

### Review: Balancing Redox Reactions

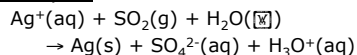
- Determine which species is oxidized and which species is reduced
  - Oxidation corresponds to an increase in the oxidation number of an element
  - Reduction corresponds to a decrease in the oxidation number of an element
- Write half reactions for oxidation and reduction processes
  - Oxidation reaction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

### Review: Balancing Redox Reactions

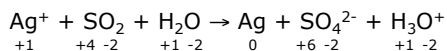
- Balance half reactions including charge balance
- Multiply each half reaction by a factor so that the total number of e<sup>-</sup>'s transferred in each reaction are equal
- Add the resulting half reactions together to get the overall balanced redox equation

### Review: Balancing Redox Reactions

#### Example:

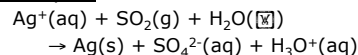


- Determine oxidation state of each element in reaction:

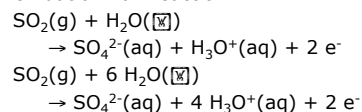


### Review: Balancing Redox Reactions

#### Example:

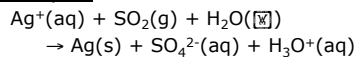


- Ag is reduced (+1 → 0)
- S is oxidized (+4 → +6)
- Oxidation half reaction:



### Review: Balancing Redox Reactions

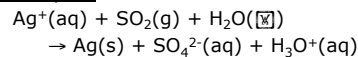
#### Example:



- Reduction half reaction:  
 $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$
- Multiply reduction reaction by 2 to balance e<sup>-</sup>'s transferred  
 $2 \text{Ag}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Ag}(\text{s})$

### Review: Balancing Redox Reactions

#### Example:



- Add balanced half reaction to get net reaction  
 $\text{SO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^-$   
 $2 \text{Ag}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Ag}(\text{s})$
- $\text{SO}_2(\text{g}) + 2 \text{Ag}^+(\text{aq}) + 6 \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 2 \text{Ag}(\text{s}) + 4 \text{H}_3\text{O}^+(\text{aq})$

## Electrochemical Cells

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

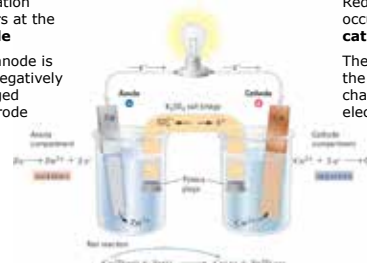
## Electrochemical Cells

Oxidation occurs at the **anode**

The anode is the negatively charged electrode

Reduction occurs at the **cathode**

The cathode is the positively charged electrode



## Electrochemical Cells

- Each half reaction has an electrical potential,  $E$
- Electrical potential is a measure of how easily a species is reduced
  - e<sup>-</sup>'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 =  $q \cdot E_{\text{cell}}$
  - Work =  $n \cdot F \cdot E_{\text{cell}}$
- The potential difference ( $E_{\text{cell}}$ ) is measured in volts
- Charge is measured in coulombs
  - 1 e<sup>-</sup> has a charge of  $1.602 \times 10^{-19}$  C
- $F = 96,470$  C/mol (Faraday's Constant)
- 1 volt = 1 Joule/1 coulomb

## Electrochemical Cells

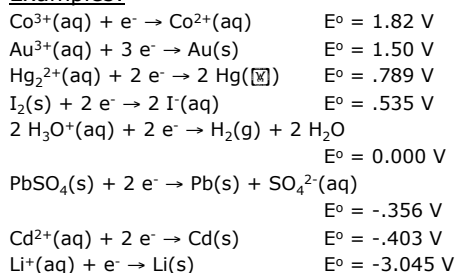
- The emf of a cell is determined by taking the difference between the potentials of the cathode and the anode:
 
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{+} - E_{-}$$
- If  $E_{\text{cell}}$  is positive the electrochemical reaction will proceed as written
- If  $E_{\text{cell}}$  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 activity of 1
- Tables give standard reduction potentials,  $E^{\circ}$  (Appendix H)

## Electrochemical Cells

### Examples:



## 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  $E^{\circ} = 0.0000000000 \text{ V}$
- Potentials of all other half reaction are measured relative to the SHE

## Electrochemical Cells

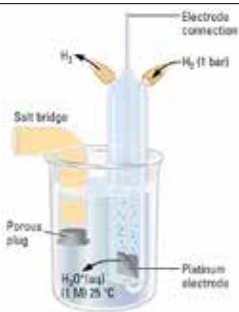


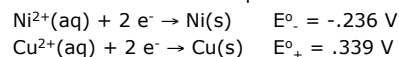
Figure 19.7

## Electrochemical Cells

### Example:

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

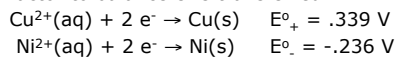
**Step 1:** write balanced half reactions for each electrode—the cathode is always the electrode with the more positive  $E^{\circ}$



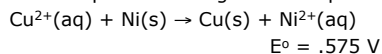
## Electrochemical Cells

### Example:

**Step 2:** if necessary, multiply half reaction by factor to balance  $\text{e}^{-}$ 's transferred



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



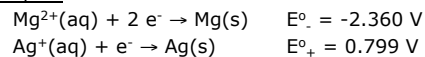
Because  $E^{\circ}$  for the cell is positive, the reaction proceeds as written

## Electrochemical Cells

### Example:

Determine  $E^{\circ}$  for a  $\text{Mg}^{2+}$  solution with Pt electrode connected to a  $\text{Ag}^{+}$  solution with a Ag electrode

**Step 1:** write balanced half reactions



## Electrochemical Cells

### Example:

Step 2: multiply anode reaction by 2 to balance e<sup>-</sup>'s



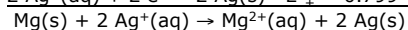
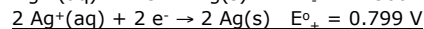
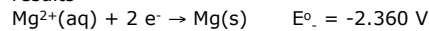
E<sup>o</sup> is a function only of the species being reduced or oxidized, not by how many there are

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

## Electrochemical Cells

### Example:

Step 3: add half reaction and E<sup>o</sup>'s to get results

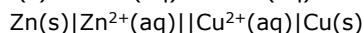
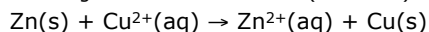


$$E^\circ_{\text{cell}} = E^\circ_{+} - E^\circ_{-} = 3.159 \text{ V}$$

## Electrochemical Cells

### o Shorthand notation for electrochemical cells

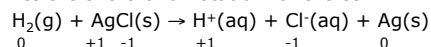
- Phase changes are represented by a single vertical line
- Salt bridges are represented by double vertical lines
- Begin with anode reaction (oxidation)



## Electrochemical Cells

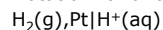
### o Example:

Write the shorthand notation for the cell:

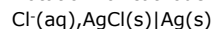


o H is oxidized; Ag is reduced

o Notation for anode:



o Notation for cathode:



o Overall:



## E<sup>o</sup> and ΔG<sup>o</sup>

o The electrochemical potential, E<sup>o</sup>, and Gibb's free energy, ΔG<sup>o</sup>, are related:

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

n = # electrons transferred

F = Faraday's Constant

$$= 96,470 \text{ C/mol}$$

## E<sup>o</sup> and ΔG<sup>o</sup>

o Reminder:

- an electrochemical rxn occurs spontaneously if E is positive
- Any rxn is spontaneous if ΔG is negative

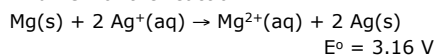
o If E<sup>o</sup> is positive, then ΔG<sup>o</sup> must be negative

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

## $E^\circ$ and $\Delta G^\circ$

### Example:

Find  $\Delta G^\circ$  for the reaction



2 e<sup>-</sup>'s are transferred in the process

$$\Delta G^\circ = -(2)(96500 \text{ C/mol})(3.16 \text{ J/C}) \\ = -609.9 \text{ kJ/mol}$$

## $E^\circ$ , $\Delta G^\circ$ , and K

- Since we know relation between  $\Delta G^\circ$  and  $E^\circ$  and between  $\Delta G^\circ$  and K, we can determine equilibrium constant for electrochemical reaction

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

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

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

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

at T = 298 K

## $E^\circ$ , $\Delta G^\circ$ , and K

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

$$E^\circ = \frac{.0592 \text{ V}}{n} \log K \quad \text{at T} = 298 \text{ K}$$

or

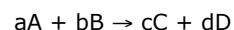
$$K = 10^{\left(\frac{nE^\circ}{.0592 \text{ V}}\right)}$$

## Concentration and $E^\circ$

- E at non-standard concentrations can be determined from our knowledge of  $\Delta G$  under non-standard conditions:

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

- Q is called the *Reaction Quotient*—same mathematical form as  $K_{eq}$



$$Q = \frac{A_C^c A_D^d}{A_A^a A_B^b} \quad A_x \text{ is activity of species X}$$

## Concentration and $E^\circ$

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

Substituting  $\Delta G = -nFE$  gives:

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

Divide by  $-nF$ :

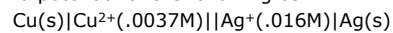
$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E_{cell}^\circ - \frac{.0592}{n} \log Q \quad \text{Nernst Equation}$$

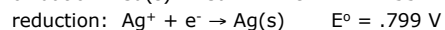
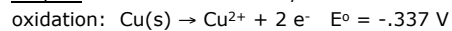
## Concentration and $E^\circ$

### Example:

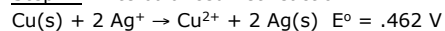
Find potential of the following cell:



**Step 1:** write half reactions w/  $E^\circ$ 's

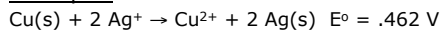


**Step 2:** write balanced net reaction



## Concentration and $E^\circ$

### Example:



Step 3: write expression for Q:

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

Step 4: solve for E

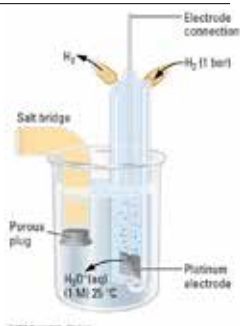
$$\begin{aligned} E &= E^\circ - \frac{.0592 \text{ V}}{n} \log Q \\ &= .462 \text{ V} - \frac{.0592 \text{ V}}{2} \log\left(\frac{.0037}{.016^2}\right) \\ &= .427 \text{ V} \end{aligned}$$

## Electrodes

- When constructing an electrochemical cell, we need two electrodes—the cathode (reduction) and the anode (oxidation)
- To use electrochemistry as an analytical technique, one electrode must serve as a reference electrode that produces a known value of E
- Total  $E_{\text{cell}}$  then depends on concentration of analyte

## Reference Electrodes

- The standard hydrogen electrode (SHE) could be used as a reference  
 $\text{Pt}|\text{H}_2(\text{g})[1 \text{ atm}]|\text{H}^+$   
 $[A=1]$   
 $E^\circ = 0.000 \text{ V}$



## Reference Electrodes

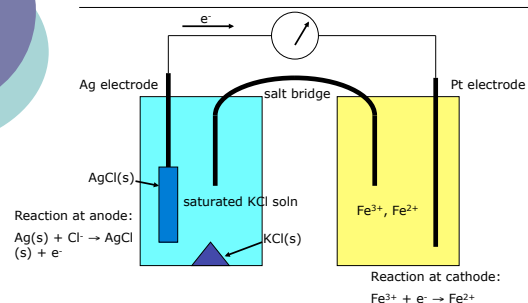
- Although  $E^\circ$ 's are measured relative to the standard hydrogen electrode, it is impractical to use the SHE in normal applications
- A number of reference electrodes have been developed that provide ease of use and stable  $E^\circ$ 's

## Reference Electrodes

### Ag|AgCl Electrode

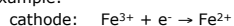
- $\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq}) \quad E^\circ = 0.222 \text{ V}$
- If the solution surrounding the electrode is saturated with KCl so the  $[\text{Cl}^-]$  remains constant, then this electrode maintains a constant potential of  $E = 0.197 \text{ V}$   
 $\text{Ag(s)}|\text{AgCl(s)}|\text{Cl}^-(\text{aq})[\text{sat'd}]$

## Reference Electrodes

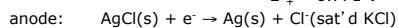


## Reference Electrodes

Example:



$$E^{\circ}_+ = 0.771 \text{ V}$$



$$E^{\circ}_- = 0.222 \text{ V}$$

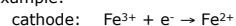
We can now write expressions for the potentials of each electrode:

$$E_+ = E^{\circ}_+ - \frac{.0592}{1} \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right)$$

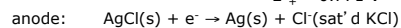
$$E_- = E^{\circ}_- - \frac{.0592}{1} \log [\text{Cl}^-] = 0.197 \text{ V}$$

## Reference Electrodes

Example:



$$E^{\circ}_+ = 0.771 \text{ V}$$



$$E^{\circ}_- = 0.222 \text{ V}$$

The potential for the cell is:

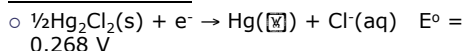
$$E_{\text{cell}} = E_+ - E_-$$

$$= .771 - .0592 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) - \{ .222 - .0592 \log [\text{Cl}^-] \}$$

However, because the anode is saturated with KCl,  $[\text{Cl}^-]$  is constant, so the cell potential depends only on the concentrations of  $[\text{Fe}^{3+}]$  and  $[\text{Fe}^{2+}]$

## Reference Electrodes

### Calomel Electrode

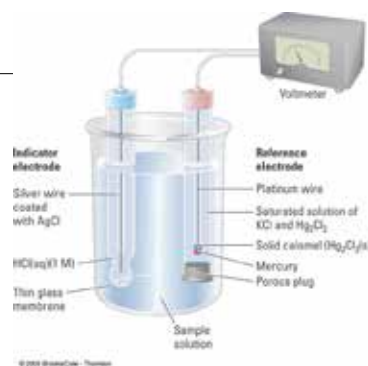


- If the solution surrounding the electrode is saturated with KCl so the  $[\text{Cl}^-]$  remains constant, then this electrode maintains a constant potential of  $E = 0.241 \text{ V}$



- This is referred to as the SCE—saturated calomel electrode

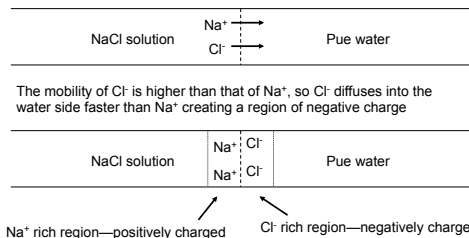
## SCE



## Junction Potentials

- Anytime electrolyte solution with different concentrations are in contact, a junction potential is formed
- The gradient in concentrations induces movement from higher concentration side of contact region to lower concentration side
- Differing mobilities of ions create regions in the solution where charge builds up

## Junction Potentials



### Junction Potentials

- The negatively charged, Cl<sup>-</sup> rich region inhibits further movement of Cl<sup>-</sup> and enhances movement of Na<sup>+</sup> to the right
- The resulting separation of charge creates an electrical potential that contributes to the potential measured for a galvanic cell
- Junction potentials are on the order of mV, but depending on E<sub>cell,r</sub>, may introduce significant error in the analysis of an analyte

### Indicating Electrodes

- The indicating electrode is designed to detect the analyte species
- There are several varieties of indicating electrodes:
  - Metal electrodes: used to detect metal ions electrode is made of metal being analyzed
  - Ion-selective electrodes: designed to detect a specific analyte ion—no redox chemistry involved

### Indicating Electrodes

- There are two types of indicating electrodes we will discuss—metal electrodes and ion specific electrodes
- Metal electrodes use the metal of interest as the electrode material and detect metal ion in solution
 

SCE || Cu<sup>+</sup>(A<sub>Cu+</sub>=unknown) | Cu(s)

$$\text{Cu}^+ + e^- \rightarrow \text{Cu}(s) \quad E^\circ = 0.518 \text{ V}$$

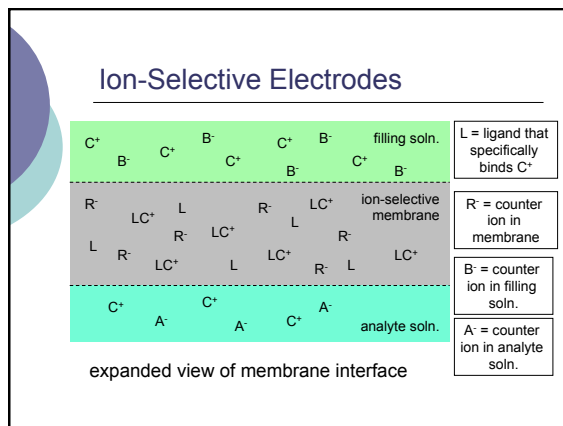
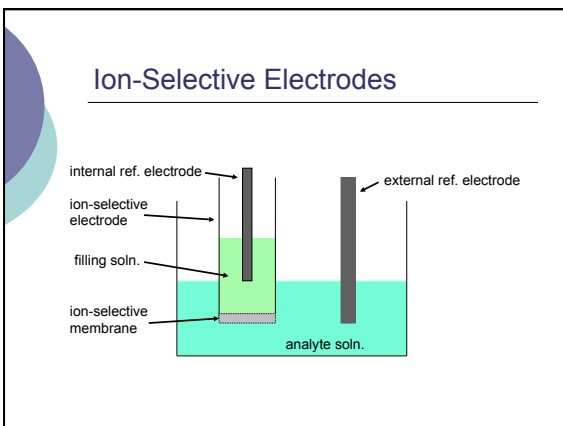
$$E_+ = .518\text{V} - .0592 \log\{1/(A_{\text{Cu}^+})\}$$

$$E_{\text{cell}} = E_+ - E_{\text{ref}} = .518\text{V} - .0592 \log\{1/(A_{\text{Cu}^+})\} - .241\text{V}$$

$$p\text{Cu} = -\log(A_{\text{Cu}^+}) = (.277 - E_{\text{cell}})/.0592$$

### Cell Potential

- The total potential of a cell containing an indicator electrode and a reference electrode is:
 
$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}}$$



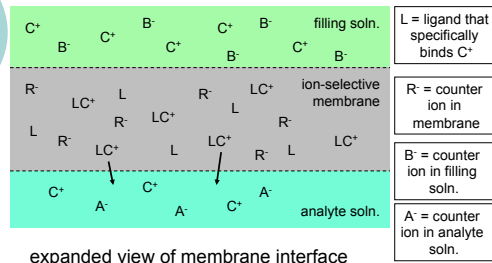


### Indicating Electrodes

- Membrane allows transport of  $C^+$  across interface, but not  $A^-$ ,  $R^-$ , or  $B^-$
- The  $[C^+]$  is greater in the membrane than in analyte solution
- As  $C^+$  moves into analyte solution, an electrical potential forms across the interface

The resulting charge imbalance in the membrane limits the amount of  $C^+$  that can move across the membrane interface

### Ion-Selective Electrodes



### Indicating Electrodes

$$\Delta G = \Delta G_{\text{solv}} + \Delta G_{\text{change in activity of } C^+}$$

$\Delta G_{\text{solv}}$  arises from difference in solvents between membrane and analyte solution

$$\Delta G = \Delta G_{\text{solv}} - RT \ln(a_{\text{Mem}}/a_{\text{Out}})$$

$a_{\text{Mem}}$  = activity of  $C^+$  in membrane  
 $a_{\text{Out}}$  = activity of  $C^+$  in outer (analyte) soln.

### Indicating Electrodes

The potential difference across the membrane interface creates a free energy contribution:

$$\Delta G = -nFE_{\text{O}} \quad n = \text{charge on } C^+$$

At equilibrium, the total free energy of the system must be zero:

$$\Delta G_{\text{solv}} - RT \ln(a_{\text{Mem}}/a_{\text{Out}}) - nFE_{\text{Out}} = 0$$

Solving for  $E_{\text{Out}}$  (the potential across the outer interface) gives:

$$E_{\text{O}} = \Delta G_{\text{solv}}/nF - (RT/nF)\ln(a_{\text{Mem}}/a_{\text{Out}})$$

### Indicating Electrodes

There is an analogous term,  $E_{\text{In}}$ , for the interface between the membrane and the filling solution, but because the concentration of  $C^+$  in the filling solution is higher, this potential is essentially constant

### Indicating Electrodes

The total potential for the cell is now:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{Out}} - E_{\text{In}} \\ &= \Delta G_{\text{solv}}/nF - (RT/nF)\ln(a_{\text{Mem}}/a_{\text{Out}}) - E_{\text{In}} \\ &= \Delta G_{\text{solv}}/nF - (RT/nF)\ln(a_{\text{Mem}}) + (RT/nF)\ln(a_{\text{Out}}) - E_{\text{In}} \end{aligned}$$

constant                      constant                      constant

Finally:

$$\begin{aligned} E_{\text{cell}} &= \text{constant} + (RT/nF)\ln(a_{\text{Out}}) \\ &= \text{constant} + (.05916/n)\log(a_{\text{Out}}) \quad \text{at } 25^\circ\text{C} \end{aligned}$$