

# Electrochemistry

Reading: Ch 18, sections 1 – 9    Homework: Chapter 18: 37, 39\*, 43, 45\*, 47, 53, 55, 61, 63, 65\*, 67, 69, 73, 77

\* = 'important' homework question

## Review of REDOX Reactions

### Background



'REDOX' reactions are chemical processes in which REDuction and OXidation simultaneously occur

Oxidation Is Loss of electrons. **An element or compound that *loses* electron(s) during a chemical process is said to be OXIDIZED**

Reduction Is Gain of electrons. **An element or compound that *gains* electron(s) during a chemical process is said to be REDUCED**



**TRICK:** Remembering the difference between oxidation and reduction is easy, just remember....

**OIL RIG of electrons**

**Oxidation Is Loss, Reduction Is Gain of electrons**

Example of a Simple REDOX reaction:



Discussion: Which chemical species has lost electrons during this process (i.e. been oxidized)? Which has gained electrons (been reduced)? How can you figure this out?



**An overall REDOX equation is the sum of two half equations – one for oxidation, one for reduction**



Summary: All REDOX equations are balanced by combining their two respective ½ equations, just like in the above example. We will learn how to perform this task for more complex reactions in the following pages

## Oxidation Numbers



Oxidation Number or Oxidation State – the ‘charge’ on an atom in a substance as if it were a monatomic ion

A *change* in oxidation state during a chemical process indicates that a specie has either been *oxidized* (number goes up), or *reduced* (number goes down). **Recall the previous NaCl example.**

### Rules for assigning oxidation numbers

1. For materials that form atomic ions, the oxidation state is the same as the ‘regular’ ionic charge

Task: State the oxidation state of the following:

Na in NaCl		Cl in AlCl <sub>3</sub>	
Mg in MgCl <sub>2</sub>		Fe in Fe <sub>2</sub> O <sub>3</sub>	



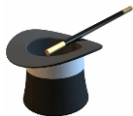
Since you know the charge of a great many atomic ions, you also know their oxidation states, i.e.:

**Group I = I (Li<sup>+</sup>, Na<sup>+</sup> ...)**      **Group VII = -I (F<sup>-</sup>, Cl<sup>-</sup> ...)**  
**Group II = II (Mg<sup>2+</sup>, Ca<sup>2+</sup> ...)**      **Group VI = -II (O<sup>2-</sup>, S<sup>2-</sup> ...)**

Note: Oxidation states / numbers are expressed with Roman Numerals (this differentiates them from ‘pure’ ionic charges)

**2. For ANY elemental atom, its oxidation state is ZERO. Why?**

E.g. Elemental chlorine, Cl<sub>2</sub>



**Any atom bonded to other *identical* atom(s) must have an oxidation state (oxidation number) of ZERO**

**ALL ELEMENTS must by definition possess zero oxidation states**

Examples: Any diatomic element (O<sub>2</sub>, F<sub>2</sub>), any metallic element (Pb(s), Al(s)) etc.

**3. All other atoms' oxidation states must be determined mathematically using the 'Sum of Oxidation States' Rule:**



For molecules: The sum of the molecule's component atoms individual oxidation numbers = ZERO

Example: Nitric acid, HNO<sub>3</sub>



For polyatomic ions ('charged molecules'): The sum of the polyatomic ion's component atoms individual oxidation numbers = overall ionic charge

Example: The nitrate ion,  $\text{NO}_3^-$

Exceptions:

- **Oxygen always has a -II oxidation state, except when bonded to either fluorine or itself.** Why? Hint: Think of the periodic trend in electronegativity (slide, appendix).

Examples:

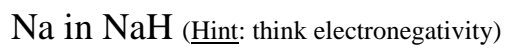


- **F always has a -I oxidation state, except when bonded to itself. Other Halogens (Cl, Br, I) are also -I, except when bonded to F or O.** Why?

Examples:



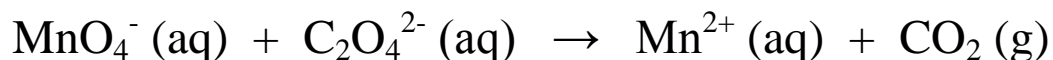
More Examples: Calculate the oxidation state of:



## Balancing 'harder' REDOX reactions

### Worked example

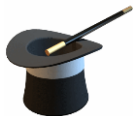
Balance the following REDOX process:



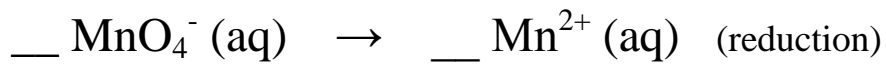
Question: Why cant we just balance these equations 'normally'

Answer:

**Step 1: Split the overall reaction into a pair of  $\frac{1}{2}$  equations and balance atoms OTHER THAN H and O.**



**Trick: assign oxidation numbers to the original unbalanced equation in order to see which species were oxidized and reduced.**



**Step 2: Balance the amount of O (oxygen atoms) in each  $\frac{1}{2}$  equation by adding  $\text{H}_2\text{O}$  (l) where necessary.**

**Step 3:** Balance the amount of H (hydrogen atoms) in each  $\frac{1}{2}$  equation by adding  $\text{H}^+$  (aq) where necessary.

**Step 4:** Balance the NET charges on both sides of each  $\frac{1}{2}$  equation by adding  $e^-$  (electrons) where necessary.



**Trick:** Electrons have a -1 charge, so add them to the more positive side of each  $\frac{1}{2}$  equation until the charge on both sides IS THE SAME



**Step 5:** Equalize the amount of  $e^-$  in each  $\frac{1}{2}$  equation by multiplying through by the appropriate LCF.

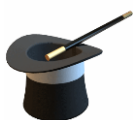


Recall: REDOX reactions are really electron exchange reactions. By completing this step you ensure that an *equal number* of  $e^-$  are transferred (lost and gained respectively) during the two  $\frac{1}{2}$  equations. This is the goal of the procedure(!)

**Step 6:** Add the two  $\frac{1}{2}$  equations, cancel any similar terms. Ensure that the conservation of mass law (same # and type of atoms b.s.) is obeyed

Background: ALL batteries utilize REDOX processes, with the electrons transferred between each  $\frac{1}{2}$  reaction being passed through a circuit in order to provide electrical power. Your cell phone most likely uses a ‘NiCad’ (Nickel/Cadmium) battery – take a look!

Task: Balance the following ‘NiCad battery’ REDOX reaction:



**Trick: Write the initial pair of  $\frac{1}{2}$  equations ONCE, but leave space for each balancing step**

## The Reactivity Series



Background: For batteries featuring similar  $\frac{1}{2}$  reactions (such as in the Cu-Zn battery), it is often difficult to know which metal undergoes oxidation and which reduction



This information is contained within the *Reactivity Series*

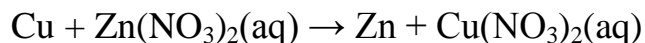
<b>K</b>	Potassium	
<b>Na</b>	Sodium	
<b>Ca</b>	Calcium	
<b>Mg</b>	Magnesium	
<b>Al</b>	Aluminium	
<b>C</b>	<i>Carbon</i>	
<b>Zn</b>	Zinc	
<b>Fe</b>	Iron	
<b>Sn</b>	Tin	
<b>Pb</b>	Lead	
<b>H</b>	<i>Hydrogen</i>	
<b>Cu</b>	Copper	
<b>Ag</b>	Silver	
<b>Au</b>	Gold	
<b>Pt</b>	Platinum	

*(added for comparison)*

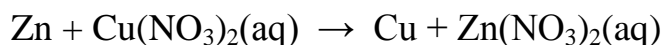


The **MOST** reactive metals are those which **LOSE** electrons (i.e. become oxidized) the most easily. These (e.g. **K**) are at the **TOP** of the reactivity series

Discussion: Which of the following is the correct REDOX reaction for the Cu-Zn battery? See slide / handout.



or



Task: Write a REDOX reaction for the Ag(s) / Ag(NO<sub>3</sub>)(aq) : Cu(s) / Cu(NO<sub>3</sub>)<sub>2</sub>(aq) battery. Hint: Decide on two  $\frac{1}{2}$  reactions, then follow 'the rules'.

## Quantitative Electrochemistry – Cell EMF



The reactivity series can be quantified using *standard reduction potentials*. Note: reduction potentials (reduction) are listed in *reverse order* to the reactivity (oxidation) series.

A standard reduction potential is the voltage of the respective half-cell reaction's reduction process compared to that of the  $2\text{H}^+(\text{aq}) / \text{H}_2(\text{g})$  half-cell (0.00 V)

	Reduction Half-Reaction	$E^\circ$ (V)	
Stronger oxidizing agent 	$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}(\text{aq})$	2.87	Weaker reducing agent 
	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$	1.78	
	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.51	
	$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33	
	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$	1.23	
	$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	1.09	
	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	0.80	
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	0.77	
	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70	
	$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	0.54	
	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$	0.40	
	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	0.34	
	$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	0.15	
	<b><math>2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})</math></b>	<b>0</b>	
	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13	
	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.26	
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40		
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.45		
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76		
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83		
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66		
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37		
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71		
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.04		



Recall your lab – the EMF (voltage or potential difference) of an electrochemical cell (voltaic cell or battery) is simply the **DIFFERENCE** (potential difference, get it!?) in the two half cell reduction potentials.

Task: Determine the *magnitude* of the voltage for a Cu-Zn battery

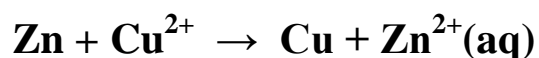


Problem: Working out the *magnitude* of a battery's EMF is straight forward, but determining if this voltage difference is 'positive' or 'negative' requires further consideration.

Recall the complication of having to 'reverse the leads' in your lab – *this was the manifestation of this issue in practice.*

### Quantitative analysis of the 'Duracell' reaction

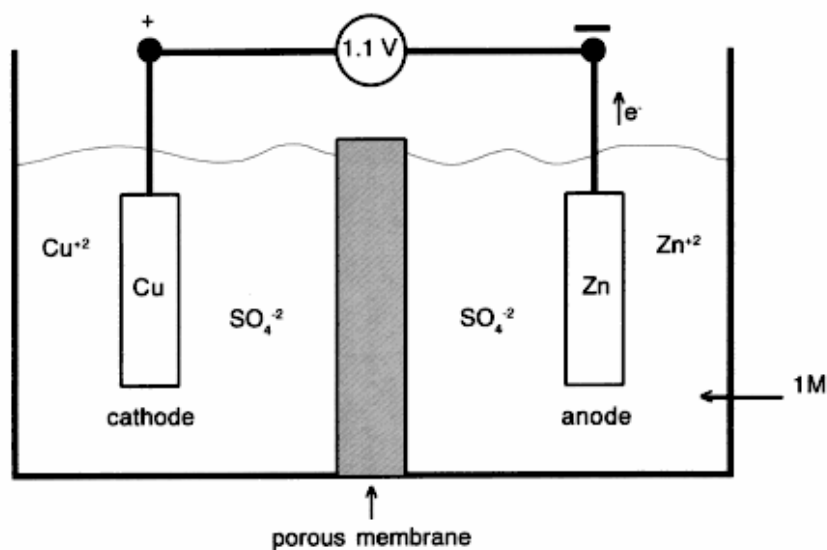
1. Recall: Since zinc is higher in the reactivity series than copper it will be oxidized, while copper ions are reduced:



2. Using a 'number line' approach, we know that the *absolute* EMF of this cell (from above) is  $0.34 \text{ V} + 0.76 \text{ V} = 1.1 \text{ V}$

3. Electrochemical conventions must now be used to determine which half-cell makes up the anode and which the cathode of the cell. This will determine the sign (+ or -) of the cell voltage.

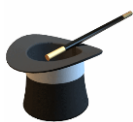
Remember that *Oxidation* occurs at the *Anode* (-ve electrode) and *Reduction* at the *Cathode* (+ve electrode)



Now, we must use the following equation to find both the magnitude and sign of the cell EMF (must remember):

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} (\text{cathode}) - E^{\circ}_{\text{red}} (\text{anode})$$

Where:  $E^{\circ}_{\text{cell}}$  = cell EMF, with correct sign  
 $E^{\circ}_{\text{red}} (\text{cathode})$  = standard reduction potential of the reduction process (at the cathode)  
 $E^{\circ}_{\text{red}} (\text{anode})$  = standard reduction potential of the oxidation process (at the anode)



Determine which half-cells make up the anode and cathode, respectively.

Recall, **Oxidation at the Anode** – the half-cell highest in the reactivity series (lowest in the reduction potential table) will be the anode.

‘Insert and evaluate’ in the above equation, once anode and cathode reduction potentials have been assigned.

For the Zn-Cu battery:

Oxidation:  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq})$   $E^{\circ}_{\text{red}} = -0.76 \text{ V}$

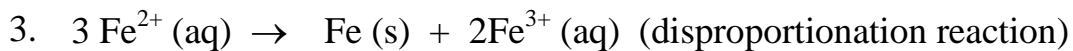
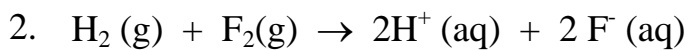
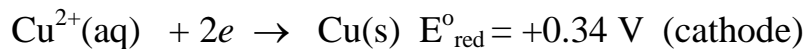
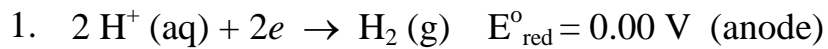
Reduction:  $\text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)}$   $E^{\circ}_{\text{red}} = +0.34 \text{ V}$

Since  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} (\text{cathode}) - E^{\circ}_{\text{red}} (\text{anode})$ :

$$E^{\circ}_{\text{cell}} = (+0.34 \text{ V}) - (-0.76\text{V}) = +1.10 \text{ V}$$

Note: The Zn-Cu battery has a positive sign for  $E^{\circ}_{\text{cell}}$  - *this is only true (for any voltaic cell) if the anode and cathode are correctly assigned.*

Group Task: Determine the magnitude and sign of the EMF for the following voltaic cells, constructed from the half-cells shown (also see appendix E or slide for standard potentials)



## EMF and Gibbs Free Energy



Clearly, voltaic cells feature *spontaneous processes* – the electrons transferred between the two half-cells do so *upon demand* in order to power your I-pod, CD player etc. This relationship is *directly proportional* in terms of EMF and  $\Delta G$ :

$$\Delta G \propto E$$

The quantitative version of the above relationship is:

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

Where:  $\Delta G^\circ$  = standard Gibbs free energy of the REDOX process

$n$  = number of electrons transferred in the redox process (from the balanced REDOX equation)

$F$  = The Faraday constant (the charge of 1 mole of electrons), where  $1 F = 96,500$  Coulombs/mole

$E^\circ$  = standard cell potential of the REDOX process



Michael Faraday – Scientific idol of Margaret Thatcher, ex Prime Minister of Great Britain



Margaret Thatcher – the only British Prime Minister to hold a bachelors degree in chemistry. ‘Maggie’ also shares a birthday with Dr. Mills (err, scary!)



Task: Determine  $\Delta G^\circ$  for:



Is this process spontaneous?

### Cell EMF Under Non-Standard Conditions



Discussion: The voltage of an AA Duracell Zn-Cu battery is 1.5 V, whereas the standard electrode potential for this pair of half-cells is only 1.1 V. Why is this?



The Nernst Equation relates the EMF of a cell to that at under standard conditions ( $E^\circ_{\text{cell}}$ ) and  $Q$ , (the reaction quotient). Recall from the equilibria topic that  $Q = [\text{products}]/[\text{reactants}]$ .

Nernst Equation:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{or} \quad E = E^\circ - \frac{RT}{nF} \ln Q$$

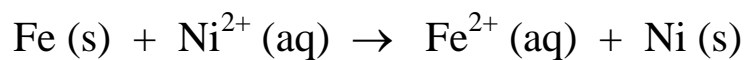


Since  $\Delta G = 0$  at equilibrium (or  $E_{\text{cell}} = \text{zero}$  when the battery goes 'flat', i.e. at *equilibrium*\*:

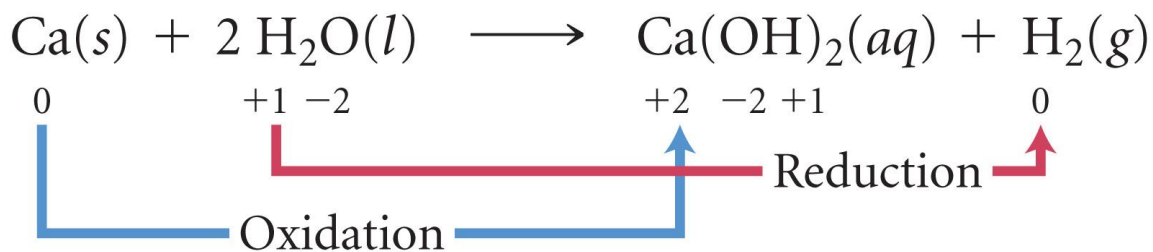
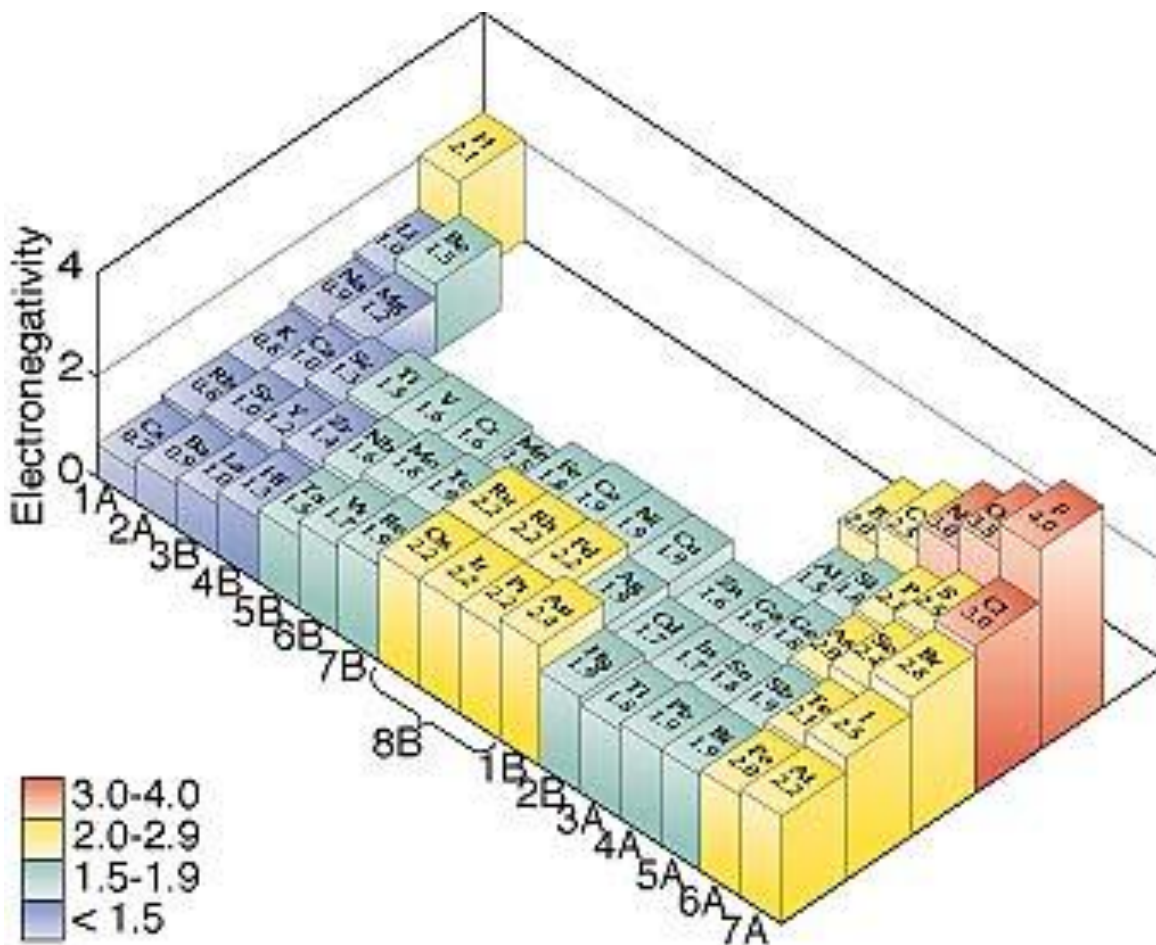
$$\Delta G = -RT \ln K$$

\*This new equation will allow for evaluation of K (equilibrium constant) for any Redox process at any temperature.

Group Task: Use your new equation to answer the following question: What is the value of the equilibrium constant, K, for the following REDOX process? See Appendix E of your notes for standard reduction potentials.

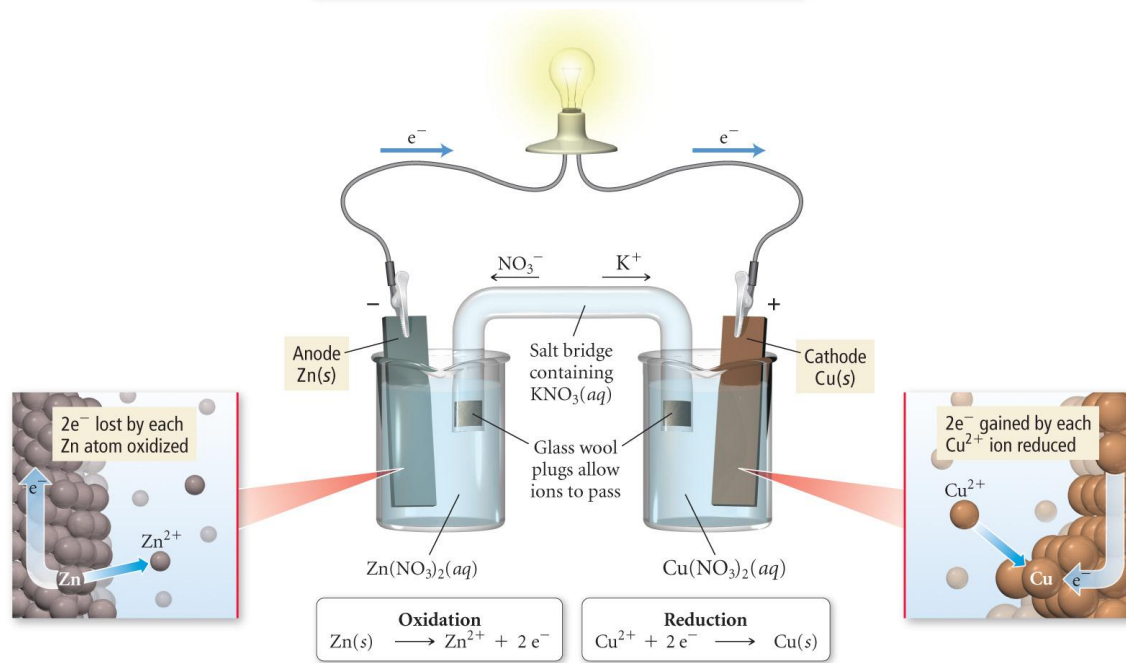
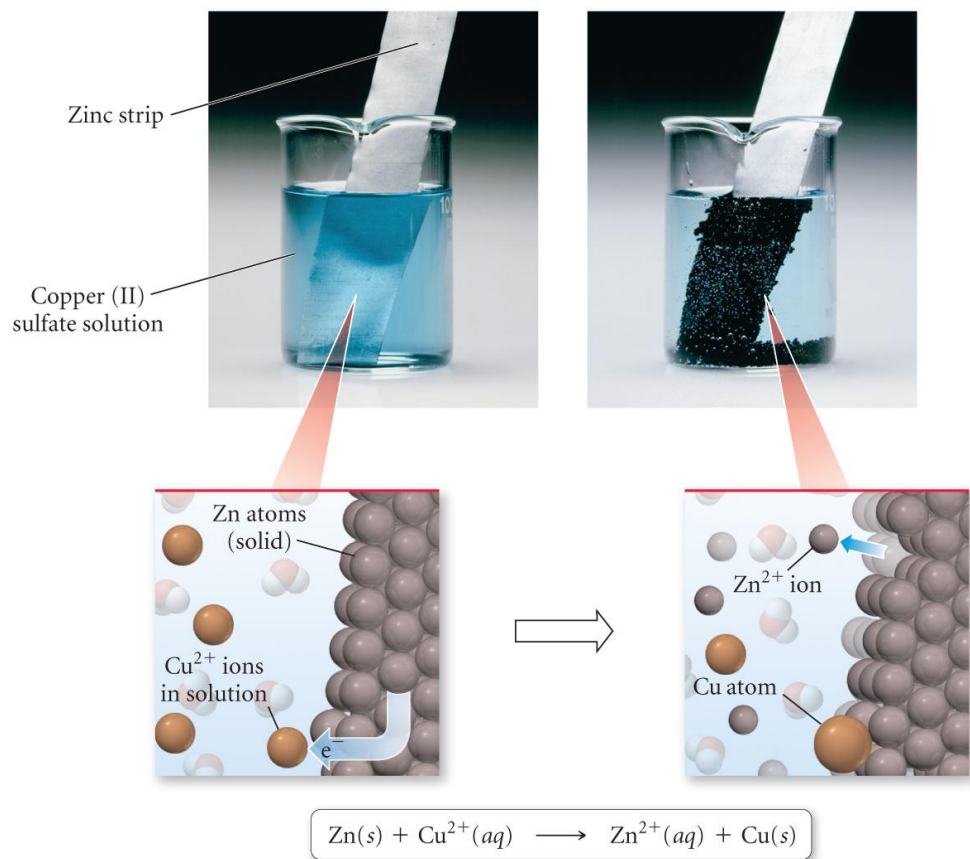


Appendix:

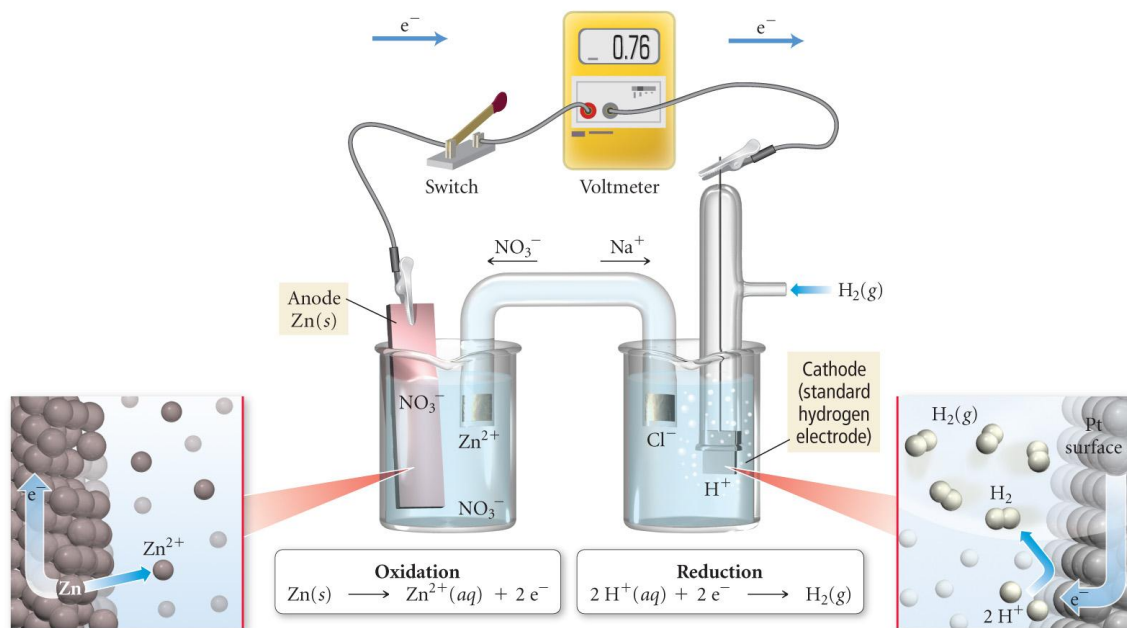




## A Spontaneous Redox Reaction: $\text{Zn} + \text{Cu}^{2+}$



### Measuring Half-Cell Potential with the SHE



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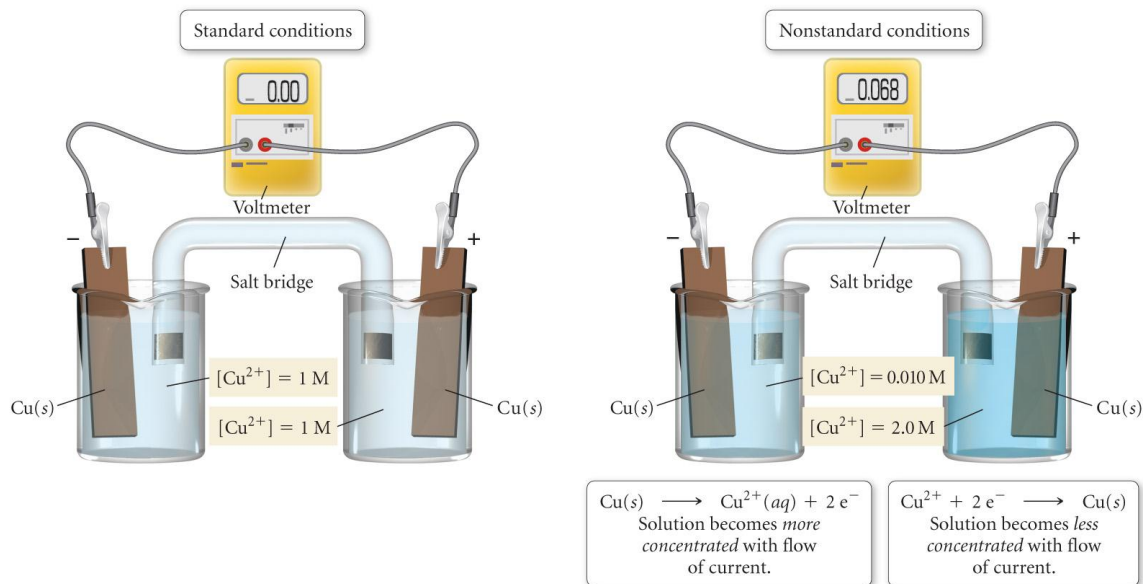
$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\
 &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log 1 \quad \leftarrow \log 1 = 0 \\
 &= E_{\text{cell}}^{\circ}
 \end{aligned}$$

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$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q && E_{\text{cell}}^{\circ} \\
 &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log K \\
 &= E_{\text{cell}}^{\circ} - E_{\text{cell}}^{\circ} \\
 &= 0
 \end{aligned}$$

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#### A Concentration Cell



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