



## Review: Balancing Redox Reactions

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- 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

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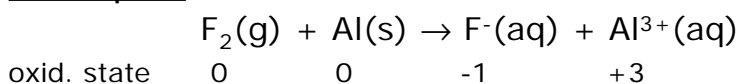
- Balance half reactions including charge balance
- Multiply each half reaction by a factor so that the total number of  $e^-$ 's transferred in each reaction are equal
- Add the resulting half reactions together to get the overall balanced redox equation



## Review: Balancing Redox Reactions

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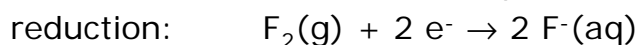
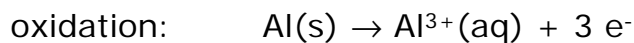
### Example:



Fluorine is reduced (0 → -1)

Aluminum is oxidized (0 → +3)

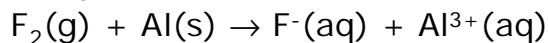
- Half reactions:



## Review: Balancing Redox Reactions

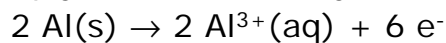
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### Example:

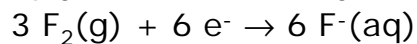


- Balance e<sup>-</sup>'s transferred:

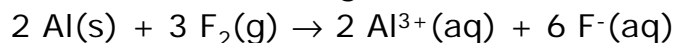
multiply oxidation rxn by 2



multiply reduction rxn by 3



- Add half reaction to get net reaction:



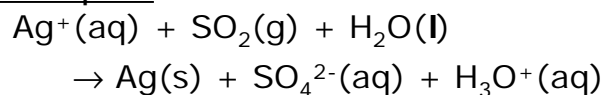
- Check atom and charge balance:



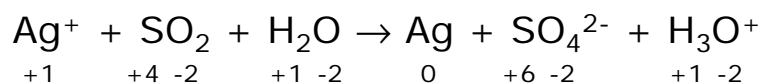
## Review: Balancing Redox Reactions

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### Example:



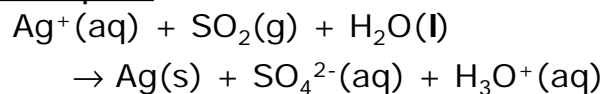
- Determine oxidation state of each element in reaction:



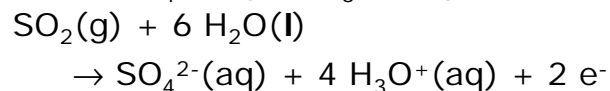
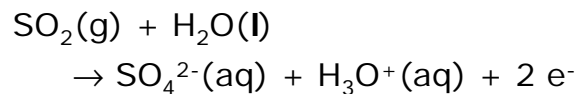
## Review: Balancing Redox Reactions

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### Example:



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

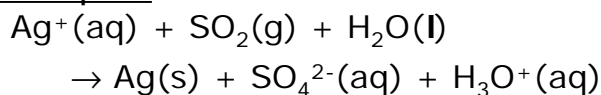




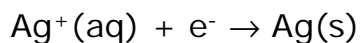
## Review: Balancing Redox Reactions

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### Example:



- Reduction half reaction:



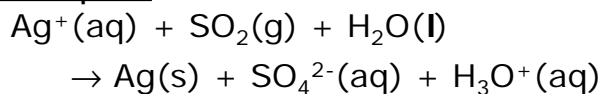
- Multiply reduction reaction by 2 to balance  $\text{e}^-$ 's transferred



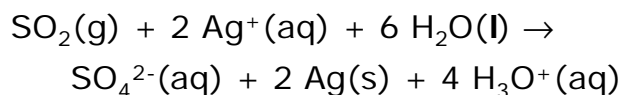
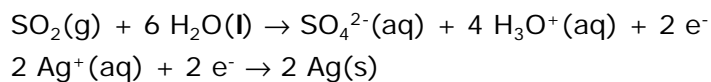
## Review: Balancing Redox Reactions

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### Example:



- Add balanced half reaction to get net reaction



## Electrochemical Cells

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

## Electrochemical Cells

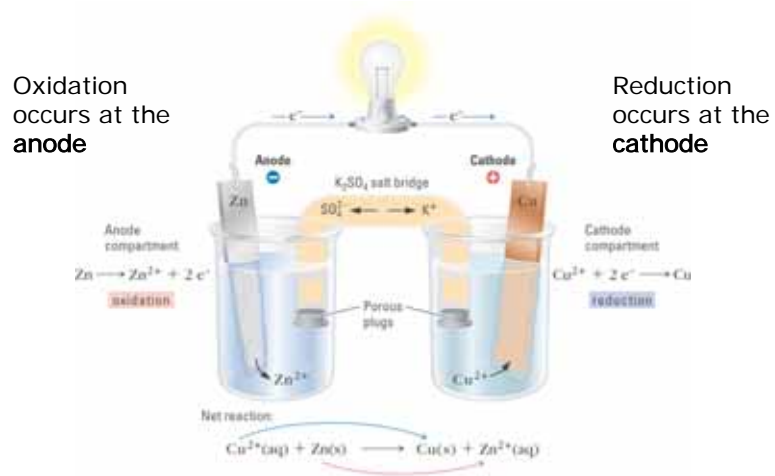


Figure 19.3



## Electrochemical Cells

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- 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

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- Work for a cell is defined as:
  - $\text{Work} = \text{charge} \cdot \Delta E$
  - $\text{Work} = \# e^- \text{'s} \cdot \Delta E$
- The potential difference ( $\Delta E$ ) is measured in volts
- Charge is measured in coulombs
  - $1 e^-$  has a charge of  $1.602 \times 10^{-19} \text{ C}$
- $1 \text{ volt} = 1 \text{ Joule}/1 \text{ coulomb}$



## Electrochemical Cells

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

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

- 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

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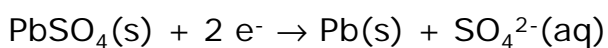
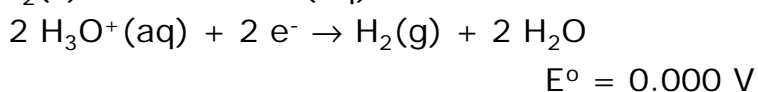
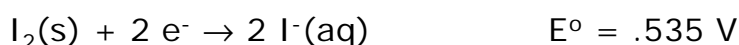
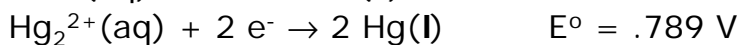
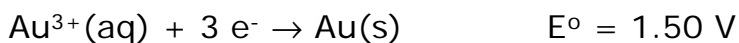
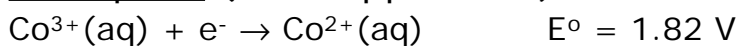
- Values for the potential of various half reactions can be found in tables
- Values are listed under standard conditions
  - Gas phase species have a pressure of 1 atm
  - Aqueous species have a concentration of 1 M
- Tables give as standard reduction potentials,  $E^{\circ}$



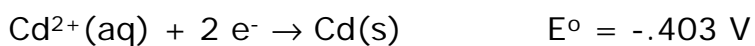
## Electrochemical Cells

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Examples: (from Appendix I)



$$E^{\circ} = -.356 \text{ V}$$



## Electrochemical Cells

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- Electrical potential cannot be measured on an absolute scale
- The standard hydrogen electrode (SHE) is defined as a reference electrode with a potential of  $E^{\circ} = 0.000000000000 \text{ V}$
- Potentials of all other half reaction are measured relative to the SHE



## Electrochemical Cells

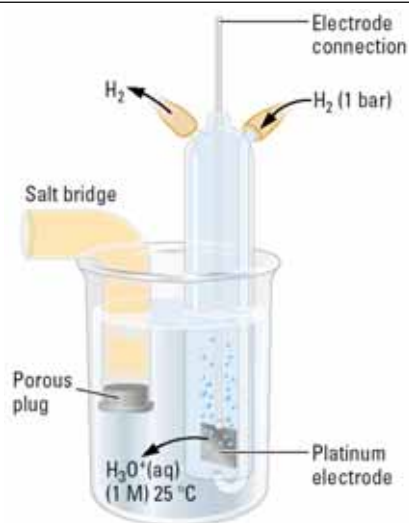


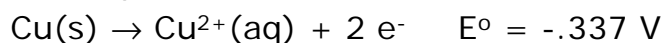
Figure 19.7

## 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)



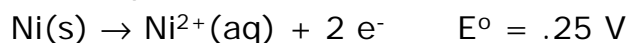
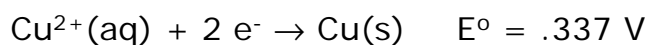
When you flip a redox eqn., you change the sign of  $E^{\circ}$

## Electrochemical Cells

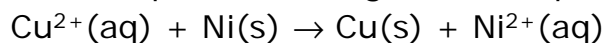
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### Example:

Step 2: if necessary, multiply half reaction by factor to balance e<sup>-</sup>'s transferred



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



$$E^{\circ} = .59 \text{ V}$$

Because E<sup>o</sup> for the cell is positive, the reaction proceeds as written

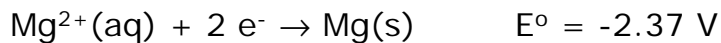
## Electrochemical Cells

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### Example:

Determine E<sup>o</sup> for a Mg<sup>2+</sup> solution with Pt electrode connected to a Ag<sup>+</sup> solution with a Ag electrode

Step 1: write balanced half reactions

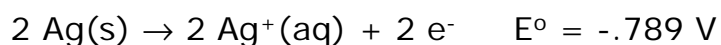


## Electrochemical Cells

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### 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

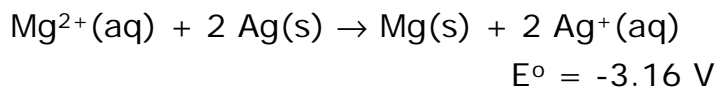
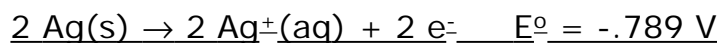
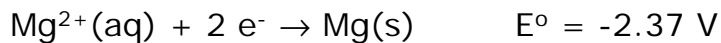
We do not multiply the value of E<sup>o</sup> by the same factor used to balance the e<sup>-</sup>'s transferred

## Electrochemical Cells

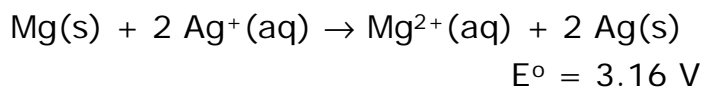
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### Example:

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



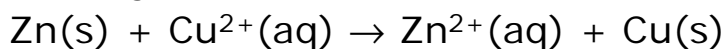
Because E<sup>o</sup> is negative, the reverse reaction occurs



## Electrochemical Cells

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- 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)

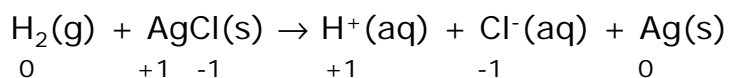


## Electrochemical Cells

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- Example:

Write the shorthand notation for the cell:



- H is oxidized; Ag is reduced
- Notation for anode:  
 $\text{H}_2(\text{g}), \text{Pt} | \text{H}^+(\text{aq})$
- Notation for cathode:  
 $\text{Cl}^-(\text{aq}), \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$
- Overall:  
 $\text{H}_2(\text{g}), \text{Pt} | \text{H}^+(\text{aq}) || \text{Cl}^-(\text{aq}), \text{AgCl}(\text{s}) | \text{Ag}(\text{s})$

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

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- The electrochemical potential,  $E^\circ$ , and Gibb's free energy,  $\Delta G^\circ$ , are related:

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

$n$  = # electrons transferred

$F$  = Faraday's Constant

= 96,485 C/mol

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

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- Reminder:
  - an electrochemical rxn occurs spontaneously if  $E$  is positive
  - Any rxn is spontaneous if  $\Delta G$  is negative
- If  $E^\circ$  is positive, then  $\Delta G^\circ$  must be negative

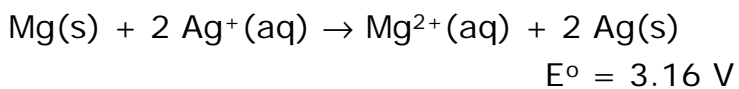
$$\Delta G^\circ = -nFE^\circ$$

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

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### Example:

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



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

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

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

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- 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 $K$

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- 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 $E^\circ$

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

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

Substituting  $\Delta G = -nFE$  gives:

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

Divide by  $-nF$ :

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

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

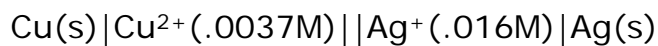
Nernst  
Equation

## Concentration and E°

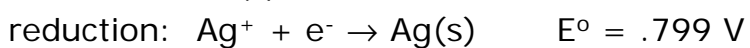
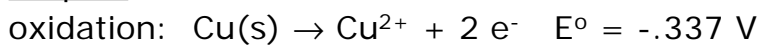
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### Example:

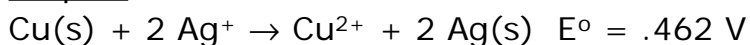
Find potential of the following cell:



Step 1: write half reactions w/ E°'s



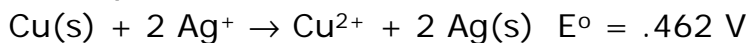
Step 2: write balanced net reaction



## Concentration and E°

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### Example:



Step 3: write expression for Q

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

Step 4: solve for E

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