

## Chem 103 lecture 7b

Last time: finished  $\Delta G$ ,  
defined redox;

balanced equations

Today: Elec. Potential,

Electroch. Cells,

Nernst Equation



## Electrochem. Potential, E

- Tendency of metals to dissolve:  
 $M(s) \rightarrow M^+(aq) + e^-$   
an example of oxidation.  
Tendency  $\approx$  oxidation potential,  
Units of potential = volts  
-It's an *intrinsic* quantity (indep. of mass)

## Properties of E

- Intrinsic quantity describing a substance's tendency to react by redox reaction.  
-just like pressure.  
-it's potential energy / charge  
-can be positive or negative.  
-changes sign when reaction is reversed.  
Example:  $Cu \rightarrow Cu^{2+} + 2e^-$   $E_{ox}^\circ = -0.34V$   
Therefore:  $Cu^{2+} + 2e^- \rightarrow Cu$   $E_{red}^\circ = +0.34V$

## Properties of E

- Intrinsic property therefore:  
 $Cu^{2+} + 2e^- \rightarrow Cu$   $+0.34V$   
Multiplying by any factor, say 3:  
 $3Cu^{2+} + 6e^- \rightarrow 3Cu$   $E^\circ = +0.34V$   
Not  $3 \times 0.34V$

## Standard Reduction Potentials

- The tables typically provide :  $E_{reduction}^\circ$  and not  $E_{oxidation}^\circ$
- Example:

	$E_{red}^\circ$ (volts)
(1) $Cu^{2+} + 2e^- \rightarrow Cu$	0.337
(2) $Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
- Which is more easily reduced,  $Cu^{2+}$  or  $Zn^{2+}$ ?
- $Cu^{2+}$
- Why? because  $E_{red}^\circ$  is more positive.

## Standard Reduction Potentials and strength of oxidant

- Continuing this example
- Example:

	$E_{red}^\circ$ (volts)
(1) $Cu^{2+} + 2e^- \rightarrow Cu$	0.337
(2) $Zn^{2+} + 2e^- \rightarrow Zn$	-0.763
- Which is the stronger oxidant,  $Cu^{2+}$  or  $Zn^{2+}$ ?
- $Cu^{2+}$
- Why? because  $E_{red}^\circ$  is more positive. It's more easily reduced.

## Standard Reduction Potentials and strength of reductant

- Continuing this example
- Example:  $E^{\circ}_{\text{red}}$  (volts)
  - (1)  $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$  0.337
  - (2)  $\text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn}$  -0.763
- Which is the stronger reductant, Cu or Zn?
- Zn
- Why? Zn is more easily oxidized. Note:
 
$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-} \quad E^{\circ}_{\text{ox}} = +0.763\text{V}$$

## Standard Reduction Potential Table and general trends

Strongest oxidant	E
$\uparrow$	
$E^{\circ}_{\text{red}}$ (volts)	
$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	+2.87
$\text{O}_2 + 4\text{H}_3\text{O}^{+} + 4\text{e}^{-} \rightarrow 6\text{H}_2\text{O}$	+1.23
$2\text{H}_3\text{O}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g}) + 2\text{H}_2\text{O}$	0.0
$\text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn}$	-0.763
$\downarrow$	
$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$	-3.045
	Strongest reductant

## The spontaneous reaction between copper and zinc:

- Example:  $E^{\circ}_{\text{red}}$  (volts)
  - (1)  $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$  0.337
  - (2)  $\text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn}$  -0.763
- One has to be reversed. Which one?
- (2)  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^{-}$  +0.763
- Then add (1) and -(2):  $E^{\circ} = E^{\circ}_1 - E^{\circ}_2$
- $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+}$  +1.100 V

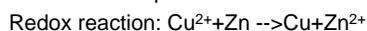
## Electrochemical cells harness the free energy available

There are 2 general types of electrochemical cells:

- Galvanic cells
  - These can do work. Example: battery
- Electrolytic cells
  - These require outside input of energy. E.g. production of aluminum metal.

## First need exergonic redox rxn.

A classic example:



$\Delta E^{\circ} = +1.10\text{V}$

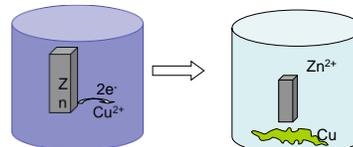
What happens if you put a piece of Zn metal into a blue solution of  $\text{CuSO}_4$  in a beaker?

The Zn dissolves, Cu metal forms at the bottom. Solution loses its blue color.

Lots of heat is generated!

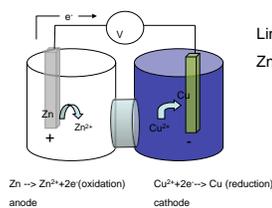
## $\text{Cu}^{2+}$ gets 2 e's from Zn

$\text{Cu}^{2+}$  pulls harder than Zn: gets 2 e's and forms Cu metal.  $\text{Zn}^{2+}$  dissolves.



## Daniell Cell

The Daniell cell uses this reaction. But it separates the Zn from the  $\text{Cu}^{2+}$  and forces the  $e^-$ 's to flow thru a wire.



Line diagram for this cell:  
 $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$

## Electrical work

Electrical work = charge x potential =  $qE$

Charge is in coulomb units (C)

Potential is in volts (V)

Electrical current (I) is in amperes (A) = C/s

$W = n f \Delta E_{\text{cell}}^{\circ}$   $f = \text{Faraday's constant} = 96485 \text{C/mol } e^-$   
 (or  $W = \Delta E I t = V I t$ )

$\Delta G^{\circ} = - n f E^{\circ}$  (So for  $E^{\circ} > 0$ ,  $\Delta G^{\circ} < 0$ ; i.e.  $E^{\circ} > 0$  means product favored)

## Standard Cell potential

For a cell:  $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cath}} - E^{\circ}_{\text{anode}}$

For the Daniell cell:

$$E^{\circ}_{\text{cell}} = 0.337\text{V} - (-.763\text{V}) = +1.100\text{V}$$

## $E^{\circ}_{\text{cell}}$ , $\Delta G^{\circ}$ and K

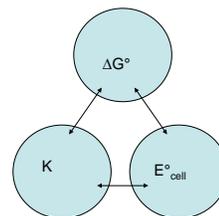
Since  $\Delta G^{\circ} = -nFE^{\circ}$

And  $\Delta G^{\circ} = -RT \ln K$

Then we get:

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

$$\text{Or, } E^{\circ}_{\text{cell}} = (RT/nF) \ln K$$



## Nernst Equation: effect of Q

For a *nonstandard* electrochem cell:

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

But  $\Delta G = -nFE$ ,  $\Delta G^{\circ} = -nFE^{\circ}$ , so

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

$$E = E^{\circ} - RT/nF \ln Q$$

The Nernst Equation gives the actual potential of a cell.