Review: Balancing Redox Reactions

- Determine which species is oxidized and which species is reduced
  - Oxidation corresponds to an increase in the oxidation number of an element
  - Reduction corresponds to a decrease in the oxidation number of an element
- Write half reactions for oxidation and reduction processes
  - Oxidation reaction will have e^-'s on the right side of equation
  - Reduction reaction will have e^-'s on the left side of the equation

Review: Balancing Redox Reactions

- Balance half reactions including charge balance
- Multiply each half reaction by a factor so that the total number of e^-'s transferred in each reaction are equal
- Add the resulting half reactions together to get the overall balanced redox equation

Review:
Balancing Redox Reactions

Example:

$F_2(g) + Al(s) \rightarrow F^-(aq) + Al^{3+}(aq)$

oxid. state 0 0 -1 +3

Fluorine is reduced ($0 \rightarrow -1$)

Aluminum is oxidized ($0 \rightarrow +3$)

- Half reactions:

  oxidation: $Al(s) \rightarrow Al^{3+}(aq) + 3\,e^-$

  reduction: $F_2(g) + 2\,e^- \rightarrow 2\,F^-(aq)$

Review:
Balancing Redox Reactions

Example:

$F_2(g) + Al(s) \rightarrow F^-(aq) + Al^{3+}(aq)$

- Balance e^-'s transferred:

  multiply oxidation rxn by 2

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

  multiply reduction rxn by 3

  $3\,F_2(g) + 6\,e^- \rightarrow 6\,F^-(aq)$

- Add half reaction to get net reaction:

  $2\,Al(s) + 3\,F_2(g) \rightarrow 2\,Al^{3+}(aq) + 6\,F^-(aq)$

- Check atom and charge balance:

Review:
Balancing Redox Reactions

Example:

$Ag^{+}(aq) + SO_2(g) + H_2O(\ell)$

$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^{+}(aq)$

- Determine oxidation state of each element in reaction:

$$\underset{+1}{Ag^{+}} + \underset{+4\ -2}{SO_2} + \underset{+1\ -2}{H_2O} \rightarrow \underset{0}{Ag} + \underset{+6\ -2}{SO_4^{2-}} + \underset{+1\ -2}{H_3O^{+}}$$

Review:
Balancing Redox Reactions

Example:

$Ag^{+}(aq) + SO_2(g) + H_2O(\ell)$

$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^{+}(aq)$

- Ag is reduced ($+1 \rightarrow 0$)
- S is oxidized ($+4 \rightarrow +6$)
- Oxidation half reaction:

  $SO_2(g) + H_2O(\ell)$

  $\rightarrow SO_4^{2-}(aq) + H_3O^{+}(aq) + 2\ e^{-}$

  $SO_2(g) + 6\ H_2O(\ell)$

  $\rightarrow SO_4^{2-}(aq) + 4\ H_3O^{+}(aq) + 2\ e^{-}$

Review: Balancing Redox Reactions

Example:

$Ag^+(aq) + SO_2(g) + H_2O(\ell)$

$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$

- Reduction half reaction:

  $Ag^+(aq) + e^- \rightarrow Ag(s)$

- Multiply reduction reaction by 2 to balance e^-'s transferred

  $2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$

Review: Balancing Redox Reactions

Example:

$Ag^+(aq) + SO_2(g) + H_2O(\ell)$

$\rightarrow Ag(s) + SO_4^{2-}(aq) + H_3O^+(aq)$

- Add balanced half reaction to get net reaction

  $SO_2(g) + 6\ H_2O(\ell) \rightarrow SO_4^{2-}(aq) + 4\ H_3O^+(aq) + 2\ e^-$

  $2\ Ag^+(aq) + 2\ e^- \rightarrow 2\ Ag(s)$

  $SO_2(g) + 2\ Ag^+(aq) + 6\ H_2O(\ell) \rightarrow$

  $SO_4^{2-}(aq) + 2\ Ag(s) + 4\ H_3O^+(aq)$

Electrochemical Cells

- When two half reactions are connected, we get an electrochemical cell that can generate a voltage potential and electrical current

Electrochemical Cells

Oxidation occurs at the **anode**

Reduction occurs at the **cathode**

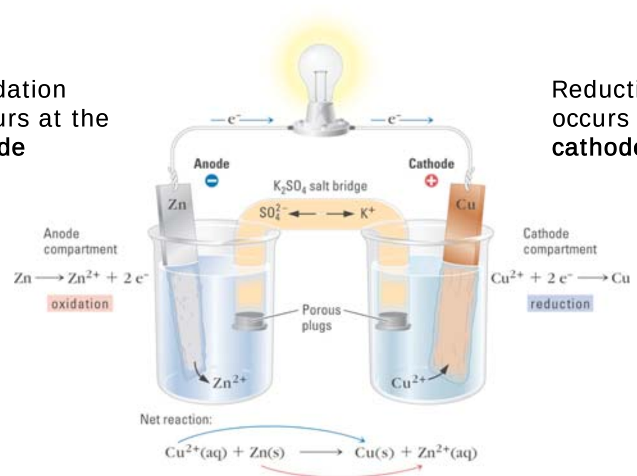

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Figure 19.3

Electrochemical Cells

- Each half reaction has an electrical potential, E
- Electrical potential is a measure of how easily a species is reduced
  - e^-'s added to the species to reduce its oxidation state
- The emf (electromotive force) of a cell is a measure of how much work that cell can do

Electrochemical Cells

- Work for a cell is defined as:
  - Work = q • E (q = charge)
- The potential difference (E) is measured in volts (V)
- Work is measured in units of joules (J)
- Charge is measured in coulombs
  - 1 e^- has a charge of 1.602×10^{-19} C
- 1 V = 1 J/1 C

Electrochemical Cells

- Power for a cell is defined as:
  - Power ≡ work/time = E • I
- I is the current of the cell (charge/unit time): I = E/R
  - R = resistance of circuit
  - I is measured in amperes (1 A = 1 C/s)
- Power is measured in watts
  - 1 W = 1 J/s = V·A

Electrochemical Cells

- The emf of a cell is determined by taking the difference between the potentials of the cathode and the anode:

  $E_{cell} = E_{cathode} – E_{anode}$
- If E_{cell} is positive the electrochemical reaction will proceed as written
- If E_{cell} is negative, the reverse reaction will occur

Electrochemical Cells

- Values for the potential of various half reactions can be found in tables
- Values are listed under standard conditions
  - Gas phase species have a pressure of 1 atm
  - Aqueous species have a concentration of 1 M
- Tables give as standard reduction potentials, E^o

Electrochemical Cells

Examples: (from Appendix I)

$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$ $E^o = 1.82$ V

$Au^{3+}(aq) + 3 e^- \rightarrow Au(s)$ $E^o = 1.50$ V

$Hg_2^{2+}(aq) + 2 e^- \rightarrow 2 Hg(\ell)$ $E^o = .789$ V

$I_2(s) + 2 e^- \rightarrow 2 I^-(aq)$ $E^o = .535$ V

$2 H_3O^+(aq) + 2 e^- \rightarrow H_2(g) + 2 H_2O$ $E^o = 0.000$ V

$PbSO_4(s) + 2 e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$ $E^o = -.356$ V

$Cd^{2+}(aq) + 2 e^- \rightarrow Cd(s)$ $E^o = -.403$ V

$Li^+(aq) + e^- \rightarrow Li(s)$ $E^o = -3.045$ V

Electrochemical Cells

- Electrical potential cannot be measured on an absolute scale
- The standard hydrogen electrode (SHE) is defined as a reference electrode with a potential of E^o = 0.00000000000 V
- Potentials of all other half reaction are measured relative to the SHE

Electrochemical Cells

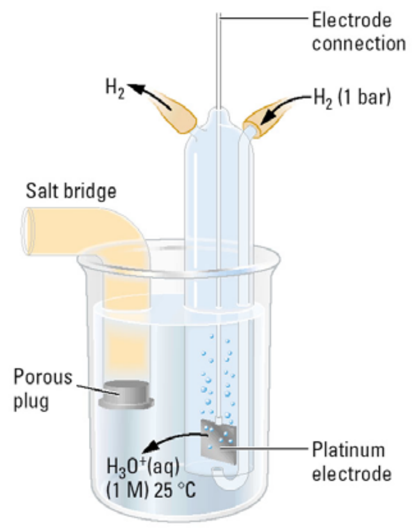

Figure 19.7

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Electrochemical Cells

Example:

Determine potential when a copper electrode in a solution of copper nitrate is connected to a nickel electrode in a solution of nickel nitrate

Step 1: write balanced half reactions for each electrode (it doesn't matter yet which electrode you select as the anode and which as the cathode)

$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$ $E^o = -.25$ V

$Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$ $E^o = -.337$ V

When you flip a redox eqn., you change the sign of E^o

Electrochemical Cells

Example:

Step 2: if necessary, multiply half reaction by factor to balance e^-'s transferred

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $E^o = .337$ V

$Ni(s) \rightarrow Ni^{2+}(aq) + 2\ e^-$ $E^o = .25$ V

Step 3: add half reactions to get net reaction, and add potentials to get net cell potential

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

$E^o = .59$ V

Because E^o for the cell is positive, the reaction proceeds as written

Electrochemical Cells

Example:

Determine E^o for a Mg^{2+} solution with Pt electrode connected to a Ag^+ solution with a Ag electrode

Step 1: write balanced half reactions

$Mg^{2+}(aq) + 2\ e^- \rightarrow Mg(s)$ $E^o = -2.37$ V

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E^o = -.789$ V

Electrochemical Cells

Example:

Step 2: multiply anode reaction by 2 to balance e^-'s

$2\ Ag(s) \rightarrow 2\ Ag^+(aq) + 2\ e^-$ $E^o = -.789$ V

E^o is a function only of the species being reduced or oxidized, not by how many there are

We do not multiply the value of E^o by the same factor used to balance the e^-'s transferred

Electrochemical Cells

Example:

Step 3: add half reaction and E°'s to get results

$Mg^{2+}(aq) + 2\,e^- \rightarrow Mg(s)$ $E^o = -2.37\ V$

$\underline{2\,Ag(s) \rightarrow 2\,Ag^+(aq) + 2\,e^- \quad E^o = -.789\ V}$

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

$E^o = -3.16\ V$

Because E° is negative, the reverse reaction occurs

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

$E^o = 3.16\ V$

Electrochemical Cells

- Shorthand notation for electrochemical cells
  - Phase changes are represented by a single vertical line
  - Salt bridges are represented by double vertical lines
  - Begin with anode reaction (oxidation)

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

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

Electrochemical Cells

- Example:

Write the shorthand notation for the cell:

$H_2(g) + AgCl(s) \rightarrow H^+(aq) + Cl^-(aq) + Ag(s)$

0 +1 -1 +1 -1 0

- H is oxidized; Ag is reduced
- Notation for anode:

$H_2(g),Pt|H^+(aq)$

- Notation for cathode:

$Cl^-(aq),AgCl(s)|Ag(s)$

- Overall:

$H_2(g),Pt|H^+(aq)||Cl^-(aq),AgCl(s)|Ag(s)$

E^o and ΔG^o

- The electrochemical potential, E^o, and Gibb's free energy, ΔG^o, are related:

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

n = # electrons transferred

F = Faraday's Constant

= $N_A \cdot$charge of electron

= $(6.022 \times 10^{23}\ mol^{-1})(1.602 \times 10^{-19}\ C)$

= 96,490 C/mol

E^o and ΔG^o

- Reminder:
  - an electrochemical rxn occurs spontaneously if E is positive
  - Any rxn is spontaneous if ΔG is negative
- If E^o is positive, then ΔG^o must be negative

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

E^o and ΔG^o

<u>Example:</u>

Find ΔG^o for the reaction

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

$E^o = 3.16$ V

2 e^-'s are transferred in the process

$\Delta G^o = -(2)(96500\ C/mol)(3.16\ J/C)$

$= -609.9$ kJ/mol

E^o, ΔG^o, and K

- Since we know relation between ΔG^o and E^o and between ΔG^o and K, we can determine equilibrium constant for electrochemical reaction

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

$\Delta G^o = -RT \ln K$

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

$$E^o = \frac{RT}{nF}\ln K = \frac{.0257\ V}{n}\ln K$$

at T = 298 K

E^o, ΔG^o, and K

- If we convert from natural log to common log (base 10), we get

$$E^o = \frac{.0592\ V}{n}\log K$$

at T = 298 K

or

$$K = 10^{\left(\frac{nE^o}{.0592\ V}\right)}$$

Concentration and E^o

- E at non-standard concentrations can be determined from our knowledge of ΔG under non-standard conditions:

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

  Substituting $\Delta G = -nFE$ gives:

  $-nFE_{cell} = -nFE^o_{cell} + RT \ln Q$

  Divide by –nF:

  $E_{cell} = E^o_{cell} - RT/nF \ln Q$

$$E_{cell} = E^o_{cell} - \frac{.0592}{n} \log Q$$

Nernst Equation

Concentration and E^o

Example:

Find potential of the following cell:

$Cu(s)|Cu^{2+}(.0037M)||Ag^{+}(.016M)|Ag(s)$

Step 1: write half reactions w/ E^o's

oxidation: $Cu(s) \rightarrow Cu^{2+} + 2e^-$ $E^o = -.337$ V

reduction: $Ag^+ + e^- \rightarrow Ag(s)$ $E^o = .799$ V

Step 2: write balanced net reaction

$Cu(s) + 2Ag^+ \rightarrow Cu^{2+} + 2Ag(s)$ $E^o = .462$ V

Concentration and E°

Example:

Cu(s) + 2 Ag$^+$ → Cu^{2+} + 2 Ag(s) E° = .462 V

Step 3: write expression for Q

$$Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Step 4: solve for E

$$E = E^o - \frac{.0592\ V}{n} \log Q$$

$$= .462\ V - \frac{.0592\ V}{2} \log\left(\frac{.0037}{.016^2}\right)$$

$$= .427\ V$$