Chapter 14 – Fundamentals of Electrochemistry *continued*

Vocabulary:

Oxidation - Loss of electrons (increase oxidation state)

Reduction – Gain of electrons (decrease oxidation state)

Oxidizing agent – Substance that takes electrons (Standard reduction potential is more positive.)

Reducing agent – Substance that gives up electrons (Standard reduction potential is more negative.)

Anode – Electrode that oxidation takes place (positive polarity)

Cathode – Electrode that reduction takes place (negative polarity)

Coulombs – unit of charge

Volt – unit of potential

Ampere – unit of current (coulomb/sec)

Joule – unit of work

Watt – unit of power (work/sec)

Review of Important Electrochem Equations

q (coulombs) = n (moles) x F (Faraday constant, coulombs/mole)

Work (joules) = E (volts) x q (coulombs)

E (volts) = I (Amp) x R (ohms, Ω)

Power (joules/sec) = E (volts) x I (Amp)

ΔG (Gibb's free energy) = - n (moles) x F (Faraday constant) x E (volts)

(This equation shows the thermodynamic importance of the cell potential.)

Cell Potential

For any cell, the measured potential between the anode and the cathode can be calculated:

$$E_{cell} = E_{+} - E_{-}$$

where E_{+} is the calculated potential

for the half - cell (electrode) connected to the (+)

terminal of the potentiometer (reduction reaction)

(the right cell and the right side of the potentiometer, usually)

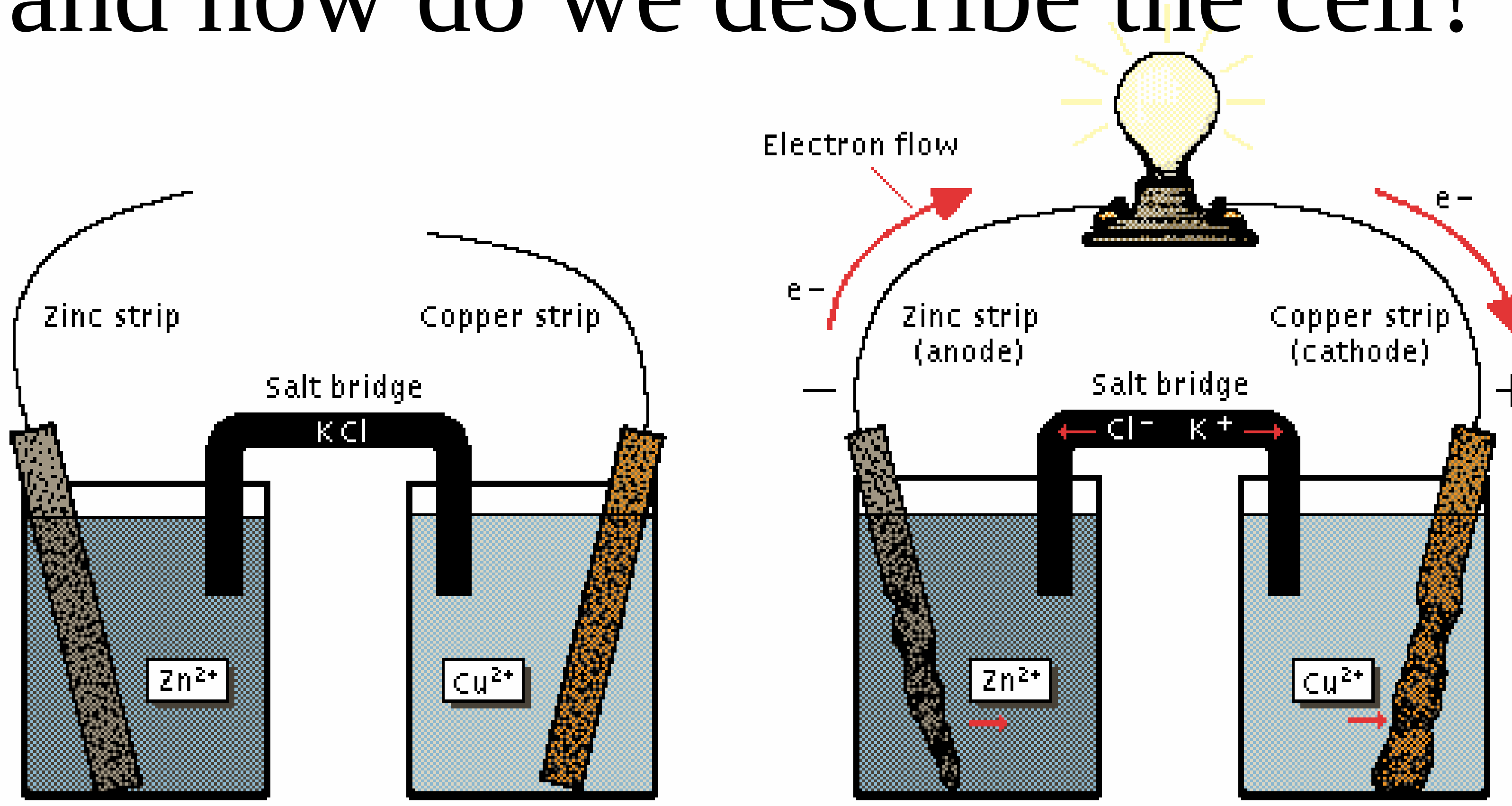
E_{-} is the potential for the half - cell (electrode)

connected to the (-) terminal of the potentiometer (oxidation reaction)

(usually the left side of the potentiometer and the left cell)

NOTE: E_{+} and E_{-} are both reduction potentials

What is happening at the electrode(s) and how do we describe the cell?



Microsoft Illustration

What is happening at the electrode(s) and how do we describe the cell?

$$\text{Anode half-rxn: } Zn^0_{(s)} \Leftrightarrow Zn^{+2}{}_{(aq)} + 2\,e^-$$

$$\text{Cathode half-rxn: } Cu^{+2}_{(aq)} + 2\,e^- \Leftrightarrow Cu^0_{(s)}$$

$$\text{Complete Cell reaction: } Zn_{(s)} + Cu^{+2}{}_{(aq)} \Leftrightarrow Zn^{+2}{}_{(aq)} + Cu^0{}_{(s)}$$

in shorthand, we use symbols!

a single vertical line marks the phase difference

a double vertical line marks the salt bridge

Anode on the left, cathode on the right

Including the counter-ions tells us something about the solutions

$$Zn_{(s)}\,|\,ZnSO_{4(aq)}\,||\,CuSO_{4(aq)}\,|\,Cu_{(s)}$$

The Standard Hydrogen Electrode (SHE)

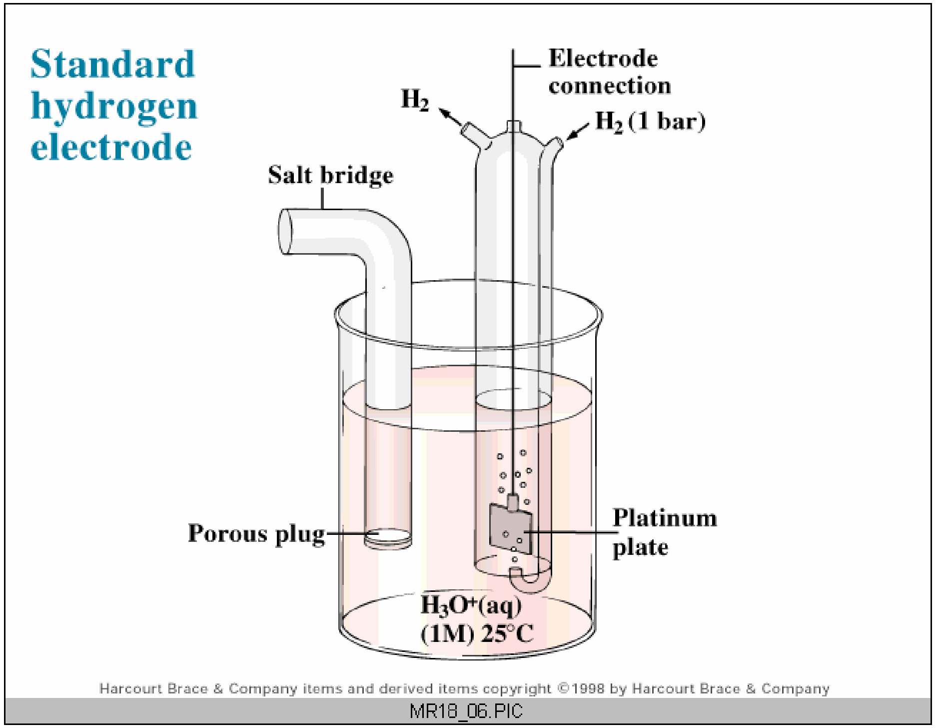
- **The basis by which all other measurements are made.**
- **Assigned a potential of zero by definition!**
- **Not practical for regular use**

Hydrogen Half-Cell

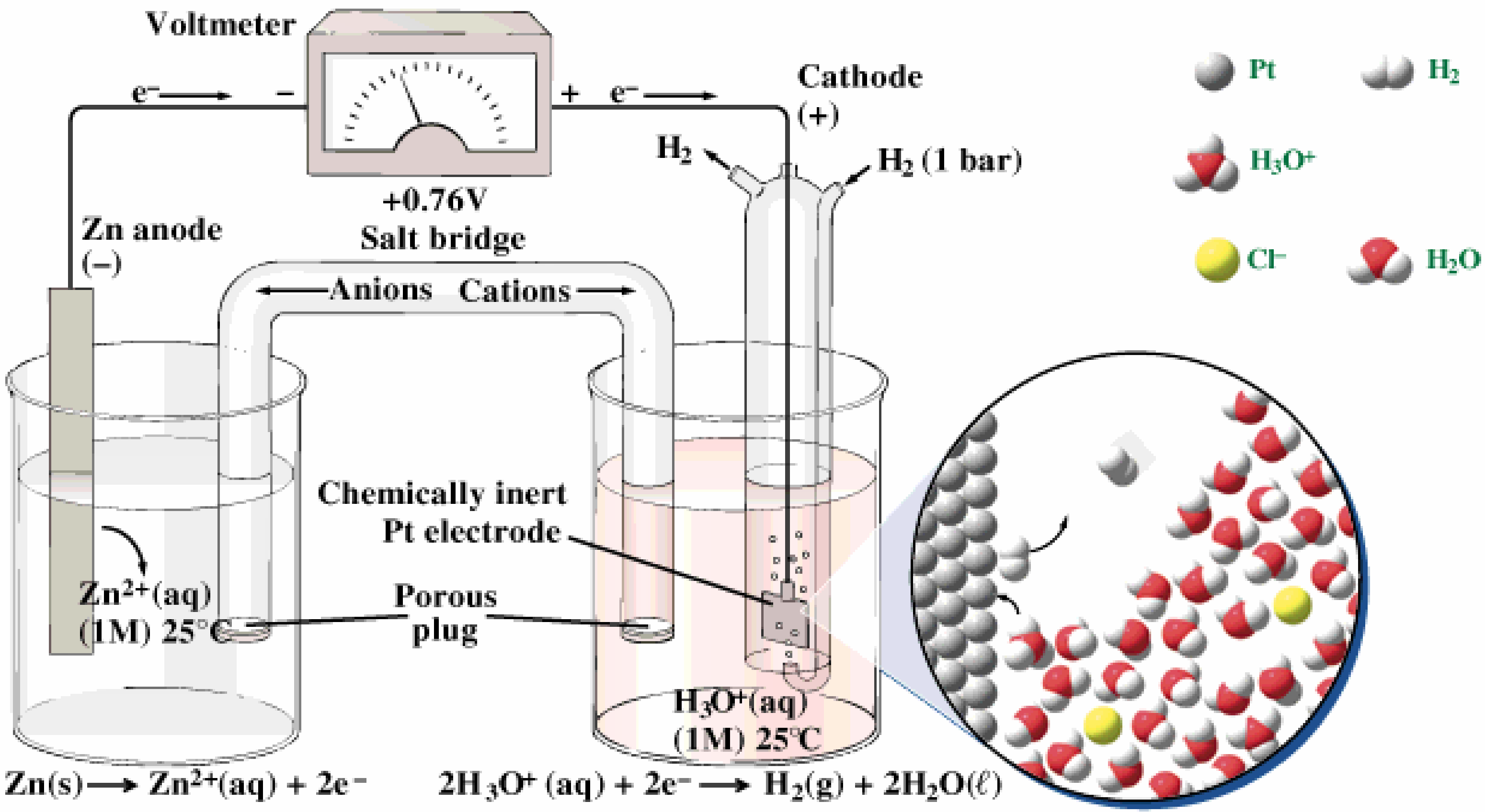
$$H_{2(g)} = 2\,H^{+}_{(aq)} + 2\,e^{-}$$

reversible reaction

SHE consists of a platinum electrode covered with a fine powder of platinum around which $H_{2(g)}$ is bubbled. Its potential is defined as zero volts.



Electrochemical cell using a $Zn^{2+}/Zn(s)$ half-cell and a standard hydrogen electrode



$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ $\quad$ $2H_3O^+(aq) + 2e^- \longrightarrow H_2(g) + 2H_2O(\ell)$

Net reaction: $Zn(s) + 2H_3O^+(aq) \longrightarrow H_2(g) + Zn^{2+}(aq) + 2H_2O(\ell)$

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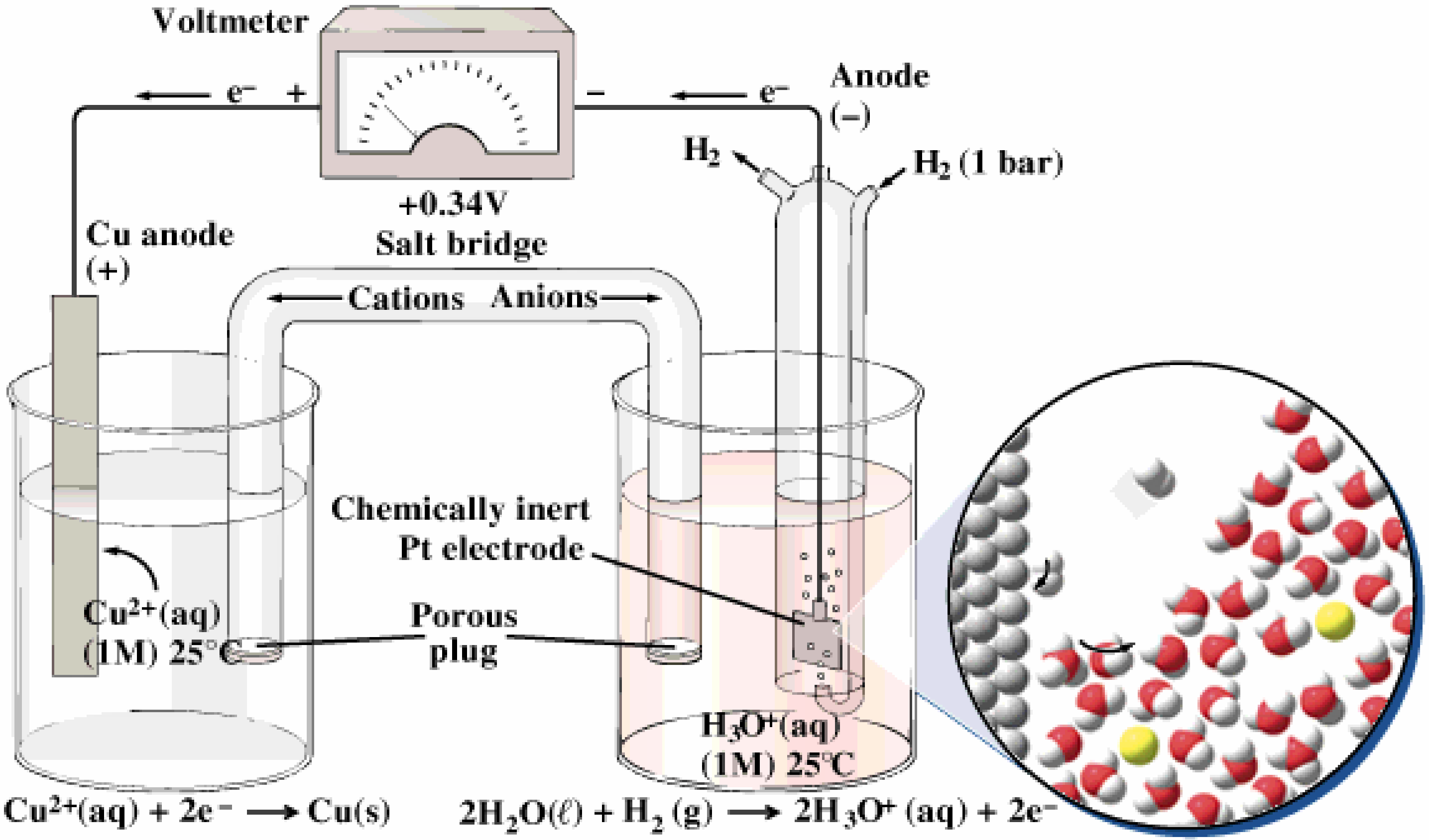
Electrochemical cell using the Cu^{2+}/Cu half-cell and the standard hydrogen electrode



$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $\quad$ $2H_2O(\ell) + H_2(g) \longrightarrow 2H_3O^+(aq) + 2e^-$

Net reaction: $2H_2O(\ell) + H_2(g) + Cu^{2+}(aq) + 2e \longrightarrow 2H_3O^+(aq) + Cu(s)$

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Standard Potentials

- **Standardized potentials (E^o), listed as reductions, for all half-reactions**
- **Measured versus the S.H.E (0)**
- **Used in predicting the action in either a galvanic cell or how much energy would be needed to force a specific reaction in a non-spontaneous cell**
- **Assumes an activity of one for the species of interest (usually a fair approximation) at a known temperature in a cell with the S.H.E.**
- **Assumes that the cell of interest is connected to the (+) terminal of the potentiometer (voltmeter) and the S.H.E. is connected to the (-) terminal**

TABLE 22-1 Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.010
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763

*See Appendix 3 for a more extensive list.

Better Oxidizing Agents in upper left hand corner.

Better Reducing Agents in lower Right hand corner

Calculating E_{cell}

- **Determine E_+ and E_-** *(Even though E_- is an oxidation reaction, the E_- is determined for the reduction reaction then subtracted.)*
- **Calculate E_{cell}**
- **Write a balanced cell reaction, by adding the two half-reactions**
  - **Write out the right cell half reaction**
  - **Write out the left cell half reaction and reverse it**
  - **Add the two reactions together to get a net, balanced cell reaction.**
- **If, you use the conventions described here,then:**
  - **If $E_{cell}>0$, the reaction is spontaneous to the right**
  - **If $E_{cell}<0$, the reaction is spontaneous to the left**

Relationship between E° and the Equilibrium Constant

Recall:

ΔG (Gibb's free energy) = - n (moles) x F (Faraday constant) x E (volts)

K (equilibrium constant) = $e^{-\Delta G/RT}$

K = $e^{-(-nFE°/RT)}$

At 25° C K = $10^{nE°/0.05916}$ or E° = (0.05916/n) log K

Problem - Calculate the E° and K for the following reaction:

$$Cr^{2+} + Fe_{(s)} \Leftrightarrow Fe^{2+} + Cr_{(s)}$$

Nernst Equation

The Nernst equation allows you to determine the cell potential when the activities of the species involved ≠ 1 ***(i.e. non-standard conditions, more typical to real-life)***

For $aA + ne^- \Leftrightarrow bB$

$$E = E° - (RT/nF) \ln (\mathcal{A}_b^{\,b} / \mathcal{A}_a^{\,a})$$

At 25° C:

$$E = E° - (0.05916/n) \log (\mathcal{A}_b^{\,b} / \mathcal{A}_a^{\,a})$$

Nernst Equation

- **Accounts for potentials of cells where the reagents are not at an activity of 1**
  - **Remember that standard potentials are at $\mathcal{A}$=1**
- **Accounts for the number of electrons transferred in a reaction, the temperature of the reaction, LeChatelier's Principle and a variety of other factors**
- **Used to calculate E_+ and E_- under non-standard conditions**
  - **Most real cases!**

The Nernst Equation for Complete Reactions…..

- **Setup two Nernst equations**
  - **One for E_+**
  - **One for E_-**

- **Solve each Nernst equation to get E_+ and E_-**

- **Solve for E_{cell} ($E_{cell} = E_+ - E_-$)**

A galvanic cell is assembled in which the left cell is the anode where cadmium metal electrode is oxidized to cadmium ion in 0.010 M cadmium nitrate. In the right cell, the cathode, silver ion is reduced to silver metal on a silver metal electrode in 0.50 M silver nitrate.

1. Draw the cell (both a picture and a schematic diagram)
2. Write the half and net cell reactions
3. Calculate the net cell voltage
4. Indicate in which direction the cell is spontaneous