a voltaic cell, electrons flow from the more negative electrode to the more positive)

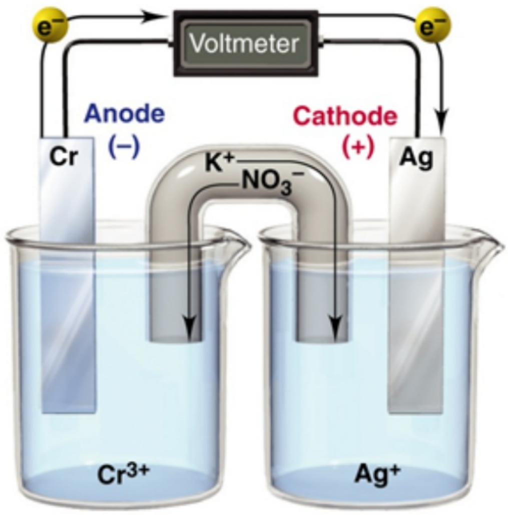
Sign Conventions:

E_{cell}	0	spontaneous rxn
E_{cell}	0	equilibrium, cell can do no more work
E_{cell}	0	spontaneous rxn

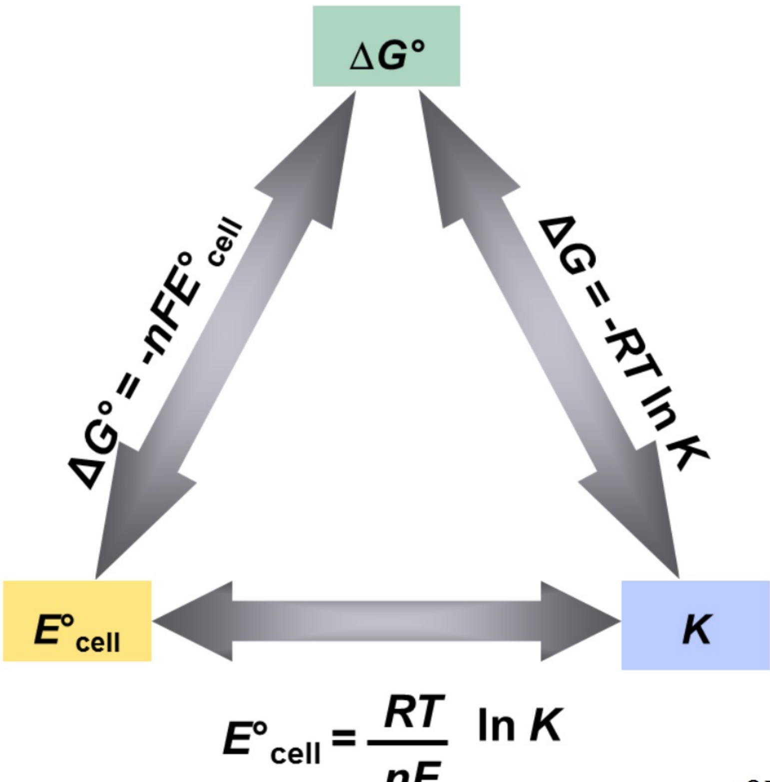
Example

Calculate the $E°_{cell}$ for the voltaic cell:

$Cr_{(s)} \mid Cr^{3+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$



Connection to Thermodynamics and Equilibrium



explain all terms

Summary of Sign Conventions

ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
< 0	> 1	> 0	*spontaneous*
0	1	0	*at equilibrium*
> 0	< 1	< 0	*nonspontaneous*

Sample Problem

Lead can displace silver from solution and silver occurs in trace amounts in the ores of lead. Calculate the $E°_{cell}$, K_{eq}, and ΔG.

The Nernst Equation

$$E_{cell} = E^{0}_{cell} + \frac{RT}{nF} \ln Q$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0592\ V}{n} \log Q$$

In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a Zn/Zn^{2+} half-cell and an H_2/H^+ half-cell under the following conditions:

$[Zn^{2+}]$ = 0.010M $[H^+]$ = 2.5M P_i (H_2) = 0.030atm

Calculate the E_{cell} at 298K.