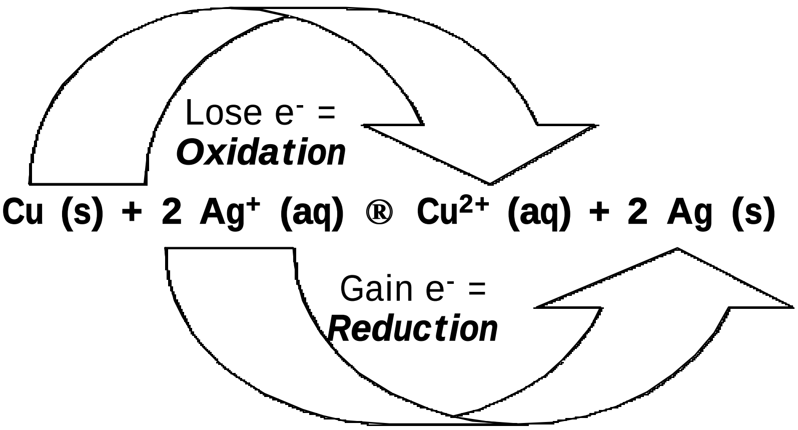
Oxidation-Reduction Chemistry

Chem 36

Spring 2002

Definitions

- Redox reactions involve *electron transfer:*



Lose e^- =
Oxidation

$Cu\ (s) + 2\ Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$

Gain e^- =
Reduction

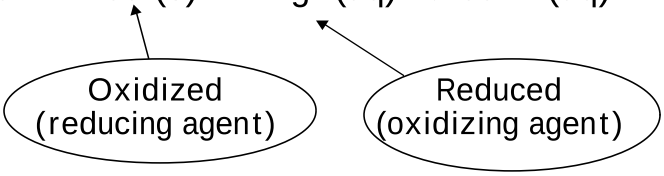
Half-Reactions

- Consider each process indivually:

Oxidation $Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2\ e^-$

Reduction $[Ag^+ + e^- \rightarrow Ag\ (s)] \times 2$

Overall: $Cu\ (s) + 2Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2Ag\ (s)$



Oxidized
(reducing agent)

Reduced
(oxidizing agent)

Balancing Redox Reactions

- **The Half-Reaction Method**

Three Steps:

1. Determine *net ionic equations* for both half-reactions
2. Balance half-reactions with respect to *mass* and *charge*
3. Combine so as that *electrons cancel*

Example

$SO_3^{2-} + H^+ + MnO_4^- \rightarrow SO_4^{2-} + Mn^{2+} + H_2O$

1. Write Skeleton Half-Reactions

Oxidation $SO_3^{2-} \rightarrow SO_4^{2-}$

Reduction $MnO_4^- \rightarrow Mn^{2+}$

2. Mass Balance

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+$

$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$

- Add H_2O to side needing oxygen
- Add H^+ to balance hydrogen

Example: Continued

3. Charge Balance (use electrons)

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

4. Combine!

$[SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$

$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$

$5SO_3^{2-} + 5H_2O + 2MnO_4^- + 16H^+ + 10e^- \rightarrow$

$5SO_4^{2-} + 10H^+ + 10e^- + 2Mn^{2+} + 8H_2O$

Example: Simplify and Verify

Collecting and cancelling gives:

$$\boxed{5SO_3^{2-} + 2MnO_4^{-} + 6H^{+} \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O}$$

Verify!

- ✓Mass Balance
- ✓Charge Balance

Done!

In Basic Solution?

- ➢**First:** Balance as though in acid
- ➢**Next:**
  - ✓Add OH^- to both sides of reaction in an amount equal to the amount of H^+
  - ✓*Change:* $H^+ + OH^-$ to H_2O
  - ✓Verify!

Example (Basic Solution)

$Cr(OH)_3 + OCl^- + OH^- \rightarrow CrO_4^{2-} + Cl^- + H_2O$

In Acid Solution

$2Cr(OH)_3 + 3OCl^- \rightarrow 2CrO_4^{2-} + 3Cl^- + H_2O + 4H^+$

$+ 4OH^-$ Add OH^- $+ 4OH^-$

Make Water

$2Cr(OH)_3 + 3OCl^- + 4OH^- \rightarrow 2CrO_4^{2-} + 3Cl^- + 5H_2O$

Example: Simplify and Verify

Collecting and cancelling gives:

$5SO_3^{2-} + 2MnO_4^- + 6H^+$ ® $5SO_4^{2-} + 2Mn^{2+} + 3H_2O$

Verify!

✓Mass Balance

✓Charge Balance

Done!

In Basic Solution?

- **First:** Balance as though in acid
- **Next:**
  - ✓Add OH^- to both sides of reaction in an amount equal to the amount of H^+
  - ✓*Change:* $H^+ + OH^-$ to H_2O
  - ✓Verify!

Example (Basic Solution)

$$Cr(OH)_3 + OCl^- + OH^- \rightarrow CrO_4^{2-} + Cl^- + H_2O$$

In Acid Solution

$$2Cr(OH)_3 + 3OCl^- \rightarrow 2CrO_4^{2-} + 3Cl^- + H_2O + 4H^+$$

$$+ 4OH^- \qquad \text{Add } OH^- \qquad + 4OH^-$$

Make Water

$$2Cr(OH)_3 + 3OCl^- + 4OH^- \rightarrow 2CrO_4^{2-} + 3Cl^- + 5H_2O$$

Back to Cu/Ag Reaction

How can we *predict* reaction spontaneity?

$Cu\ (s) + 2\ Ag^{+}\ (aq)$ ® $Cu^{2+}\ (aq) + 2\ Ag\ (s)$

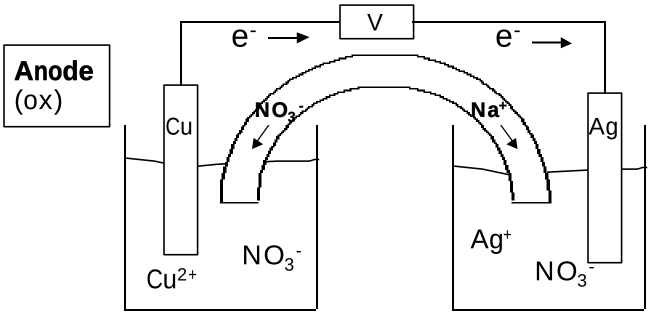
versus

$Cu^{2+}\ (aq) + 2\ Ag\ (aq)$ $\cancel{\text{®}}$ $Cu\ (s) + 2\ Ag^{+}\ (s)$

ΔG? K? Direction/Extent of Reaction?

The Galvanic Cell

- Set up, literally, two half-cells for the reaction:



Cathode
(red)

Cell Potential:

0.463 volts

$1.0\ M\ Cu(NO_3)_2$ | $1.0\ M\ AgNO_3$

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$ | $Ag^+ + e^- \rightarrow Ag\ (s)$

Electromotive Force

- What is the **Cell Potential**?
  - Recall: 1 Joule = 1 volt x 1 coulomb

    (work) (potential) (charge)
  - *Driving Force* of reaction
  - The *Electromotive Force* (EMF)
  - **E^o_{cell}** (all species in standard states)

Galvanic Cell shorthand:

$Cu\ (s)|Cu^{2+}\ (aq)||Ag^{+}\ (aq)|Ag\ (s)$ E^o_{cell} = 0.463 volts

Anode	Cathode
(oxidation)	(reduction)

Another system

- Now, consider this cell:

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

E^o_{cell} = -1.100 volts

- What does a *negative* potential mean?
  - ✓ Electrons *want* to flow from Cathode (Zn) to Anode (Cu)
  - ✓ So, reaction is *spontaneous* in the “reverse” direction:

Cu^{2+} (aq) + Zn (s) ® Cu (s) + Zn^{2+} (aq)

Pulling Rank

- Rank Ag, Cu and Zn based on their ability to *cause reduction:*
  - ✓ Cu reduces Ag^+
  - ✓ Zn reduces Cu^{2+}
- So, as reducing agents:

Zn > **Cu** > **Ag**

How can we ***quantify*** this?

Quantifying Reduction

By definition

- Measure E^o_{cell} for *reduction ½-cells* with a **reference ½-cell**:

$2H^+$ (aq) + $2e^-$ ® H_2 (g) E^o_H = 0.0000 volts

Standard Hydrogen Electrode (SHE)

Tabulate as ***Standard Reduction Potentials*** (oxidizing power):

	Ag	>	**Cu**	>	**Zn**
E°	+0.800 v		+0.337 v		-0.763 v

Calculating E^o_{cell}

$Cu\ (s)|Cu^{2+}\ (aq)||Ag^{+}\ (aq)|Ag\ (s)$

Anode (oxidation)	**Cathode (reduction)**
$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$	$Ag^+ + e^- \rightarrow Ag\ (s)$
$E^o_{ox} = -E^o_{Cu} = -0.337$ v	$E^o_{red} = E^o_{Ag} = +0.800$ v

$2 \times [Ag^+ + e^- \rightarrow Ag\ (s)]$ +0.800 v

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e$ -0.337 v

$Cu\ (s) + 2Ag^+\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s)$ ***0.463 v = E^o_{cell}***

Or: $\boxed{E^o_{cell} = E^o_{Cathode} - E^o_{Anode}}$

(right) (left)

reduction potentials

The Thermodynamics Connection!

Recall that:

work = charge x potential

Which gives:

$$w_{electr} = n\ FE_{cell}$$

mol e^-/mol rxn

Faraday's Constant = *9.6487×10^4 C/mol e^-*

For a reversible system at constant Temp and Pressure:

$$w_{max} = -\Delta G$$

So: $\boxed{\Delta G^o = -n\ FE^o_{cell}}$

What about K?

Simple!

$$\Delta G^o = -RTLnK = -n\ FE^o_{cell}$$

Rearranging gives:

$$E^o_{cell} = \frac{RTLnK}{n\ F}$$

At 298.15K:

$$\boxed{E^o_{cell} = (0.0592/n)LogK}$$

Example

$$2Al\ (s) + 3Cu^{2+}\ (aq) \rightarrow 3Cu\ (s) + 2Al^{3+}\ (aq)$$

E^o_{cell}? ΔG^o? K?

E^o_{cell}:

$2 \times [Al(s) \rightarrow Al^{3+}\ (aq) + 3e^-]$ -(-1.66 v)

$3 \times [Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)]$ +0.337 v

$2Al\ (s) + 3Cu^{2+}\ (aq) \rightarrow 3Cu\ (s) + 2Al^{3+}\ (aq)$ ***+2.00 v***

reaction is *spontaneous*

Now for ΔG^o

$\mathbf{DG^{o} = -n\ FE^{o}_{cell}}$

$\Delta G^o = -(6 \text{ mol e-/mol})(9.6487 \times 10^4 \text{ C/mol e}^-)(2.00 \text{ v})$

$\Delta G^o = -1.158 \times 10^6$ C-v/mol

Joules

$\Delta G^o =$ *$\underline{-1.16 \times 10^3 \text{ kJ/mol}}$*

Equilibrium at last

- Two paths:
  - From ΔG^o (= -RTLnK)
  - From $\mathbf{E^{o}_{cell} = (0.0592/n)LogK}$

$$\text{LogK} = \frac{(E^o_{cell})n}{0.0592}$$

$$\text{Log K} = \frac{(2.00 \text{ v})(6 \text{ mol e}^-)}{0.0592} = 202.703$$

$$K = 10^{202.703} = 5.043 \times 10^{203} = \mathbf{10^{203}}$$

Non-Standard States?

Recall: $\mathbf{DG = DG^o + RTLnQ}$

Since: $\Delta G = -n\ FE_{cell}$

Substituting:

$$\boxed{\mathbf{E_{cell} = E^o_{cell} - \frac{RT}{n\ F} LnQ}}$$

The Nernst Equation

At 298.15 K: $\boxed{\mathbf{E_{cell} = E^o_{cell} - (0.0592/n)LogQ}}$

Nernst Example

Pt (s)|Fe^{2+} (0.10 *M*), Fe^{3+} (0.20 *M*)||Ag^+ (1.0 *M*)|Ag (s)

Calculate E_{cell}

First, determine $\mathbf{E^o_{cell}}$**:**

Ox	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	-(0.771 v)
Red	$Ag^+ + e^- \rightarrow Ag\ (s)$	+0.800 v
	$Ag^+ + Fe^{2+} \rightarrow Ag\ (s) + Fe^{3+}$	*+0.029 v*

$\mathbf{E^o_{cell}}$

Example Continues

Next, find value of ***Q:***

$$Q = \frac{[Fe^{3+}]}{[Ag^{+}][Fe^{2+}]} = \frac{(0.20)}{(1.0)(0.10)} = \boldsymbol{2.0}$$

Lastly, into the *Nernst Equation:*

$$\mathbf{E_{cell} = E^{o}_{cell} - (0.0592/n)LogQ}$$

$$\mathbf{E_{cell}} = 0.029 - (0.0592/1)Log(2.0)$$

$$\mathbf{E_{cell}} = 0.029 - 0.01782 = \mathit{0.01179\ volts}$$

$$\mathbf{E_{cell}} = \underline{\boldsymbol{0.012\ volts}}$$

Nernst (huh!)
. . . What is it good for?

- Concentration Determinations

Pt, H_2 (1 atm)$|H^+$ (x *M*)$||H^+$ (1 *M*)$|H_2$ (1 atm), Pt

Unknown $[H^+]$
(Anode)

Std Hydrogen Electrode
(Cathode)

Ox $H_2 (g) \rightarrow 2H^+ (aq) + 2e^-$

Red $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

concentration cell

$$\underset{(1\ M)}{2H^+ (aq)} \rightarrow \underset{(x\ M)}{2H^+ (aq)}$$

Using Nernst

$$E_{cell} = E^{o}_{cell} - (0.0592/n)\text{Log}Q$$

$$Q = \frac{[H^+]^2_{anode}}{[H^+]^2_{cathode}} = \frac{[H^+]^2_{anode}}{1\ M}$$

$$E_{cell} = 0.000 - (0.0592/2)\text{Log}[H^+]^2_{anode}$$

$$E_{cell} = \frac{-2(0.0592)}{2}\ \text{Log}[H^+]_{anode}$$

$$E_{cell} = -0.0592\ \text{Log}\ [H^+]_{anode}$$

$$\boxed{E_{cell} = 0.0592\ \text{pH}}$$

More Uses for Nernst

- Equilibrium Constant Determinations

Pb (s)|Pb^{2+} (sat'd $PbCl_2$ (aq))||Pb^{2+} (0.100 *M*)|Pb (s)

Another concentration cell

Ox $Pb (s) \rightarrow Pb^{2+} (aq) + 2e^-$

Red $Pb^{2+} (aq) + 2e^- \rightarrow Pb (s)$

Pb^{2+} (0.100 *M*) $\rightarrow$ Pb^{2+} (sat'd)

Measure E_{cell}: ***0.0237 volts***

What is K_{sp} for $PbCl_2$?

The Nernst Solution

- Nernst will provide $[Pb^{2+}]$:

$$E_{cell} = E^{o}_{cell} - (0.0592/n)\log Q$$

$$Q = \frac{[Pb^{2+}]_{anode}}{[Pb^{2+}]_{cathode}} = \frac{[Pb^{2+}]_{sat'd}}{0.100\ M}$$

$$0.0237 = 0.000 - (0.0592/2)\log([Pb^{2+}]/0.100)$$

$$[Pb^{2+}] = 1.6 \times 10^{-2}\ M$$

Finally, Equilibrium

- Solubility Equilbrium:

$$PbCl_2\ (s) \leftrightarrows Pb^{2+}\ (aq) + 2Cl^{-}\ (aq)$$

$$\qquad\qquad S \qquad\qquad 2S$$

Substitute into K_{sp} expression:

$$K_{sp} = [Pb^{2+}][Cl^{-}]^2 = S(2S)^2 = 4S^3$$

$$K_{sp} = 4(\mathbf{1.6 \times 10^{-2}})^3 = \underline{\mathbf{1.6 \times 10^{-5}}}$$

Batteries

- ➢ What happens if we *allow current to flow* in a Galvanic Cell?
  - ✓Oxidation and Reduction reactions occur
  - ✓Concentrations change
  - ✓$Q \rightarrow K$ (equilibrium)
  - ✓$E_{cell} \rightarrow 0$ (*dead battery!*)
- ➢ Is the reaction ***reversible***?
  - ✓Battery can be recharged
  - ✓Apply a potential sufficient to drive the *reverse reaction*

Example: Pb-Acid Battery

Anode: Pb-Sb alloy grid filled with spongy Pb

Cathode: PbO_2 coating

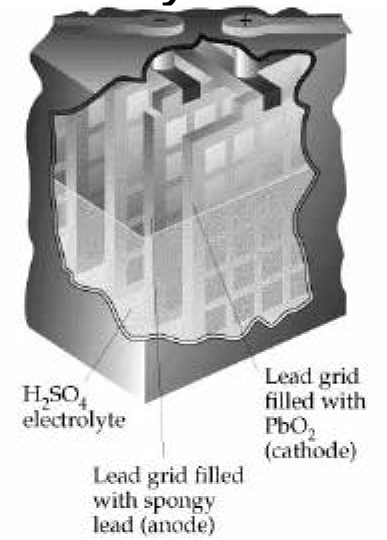
$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow$$

$$2PbSO_4 + 2H_2O$$

$$E_{cell} \approx 2.0 \text{ volts}$$

As it discharges:

- •$PbSO_4$ coats electrodes
- •Electrolyte gets diluted



Charge it up!

- Apply a potential > E_{cell} (opposite polarity)

  Forces the *reverse reaction*:

$$PbSO_4 \rightarrow Pb + PbO_2 + H^+ + SO_4^{2-}$$

When battery discharges *completely:*

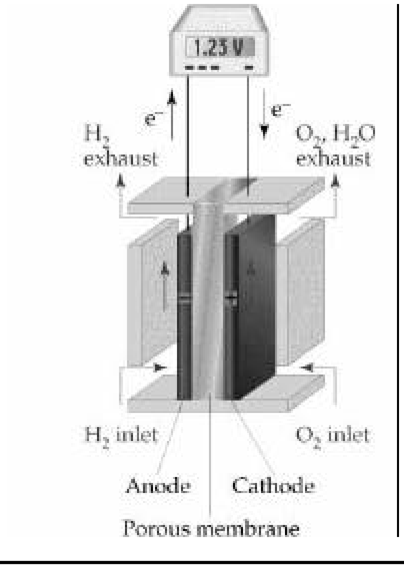
- $PbSO_4$ completely covers electrodes
- Can't recharge!
- ***Dead Battery***

When battery is *overcharged:*

- No $PbSO_4$ left to react
- Electrolysis of water
- H_2 and O_2 form
  - ✓Ruins Pb and PbO_2 coatings
  - ✓***Explosive!***

Fuel Cells

- Just an "Open" system battery
- Products and reactants are continuously replenished



Electrolysis

- ➢ Force a *nonspontaneous reaction* to occur by applying a potential:
  - ✓Greater than E_{cell}
  - ✓Opposite polarity
- ➢ Why Do It?
  - ✓Useful chemistry can happen
  - ✓Can *quantify* the extent of the reaction

Quantifying Electrolysis: Faraday's Laws

1. The amount of chemical change is proportional to the quantity of electrical charge that passes through an electrolytic cell

   Measure current: 1 Ampere = 1 Coulomb/sec
   Get charge: # Coulombs = current (Amps) x time (sec)

2. A given quantity of electricity produces the *same number of equivalents of any substance* in an electrolysis process:

   1 equivalent = 1 mol e^- in a half-reaction

   - ✓ *Relate charge (Coulombs) to equivalents using Faraday's Constant* (96,487 C/mol e^-)

Illustrative Example

- What mass of Cu is deposited if a current of **1.50 A** flows for **1.00 hour** in the electrolysis of a $CuSO_4$ solution?

The reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$$\text{time} \rightarrow \text{charge} \rightarrow \text{mol e}^- \rightarrow \text{mol Cu} \rightarrow \text{g Cu}$$

$$1.00\text{ hr} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ sec}}{1\text{ min}} \times \frac{1.5\text{ C}}{\text{sec}} \times \frac{1\text{ mol e}^-}{96{,}487\text{ C}} \times \frac{1\text{ mol Cu}}{2\text{ mol e}^-} \times \frac{63.55\text{ g Cu}}{1\text{ mol Cu}} =$$

= ***1.78 g Cu***

But what about . . . Aluminum?

- One of the most abundant elements (8% of the Earth's crust)
- Found almost *exclusively* as Al^{3+} in nature
- Can't do electrolysis reduction in aqueous solution:

$$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad E^o = -1.706\text{ V}$$

$$\boxed{2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^o = -0.83\text{ V}}$$

This is what happens!

The Hall-Hêroult Process

- 1885: Charles Martin Hall
  - ✓ 22 year-old student at Oberlin College
  - ✓ Electrolysis in a *molten salt* (Na_3AlF_6 at 1000 °C):

$$Al_2O_3\ (s) + 3C\ (s) \rightarrow 2Al\ (l) + 3CO\ (g)$$

  - ✓ Result: *inexpensive Al metal*
- **LOTS of energy is stored in Al metal**
  - ✓ ~3 billion pounds of Al thrown away each year
  - ✓ ΔG (Hall Process) = 300 - 600 kJ/mol Al
  - ✓ ΔG (Al Recycling) = 25 kJ/mol Al

Corrosion

- O_2 is a strong oxidizing agent and can oxidize many metals
- **Rust!** Fe + O_2
  - Solution? Coat Fe with a more easily oxidizable metal: Zn (galvanization)

$$E^o_{Zn} = -0.763\text{ V versus } E^o_{Fe} = -0.440\text{ V}$$

- Why doesn't Al oxidize ("rust")? $E^o_{Al} = -1.66$ V
  - It does! All Al metal has a thin coating of Al_2O_3
  - Al_2O_3 adheres to the surface and protects it