

Chapter 14 – Fundamentals of Electrochemistry

Homework - Due Wednesday, March 11

**Problems: 14-5, 14-8, 14-12, 14-15, 14-17,
14-18, 14-25, 14-26, 14-41,**

Electrochemistry

Review of the Basics

- **Oxidation**
 - Loss of electrons
 - Always occurs at the anode
 - Happens because of the action of a reducing agent
- **Reduction**
 - Gain of electrons (charge is reduced)
 - Always occurs at the cathode
 - Happens because of the action of the oxidizing agent



Redox Reaction



Example:





So... $\text{ox}_1 = \text{Fe}^{+3}$, $\text{red}_2 = \text{Sn}^{+2}$, $\text{red}_1 = \text{Fe}^{+2}$, $\text{ox}_2 = \text{Sn}^{+4}$

Electric Charge (in Coulombs) and Work

- The charge in coulombs (q) is equal to the number of moles of electrons (n) times the Faraday Constant (F)
- Voltage represents electrical potential (potential to do work)
- If some total charge in coulombs (q) is moved through some electrical potential (E, in volts V) then work is done!

$$q \text{ (coulombs)} = n \text{ (moles)} \times F \text{ (Faraday Constant)}$$

$$F = \frac{9.649 \times 10^4 \text{ Coulombs}}{\text{mole of } e^-}$$

$$\text{Work (joules)} = E \text{ (volts)} \times q \text{ (coulombs)}$$

Ohm's Law and Power

- Ohm's law relates electrical resistance, current and potential!
- Power is the work done in some unit time (e.g. joules of work per second)
- The units of Power are Watts (W)
- Ohm's law and power are related!

E(potential) = I (current) x R (resistance, in Ohms, Ω)

$$\text{Power (in Watts)} = \frac{\text{Work (joules)}}{\text{second}} = \frac{E \times q}{s}$$

$$\frac{E \times q}{s} = E \times \frac{q}{s} = E \times I$$

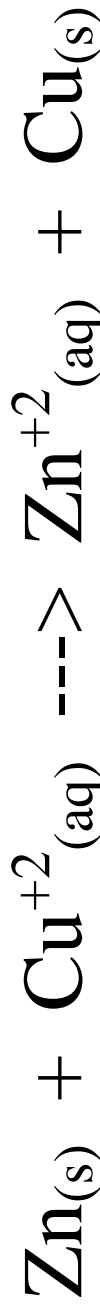
Electrochemical Cells

- A complete cell contains:
 - anode
 - cathode
 - completed circuit (for electrons to flow)
 - a salt bridge (usually!)
 - an electrolyte solution
 - chemical species that undergo reaction.
- There are two basic electrochemical cells:
 - A *GALVANIC* cell uses spontaneous chemical reactions to generate electricity
 - A *ELECTROLYTIC* cell requires an electrical potential to be applied to the cell to drive some reaction.

Galvanic Cell

Cells and Cell Reactions

Overall Cell Reaction

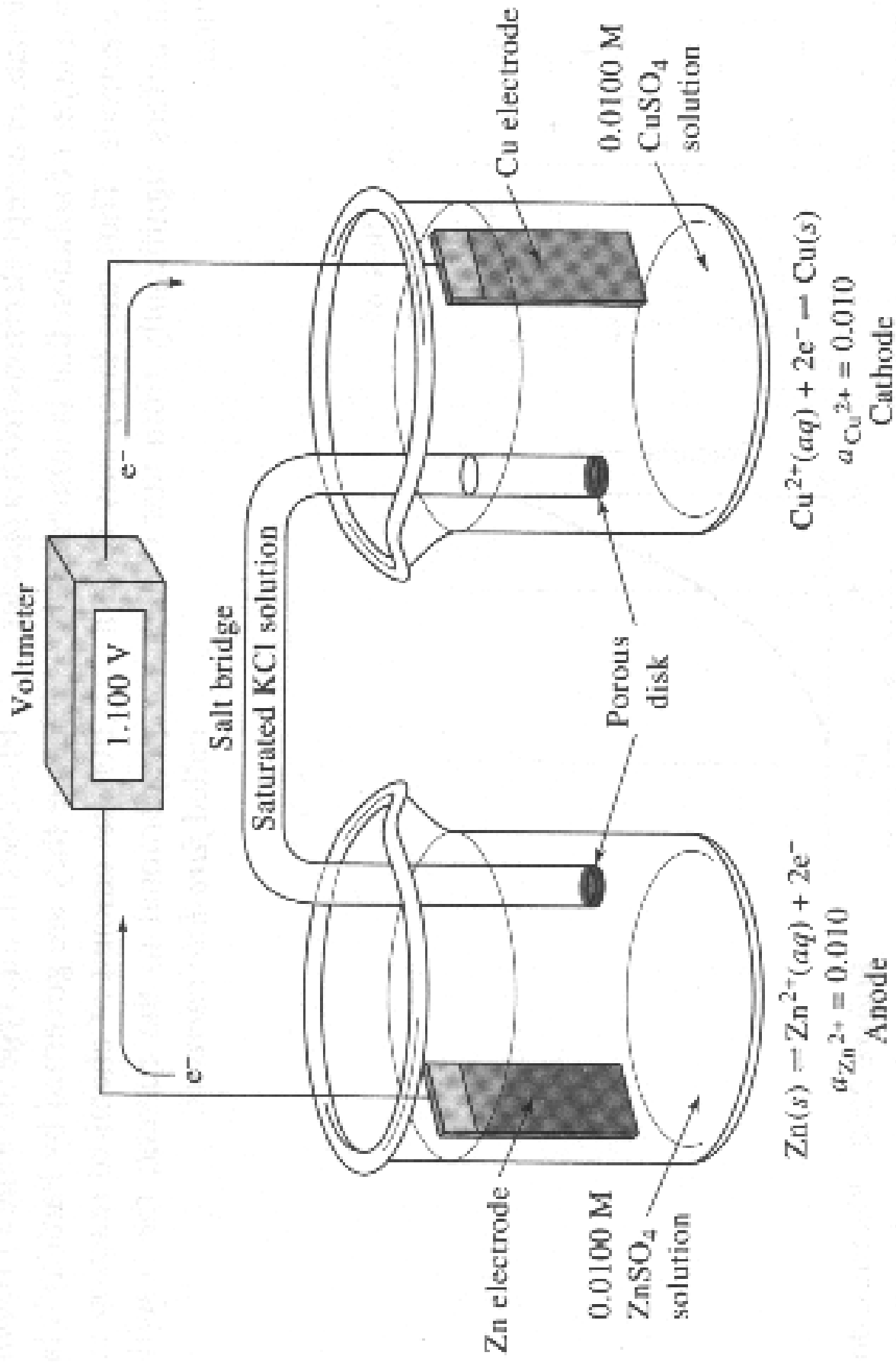


oxidation half reaction



reduction half reaction





Cell Potential

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

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

where E_{+} is the calculated potential

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

terminal of the potentiometer (reduction reaction)

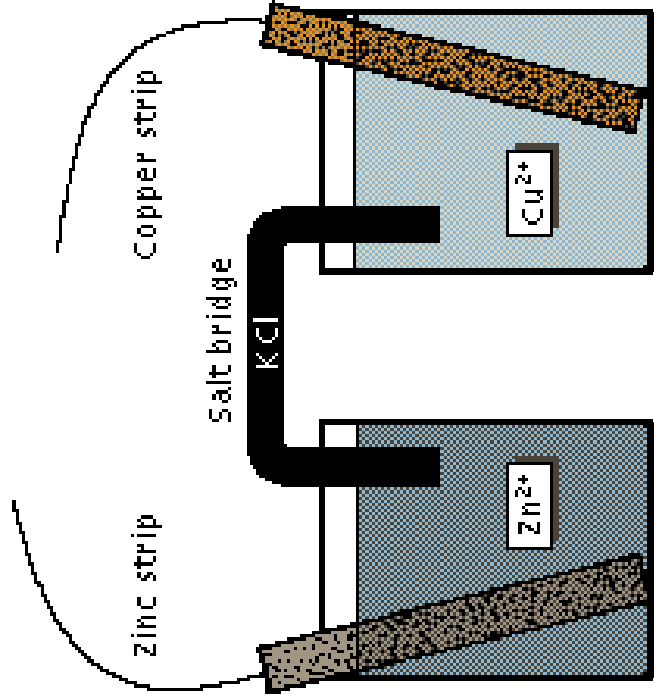
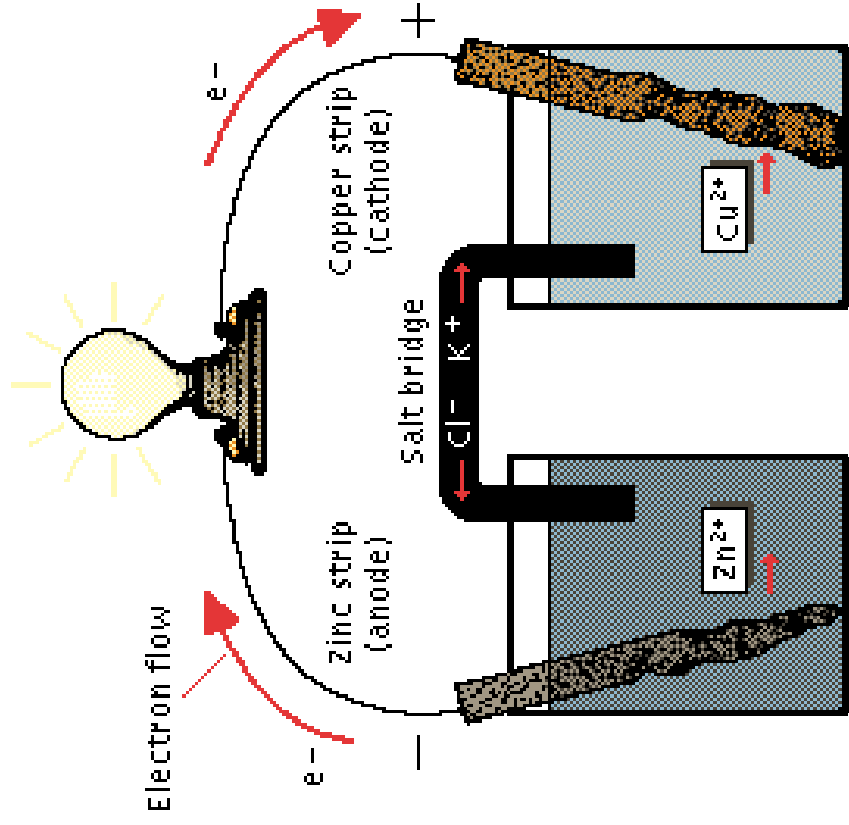
(the right cell and the right side of the potentiometer, usually)

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



Microsoft Illustration

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



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



The Standard Hydrogen Electrode (SHE)

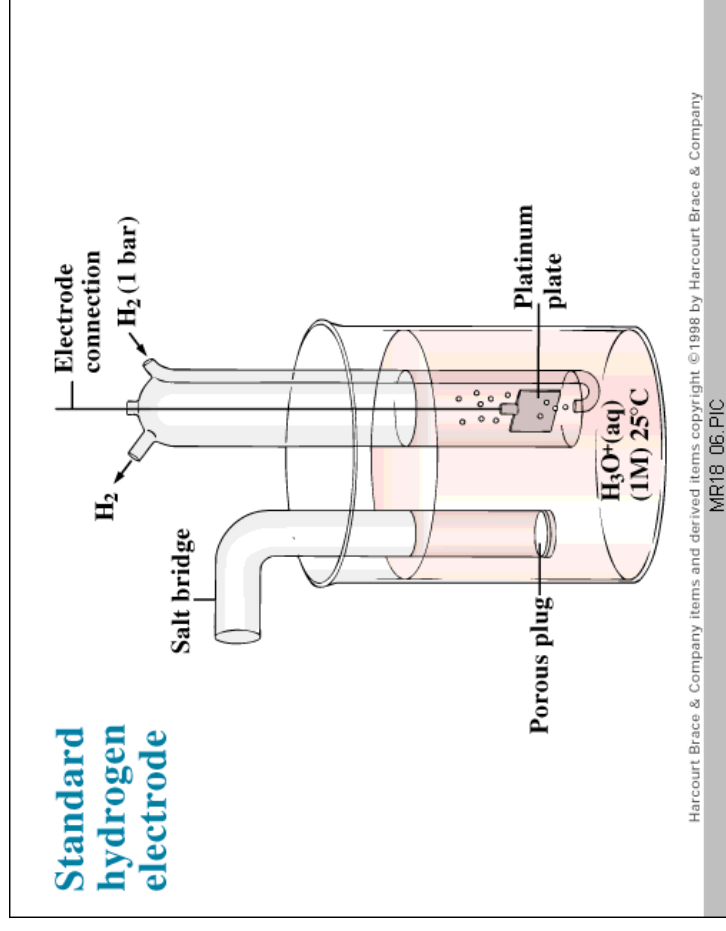
- The basis by which all other measurements are made.
- Assigned a potential of zero by definition!
- Not practical for regular use

Hydrogen Half-Cell

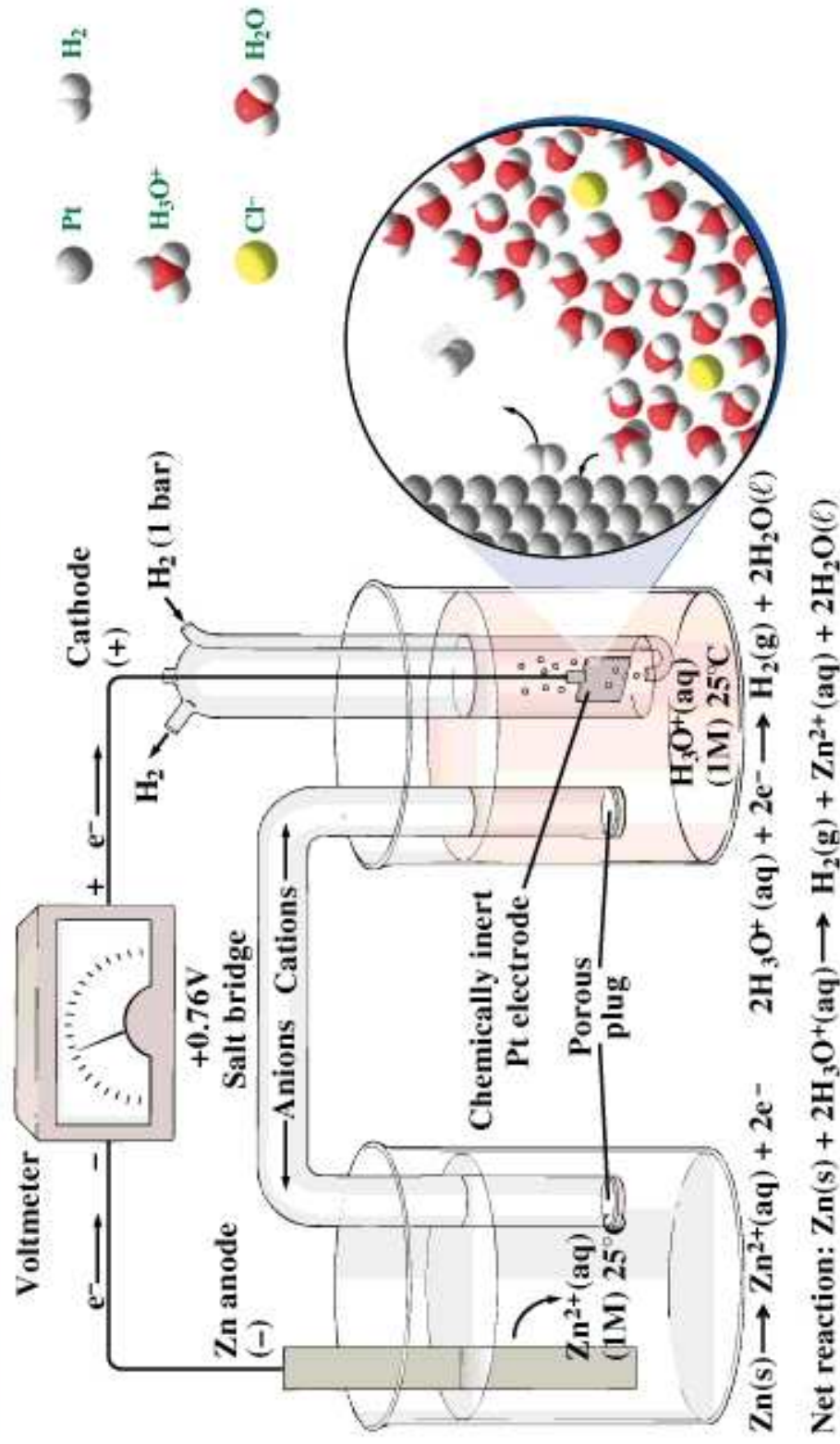


reversible reaction

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



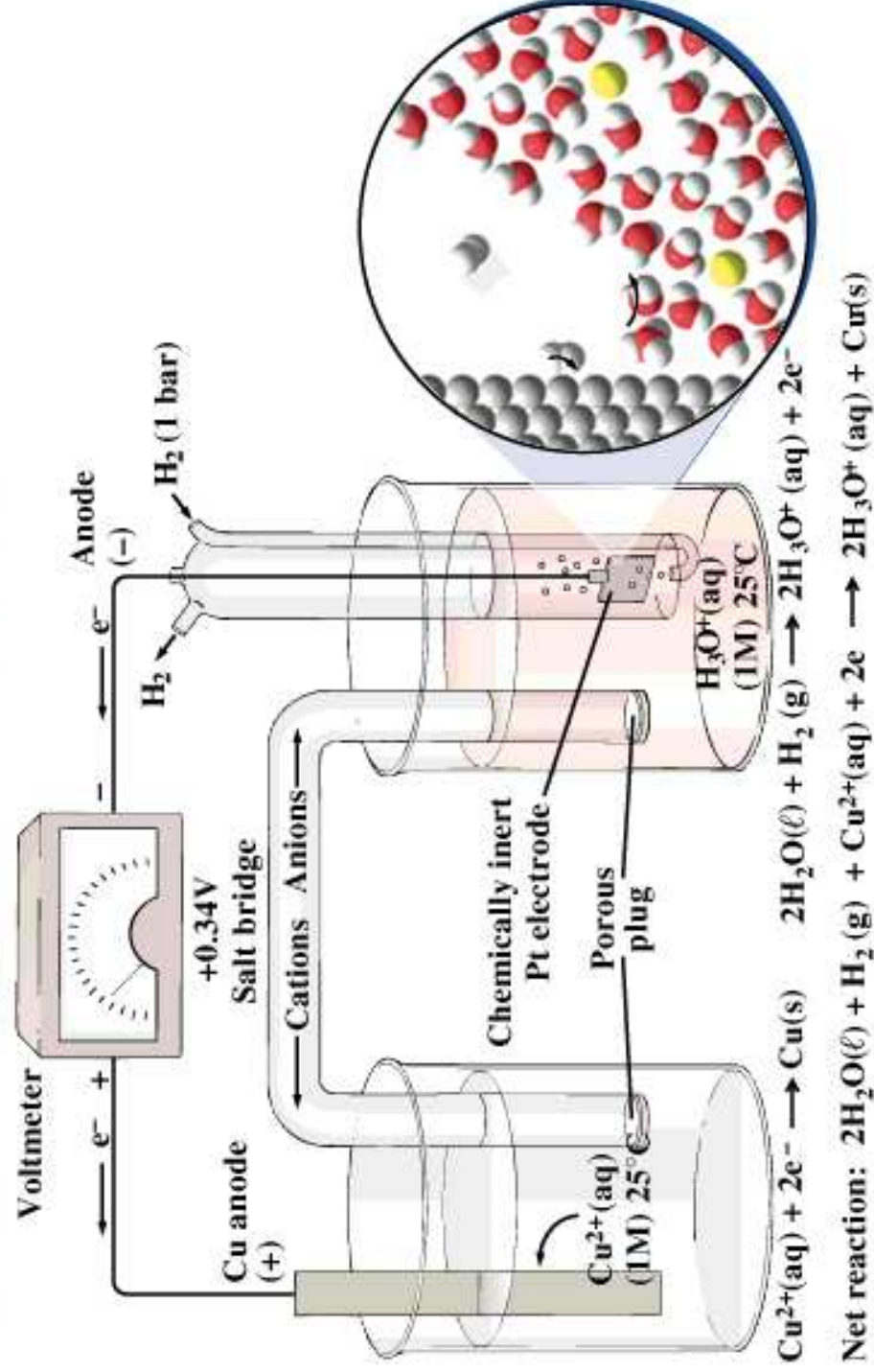
Electrochemical cell using a $Zn^{2+}/Zn(s)$ half-cell and a standard hydrogen electrode



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



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Standard Potentials

- **Standardized potentials (E°), 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
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+ 1.359
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+ 1.229
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+ 1.087
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+ 1.065
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+ 0.799
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+ 0.771
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+ 0.536
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+ 0.337
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+ 0.268
$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+ 0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+ 0.010
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{AgI}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	- 0.151
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	- 0.350
$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$	- 0.403
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	- 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 $E_{\text{cell}} > 0$, the reaction is spontaneous to the right
 - If $E_{\text{cell}} < 0$, the reaction is spontaneous to the left

Relationship between E° and the Equilibrium Constant

Recall:

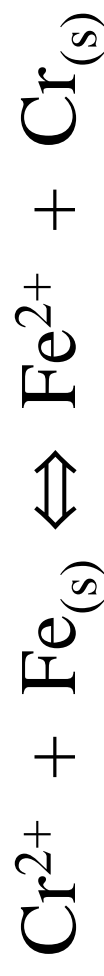
$$\Delta G \text{ (Gibb's free energy)} = - n \text{ (moles)} \times F \text{ (Faraday constant)} \times E \text{ (volts)}$$

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

$$K = e^{-(-nFE^\circ/RT)}$$

$$\text{At } 25^\circ \text{ C} \quad K = 10^{nE^\circ/0.05916} \quad \text{or} \quad E^\circ = (0.05916/n) \log K$$

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



Nernst Equation

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

For



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

At 25° C:

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

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!**