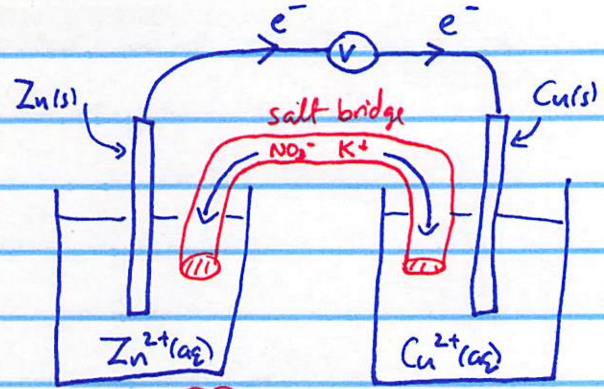
4/22/2019

from last time:



Salt bridge
- keeps solutions elec. neutral

$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ — oxidation — ANODE

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ — reduction — CATHODE

° ← STD. conditions (s/pure, l/pure, g/1atm, aq/1M)

$$E^\circ_{cell} = +1.10V$$

rxn: $Zn(s) + Cu^{2+}(aq) \xrightarrow{2e^-} Zn^{2+}(aq) + Cu(s)$; $E^\circ_{cell} = 1.10V$

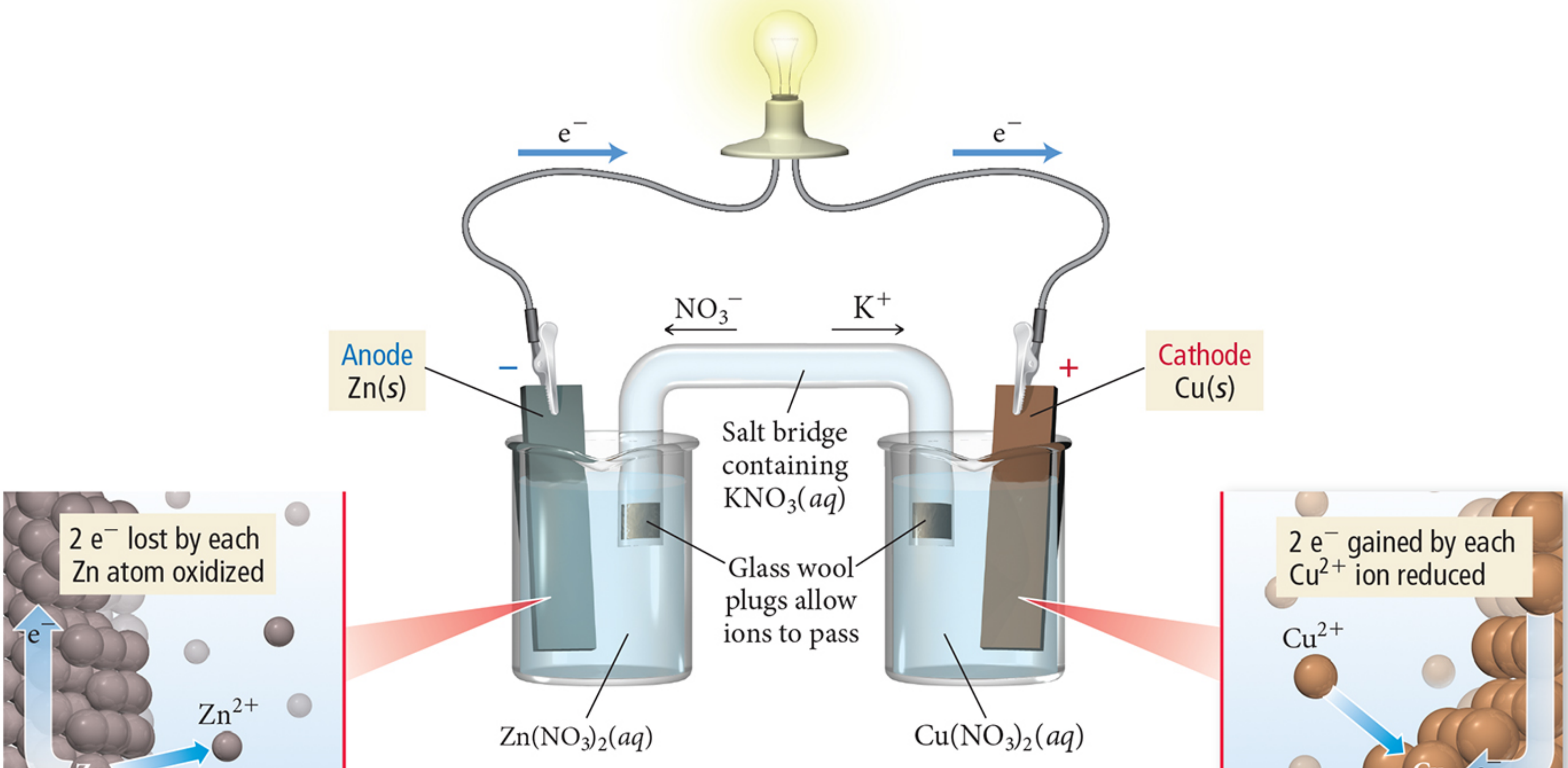
electrodes

Cell notation: $Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)$

ANODE (ox) — CATHODE (red)

each "|" = phase boundary

A Voltaic Cell



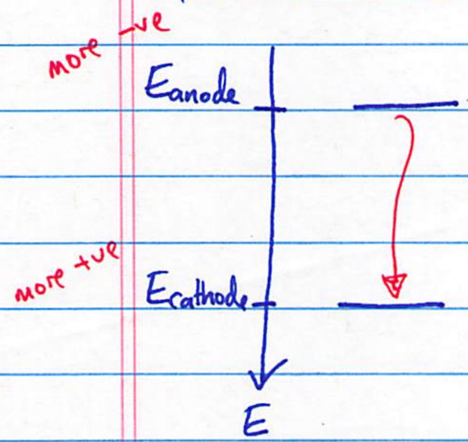
Oxidation

$Zn(s) \longrightarrow Zn^{2+}$ ions $+ 2e^-$

Reduction

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Standard Electrode Potentials



"RHS" − "LHS"

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

(red, gain e⁻s) (ox, losing e⁻s)

can measure E°_{cell}, but there are two unknowns
(1) (2)

So we define a Standard Hydrogen Electrode (SHE)
@ 0.00V
(sea level)

table 19.1 lists all of our std. electrode potentials
(referenced vs. ~~SE~~ SHE @ 0.00V)

- convention:

(1) Write all rxns as reductions (cathode rxn)
- more +ve potential = more favorable rxn
- more −ve potential = more unfavorable rxn is as written (more likely to be reversed)

really good @ stealing e^- → good ox. agents.

$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	$E^\circ = +1.50V$	
$Cu^{2+} + 2e^- \longrightarrow Cu$	$E^\circ = +0.34V$	
$2H^+ + 2e^- \longrightarrow H_2(g)$	$E^\circ = 0.00V$	(SHE)
$Zn^{2+} + 2e^- \longrightarrow Zn$	$E^\circ = -0.76V$	
$Li^+ + e^- \longrightarrow Li$	$E^\circ = -3.04V$	

good @ forming e^-s / giving up e^-s
good reducing agents.

Standard Hydrogen Electrode (SHE)

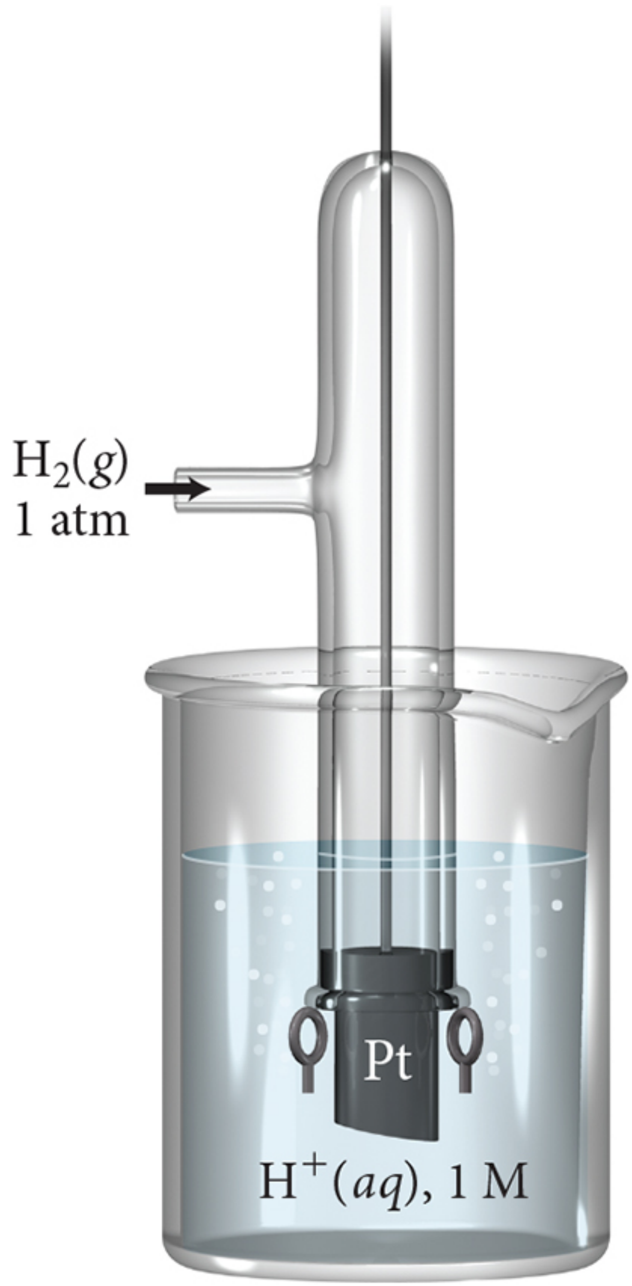


TABLE 19.1 Standard Electrode Potentials at 25 °C

	Reduction Half-Reaction		$E°$(V)	
Stronger oxidizing agent ↑	$F_2(g) + 2\,e^-$	$\longrightarrow 2\,F^-(aq)$	2.87	Weaker reducing agent ↓
	$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.78	
	$PbO_2(s) + 4\,H^+(aq) + SO_4^{2-}(aq) + 2\,e^-$	$\longrightarrow PbSO_4(s) + 2\,H_2O(l)$	1.69	
	$MnO_4^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow MnO_2(s) + 2\,H_2O(l)$	1.68	
	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$	$\longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	1.51	
	$Au^{3+}(aq) + 3\,e^-$	$\longrightarrow Au(s)$	1.50	
	$PbO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Pb^{2+}(aq) + 2\,H_2O(l)$	1.46	
	$Cl_2(g) + 2\,e^-$	$\longrightarrow 2\,Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^-$	$\longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	1.33	
	$O_2(g) + 4\,H^+(aq) + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$	1.23	
	$MnO_2(s) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	1.21	
	$IO_3^-(aq) + 6\,H^+(aq) + 5\,e^-$	$\longrightarrow \frac{1}{2}I_2(aq) + 3\,H_2O(l)$	1.20	
	$Br_2(l) + 2\,e^-$	$\longrightarrow 2\,Br^-(aq)$	1.09	
	$VO_2^+(aq) + 2\,H^+(aq) + e^-$	$\longrightarrow VO^{2+}(aq) + H_2O(l)$	1.00	
	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^-$	$\longrightarrow NO(g) + 2\,H_2O(l)$	0.96	
	$ClO_2(g) + e^-$	$\longrightarrow ClO_2^-(aq)$	0.95	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$MnO_4^-(aq) + e^-$	$\longrightarrow MnO_4^{2-}(aq)$	0.56	
	$I_2(s) + 2\,e^-$	$\longrightarrow 2\,I^-(aq)$	0.54	
	$Cu^+(aq) + e^-$	$\longrightarrow Cu(s)$	0.52	
	$O_2(g) + 2\,H_2O(l) + 4\,e^-$	$\longrightarrow 4\,OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2\,e^-$	$\longrightarrow Cu(s)$	0.34	
	$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2SO_3(aq) + H_2O(l)$	0.20	
	$Cu^{2+}(aq) + e^-$	$\longrightarrow Cu^+(aq)$	0.16	
	$Sn^{4+}(aq) + 2\,e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2\,H^+(aq) + 2\,e^-$	$\longrightarrow H_2(g)$	0	
	$Fe^{3+}(aq) + 3\,e^-$	$\longrightarrow Fe(s)$	−0.036	
	$Pb^{2+}(aq) + 2\,e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Sn^{2+}(aq) + 2\,e^-$	$\longrightarrow Sn(s)$	−0.14	
	$Ni^{2+}(aq) + 2\,e^-$	$\longrightarrow Ni(s)$	−0.23	
	$Cd^{2+}(aq) + 2\,e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2\,e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Cr^{3+}(aq) + e^-$	$\longrightarrow Cr^{2+}(aq)$	−0.50	
	$Cr^{3+}(aq) + 3\,e^-$	$\longrightarrow Cr(s)$	−0.73	
	$Zn^{2+}(aq) + 2\,e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2\,H_2O(l) + 2\,e^-$	$\longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83	
	$Mn^{2+}(aq) + 2\,e^-$	$\longrightarrow Mn(s)$	−1.18	
	$Al^{3+}(aq) + 3\,e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2\,e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
	$Ca^{2+}(aq) + 2\,e^-$	$\longrightarrow Ca(s)$	−2.76	
	$Ba^{2+}(aq) + 2\,e^-$	$\longrightarrow Ba(s)$	−2.90	
	$K^+(aq) + e^-$	$\longrightarrow K(s)$	−2.92	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

Ex: what will be the spont rxn + E°_{cell} + cell diagram given:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E^\circ = +0.80V$$

$$Au^{3+}(aq) + 3e^- \longrightarrow Au(s) \qquad E^\circ = +1.50V$$ * more +ve.

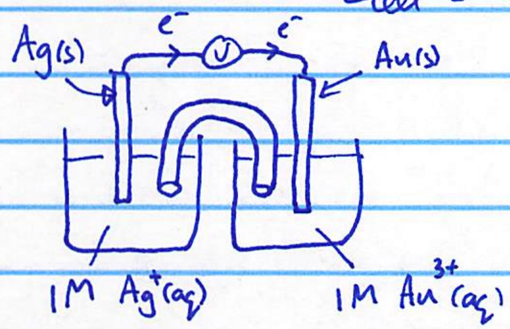
$1\times\left(Au^{3+}(aq) + 3e^- \longrightarrow Au(s)\right)$; $E^\circ = +1.50V$ red, cathode

$3\times\left(Ag(s) \longrightarrow Ag^+(aq) + e^-\right)$ $E^\circ = +0.80V$ ox, anode

$$Au^{3+}(aq) + 3Ag(s) \xrightarrow{3e^-} Au(s) + 3Ag^+(aq)$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= E^\circ_{red} - E^\circ_{ox}$$
$$= E^\circ_{RHS} - E^\circ_{LHS}.$$

$$\Rightarrow E^\circ_{cell} = +1.50V - 0.80V = +0.70V$$



$Ag(s) \,|\, Ag^+(aq, 1M) \,||\, Au^{3+}(aq, 1M) \,|\, Au(s)$

anode — cathode

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

$$\Delta G^\circ = -RT\ln K \qquad (K \gg 1,\ \Delta G^\circ < 0)$$

Physics: Electrical free energy = charge × pot. diff.

(J) (C) (V)

└ coulombs (unit of charge) └ volt ($1 V = 1 J/C$)

Michael Faraday measured |charge| on 1 mol e^- in 1800's

$$1 F = 96{,}500 C/mol$$

(faraday)

$$\Rightarrow \Delta G = \text{charge} \times \text{voltage}.$$

$$= -nF \times E_{cell}$$

- ($-$): e^-'s are $-ve$
- n: # mol e^-
- F: |charge| per 1 mol e^-

$$\Delta G = -nFE \quad // \quad \left. \begin{array}{l} \Delta G^\circ = -nFE^\circ_{cell} \\ \Delta G^\circ = -RT \ln K \end{array} \right\}$$