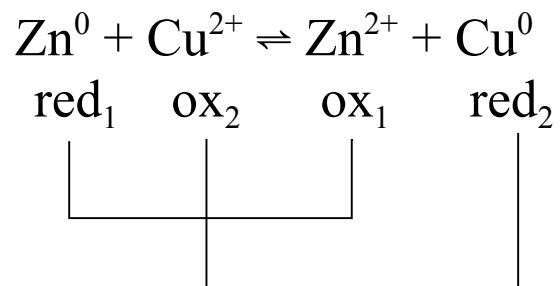
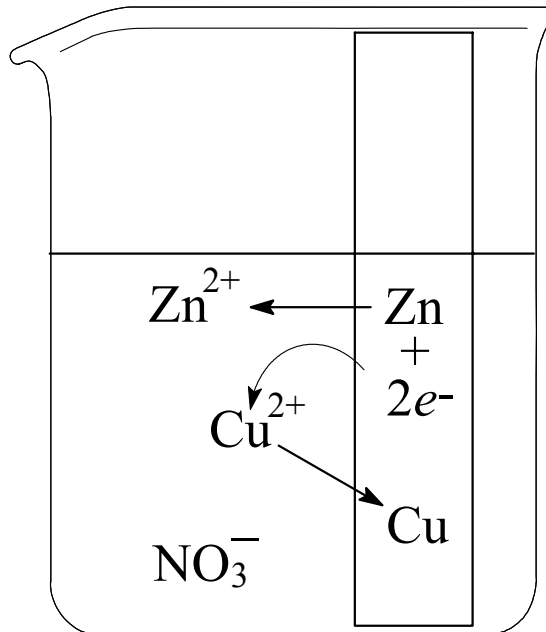
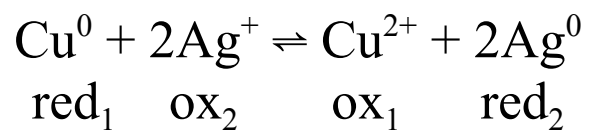
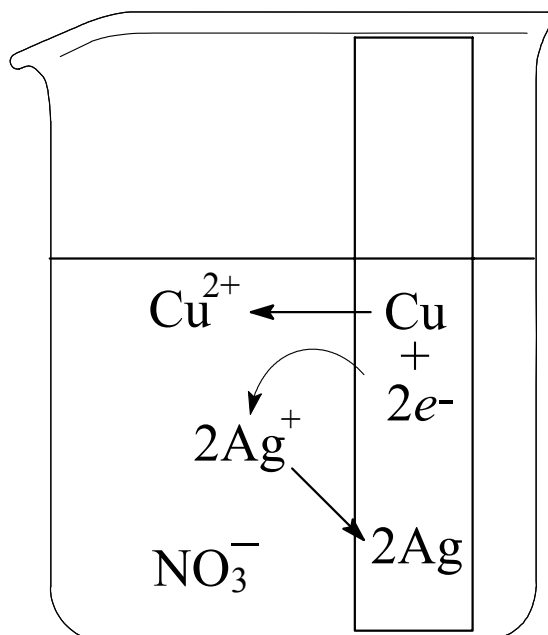


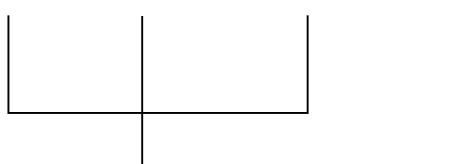
# Spontaneous Redox Between Zinc Metal and Copper(II) Ions



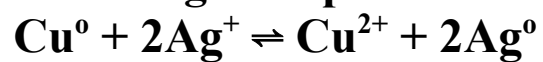
# Spontaneous Redox Between Copper Metal and Silver Ions



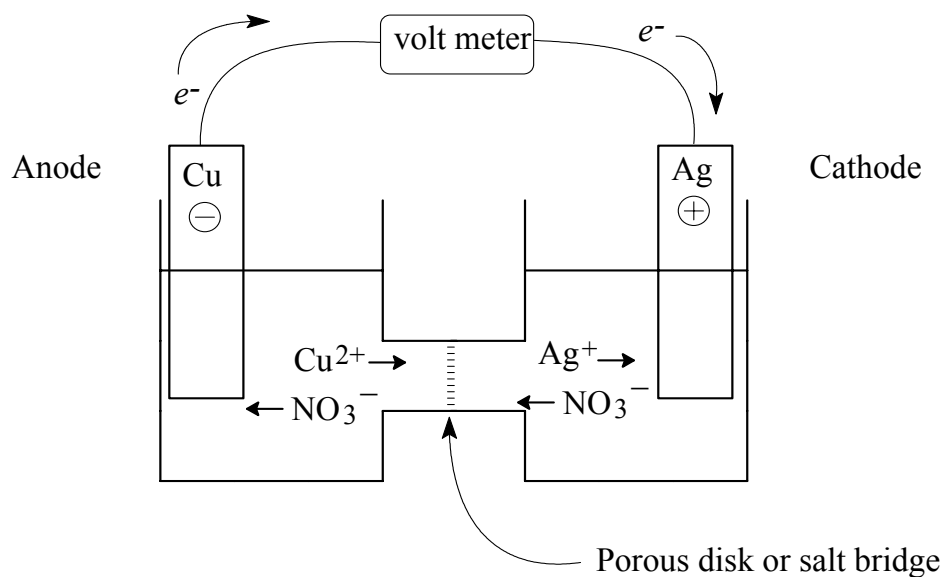
spontaneous



## Galvanic Cell Using the Spontaneous Reaction



meter reading = +0.462 V



Anode reaction:  $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$  oxidation

Cathode reaction:  $\text{Ag}^+ + e^- \rightarrow \text{Ag}$  reduction

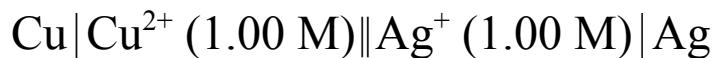
cell potential = +0.462 V

## Conventions for Galvanic Cells

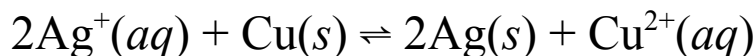
1. Reduction occurs at the cathode; oxidation occurs at the anode.
2. The cathode is given a positive sign ( $\oplus$ ), and the anode is given a negative sign ( $\ominus$ ).
3. Electrons flow through the external circuit (wire) from the anode to the cathode.
4. Positive ions (cations) migrate toward the cathode; negative ions (anions) migrate toward the anode.
5. A porous disk or salt bridge separating the two sides of the cell allows ion migration between the two compartments, thereby maintaining electrical neutrality as the cell runs.
6. The voltage of the cell is taken to be positive. If a meter gives a negative reading, the probes have been attached in reverse, or the direction of electron flow in the external circuit has been reversed, owing to a change in the concentrations of reactants and/or products in the cell.
7. Electrodes are usually conductive solids (sometimes liquid mercury is used), which may or may not be participants in the cell reaction. If neither the oxidized nor reduced form of a couple is a suitable conductive material for fabricating an electrode (e.g.,  $\text{H}^+/\text{H}_2$ ,  $\text{Cl}_2/\text{Cl}^-$ ), an inert electrode (e.g., Pt wire, graphite rod) must be used to make electrical contact with the species of the couple.
8. When using *standard cell notation*, the anode is shown on the left and the cathode is shown on the right. Vertical lines ( $|$ ) represent phase boundaries (e.g., solid-to-liquid, solid-to-gas). Double vertical lines ( $\parallel$ ) represent a salt bridge connecting the two halves of the cell. Sometimes, the composition of the salt bridge is given in the area between the double lines (expanded). A porous disk, used in place of a salt bridge, is sometimes indicated by a series of vertical dots ( $\vdots$ ) or the double vertical line notation.

## Examples of Standard Galvanic Cell Notation

Example (porous disk or unspecified salt bridge; anions not specified):



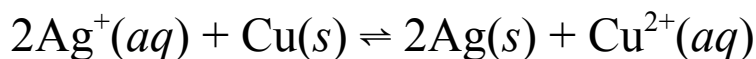
Cell reaction:



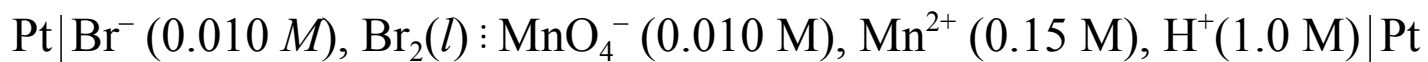
Example (anions included; salt bridge contents specified):



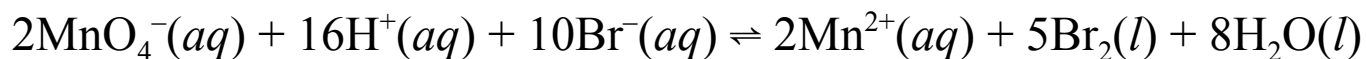
Cell reaction:



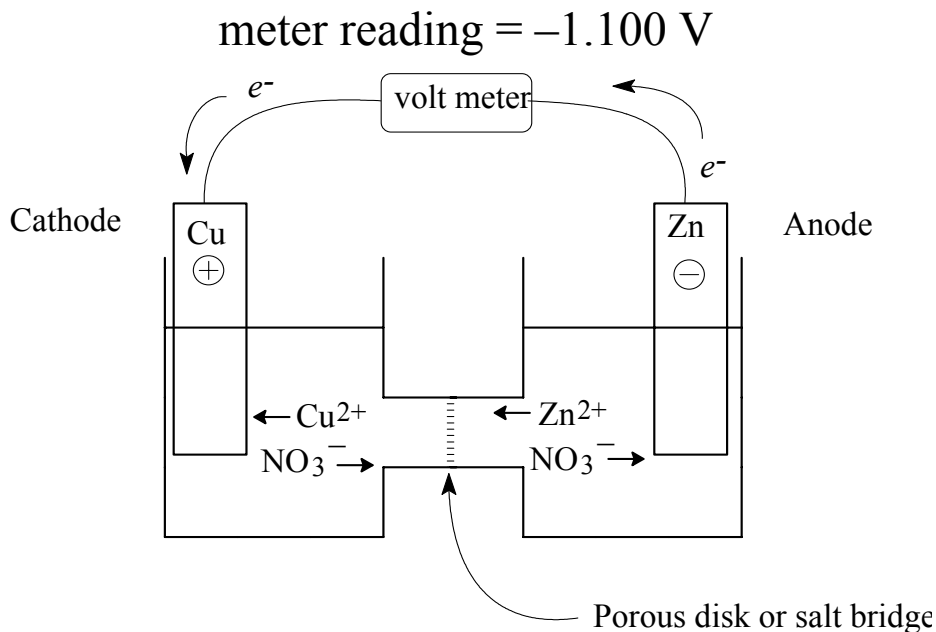
Example (porous disk; spectator ions not specified; inert electrodes used):



Cell reaction:



## Galvanic Cell Using the Spontaneous Reaction

$$\text{Zn}^0 + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}^0$$


Anode reaction:  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$       oxidation

Cathode Reaction:  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0$       reduction

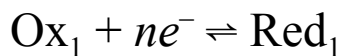
Standard Cell Notation:



cell potential = +1.100 V

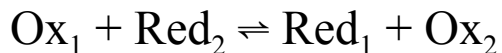
## Electromotive Force (emf)

- ☞ Electrons flow between electrodes in a galvanic cell as a result of **electromotive force** (emf).
- ☞ Cell voltage (or cell potential) is a measure of this emf,  $E_{\text{cell}}$ .
- ☞ Electromotive force results from the combined abilities of the oxidant ( $\text{Ox}_1$ ) to "pull" electrons and the reductant ( $\text{Red}_2$ ) to "push" electrons:



"pull" (reduction)

"push" (oxidation)



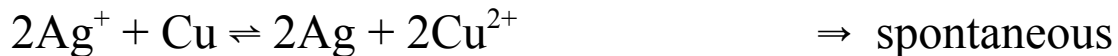
redox  $\Rightarrow$  emf =  $E_{\text{cell}}$

## Comparison of Oxidant Strengths

- ☞ By convention, we compare redox couples on the basis of their oxidant strength; i.e., their tendency to be reduced in a redox reaction.
- ☞ Oxidant strength (or reductant strength) depends on concentration, so we define **Standard Conditions** as 1 M concentrations and/or 1 atm partial pressure for all species at 25°C.
- ☞ In a competition between two couples, the couple with the stronger oxidant will run as a reduction, and the couple with the weaker oxidant (stronger reductant) will run as an oxidation in a spontaneous redox reaction.



Predicted Reactions:



## Table of Oxidants

- ☞ Through comparisons such as this, it is possible to construct a table of oxidants in order of decreasing oxidizing power (oxidant strength) from top to bottom.
- Strong oxidants are in the upper part of the left column.
  - Strong reductants are in the lower part of the right column.
  - Spontaneous redox reactions occur between oxidants in the upper left and reductants in the lower right positions on the table.

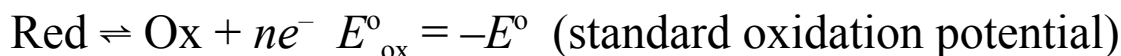
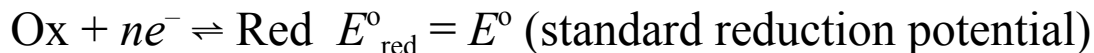
**TABLE OF OXIDIZING AND REDUCING AGENTS**

Oxidizing Agents (strong)	$\rightleftharpoons$	Reducing Agents (weak)	$E^\circ$ (volts)
$F_2(g) + 2e^-$	$\rightleftharpoons$	$2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$O_2(g) + H_2O(l)$	+2.07
$S_2O_8^{2-}(aq) + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}(aq)$	+2.01
$Co^{3+}(aq) + e^-$	$\rightleftharpoons$	$Co^{2+}(aq)$	+1.808
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$2H_2O(l)$	+1.776
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^-$	$\rightleftharpoons$	$PbSO_4(s) + 2H_2O(l)$	+1.682
$Ce^{4+}(aq) + e^-$	$\rightleftharpoons$	$Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Au(s)$	+1.498
$Cl_2(g) + 2e^-$	$\rightleftharpoons$	$2Cl^-(aq)$	+1.3595
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^-$	$\rightleftharpoons$	$2H_2O(l)$	+1.229
$IO_3^-(aq) + 6H^+(aq) + 5e^-$	$\rightleftharpoons$	$\frac{1}{2}I_2(s) + 3H_2O(l)$	+1.20
$Br_2(l) + 2e^-$	$\rightleftharpoons$	$2Br^-(aq)$	+1.065
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	$\rightleftharpoons$	$NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Hg_2^{2+}(aq)$	+0.920
$Hg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Hg(l)$	+0.854
$2NO_3^-(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$N_2O_4(g) + 2H_2O(l)$	+0.803
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.7991
$Hg_2^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$2Hg(l)$	+0.788
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.771
$O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O_2(aq)$	+0.6824
$MnO_4^-(aq) + e^-$	$\rightleftharpoons$	$MnO_4^{2-}(aq)$	+0.564
$I_2(s) + 2e^-$	$\rightleftharpoons$	$2I^-(aq)$	+0.5355
$Cu^+(aq) + e^-$	$\rightleftharpoons$	$Cu(s)$	+0.521
$Fe(CN)_6^{3-}(aq) + e^-$	$\rightleftharpoons$	$Fe(CN)_6^{4-}(aq)$	+0.361
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu$	+0.337
$HSO_4^-(aq) + 3H^+(aq) + 2e^-$	$\rightleftharpoons$	$SO_2(g) + 2H_2O(l)$	+0.172
$Cu^{2+}(aq) + e^-$	$\rightleftharpoons$	$Cu^+(aq)$	+0.158
$Sn^{4+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn^{2+}(aq)$	+0.154
$S(s) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2S(aq)$	+0.142
$S_4O_6^{2-}(aq) + 2e^-$	$\rightleftharpoons$	$2S_2O_3^{2-}(aq)$	+0.09
$2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2(g)$	0.000
$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$	-0.126
$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$	-0.136
$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$	-0.250
$Co^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Co(s)$	-0.277
$PbSO_4(s) + H^+(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s) + HSO_4^-(aq)$	-0.356
$Cd^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cd(s)$	-0.403
$Cr^{3+}(aq) + e^-$	$\rightleftharpoons$	$Cr^{2+}(aq)$	-0.408
$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	-0.4402
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	-0.7628
$2H_2O(l) + 2e^-$	$\rightleftharpoons$	$H_2(g) + 2OH^-(aq)$	-0.828
$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$	-1.029
$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	-1.676
$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$	-1.180
$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	-2.375
$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$	-2.712
$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$	-2.76
$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$	-2.924
$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$	-3.045

## STANDARD REDUCTION POTENTIALS, $E^\circ$

☞ The measure of a substance's relative oxidizing power is its **standard reduction potential,  $E^\circ$** , defined by the following conventions:

1. The *standard reduction potential,  $E^\circ$* , is defined for a half reaction of the type  $\text{Ox} + ne^- \rightleftharpoons \text{Red}$
2. All  $E^\circ$  values assume 1 M concentrations and/or 1 atm partial pressure for all species at 25°C. These define *standard conditions*.
3. For the half reaction  $2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2(\text{g})$  under standard conditions, we define  $E^\circ \equiv 0$  volt (exactly). All other standard reduction potentials for other couples are determined relative to this arbitrary standard.
4. Oxidants that gain electrons better than  $\text{H}^+(\text{aq})$  [stronger oxidants than  $\text{H}^+(\text{aq})$ ] have  $E^\circ > 0$  (i.e., +) for their reduction  $\text{Ox} + ne^- \rightleftharpoons \text{Red}$ .
5. Oxidants that gain electrons worse than  $\text{H}^+(\text{aq})$  [weaker oxidants than  $\text{H}^+(\text{aq})$ ] have  $E^\circ < 0$  (i.e., -) for their reduction  $\text{Ox} + ne^- \rightleftharpoons \text{Red}$ .
6. The *standard oxidation potential* is the negative of the standard reduction potential and refers to the potential of the half reaction  $\text{Red} \rightleftharpoons \text{Ox} + ne^-$ . Thus,



☞ We will always use  $E^\circ$  (without subscript) to refer to the reduction potential of a couple.

## Emf of a Cell Under Standard Conditions, $E^\circ_{\text{cell}}$

- The values of  $E^\circ$  for individual half-reactions can be found by setting up a series of cells under standard conditions.
- Ideally, the potential of any galvanic cell under standard conditions is given by

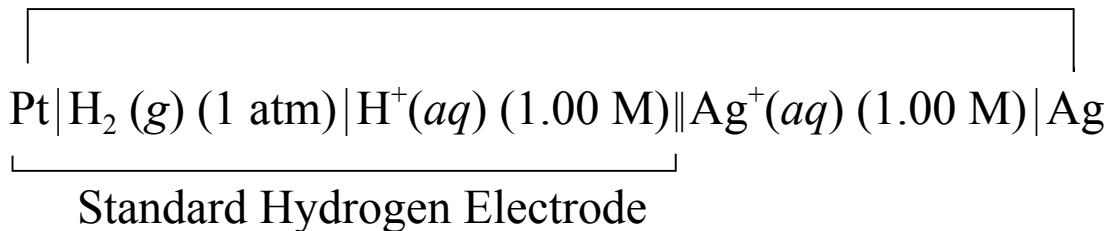
$$\begin{aligned}\text{emf} &= E^\circ_{\text{cell}} = E^\circ_{\text{red}} + E^\circ_{\text{ox}} \\ &= [E^\circ]_{\text{cathode couple}} - [E^\circ]_{\text{anode couple}}\end{aligned}$$

This is the sum of the potentials of the half-reactions that actually take place under standard conditions.

- ⊗ In reality, the actual voltage observed for the cell will be less than the ideal value, due to resistance within the electrical circuit and the cell itself. Nonetheless, if corrections are made, the emf can be taken as the  $E^\circ_{\text{cell}}$  resulting from the redox reaction.

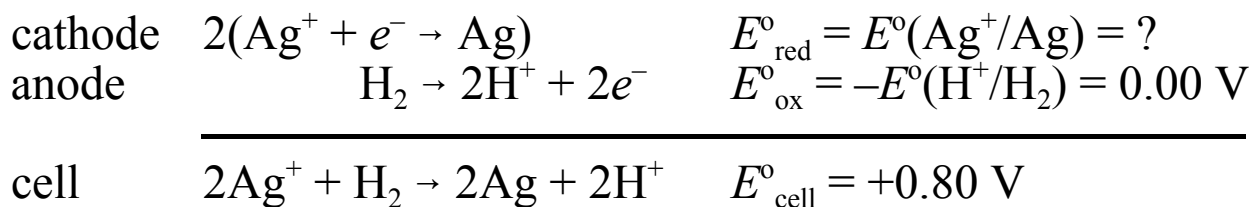
## Galvanic Cell to Determine $E^\circ(\text{Ag}^+/\text{Ag})$

$$e^- \rightarrow \quad \text{Meter} = +0.80 \text{ V} \quad e^- \rightarrow$$



anode

cathode

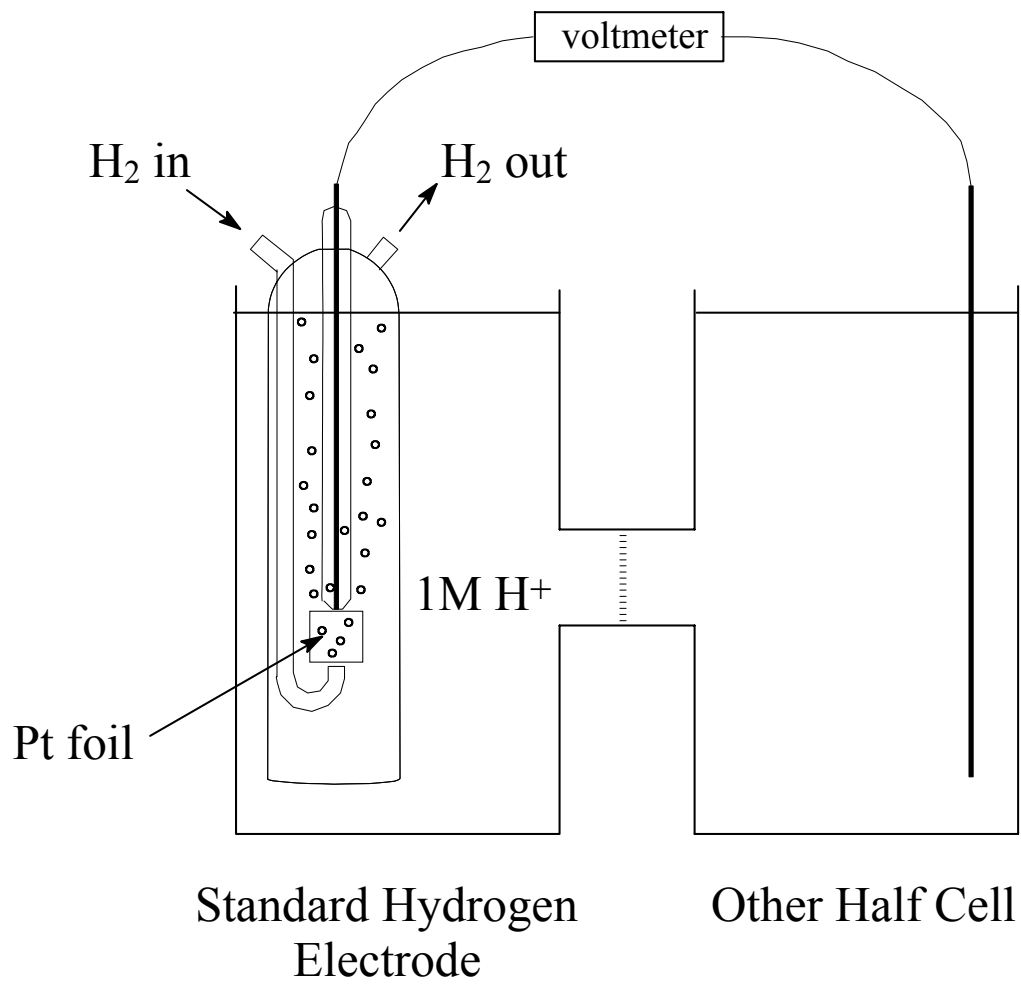


$$E^\circ_{\text{cell}} = +0.80 \text{ V} = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = 0.00 + E^\circ(\text{Ag}^+/\text{Ag})$$

$$E^\circ(\text{Ag}^+/\text{Ag}) = E^\circ_{\text{cell}} - 0.00 = +0.80 \text{ V} - 0.00$$

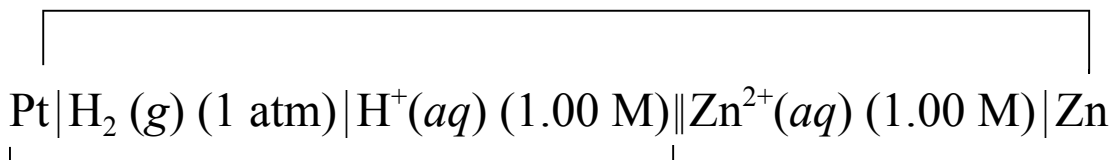
$$E^\circ(\text{Ag}^+/\text{Ag}) = +0.80 \text{ V}$$

# The Standard Hydrogen Electrode



## Galvanic Cell to Determine $E^\circ(\text{Zn}^{2+}/\text{Zn})$

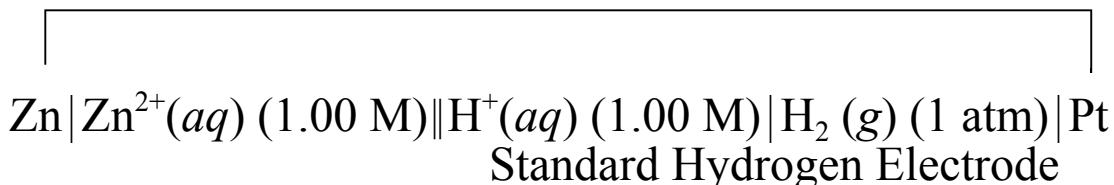
$$\leftarrow e^- \quad \text{Meter} = -0.76 \text{ V} \quad \leftarrow e^-$$



Standard Hydrogen Electrode

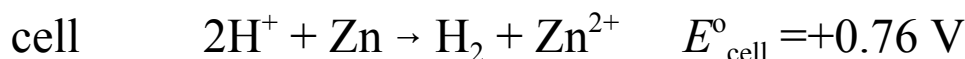
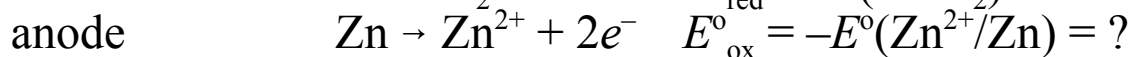
- ☞ All  $E_{\text{cell}}$  values are positive for galvanic cells, so the negative reading simply means the electrons are running the opposite way through the external circuit. **Thus,  $E_{\text{cell}} = +0.76 \text{ V}$ .**
- ☞ The cathode is now on the left, and the anode is now on the right. In standard cell notation, with the voltmeter properly attached, the cell would be shown as follows:

$$e^- \rightarrow \quad \text{Meter} = +0.76 \text{ V} \quad e^- \rightarrow$$



anode

cathode



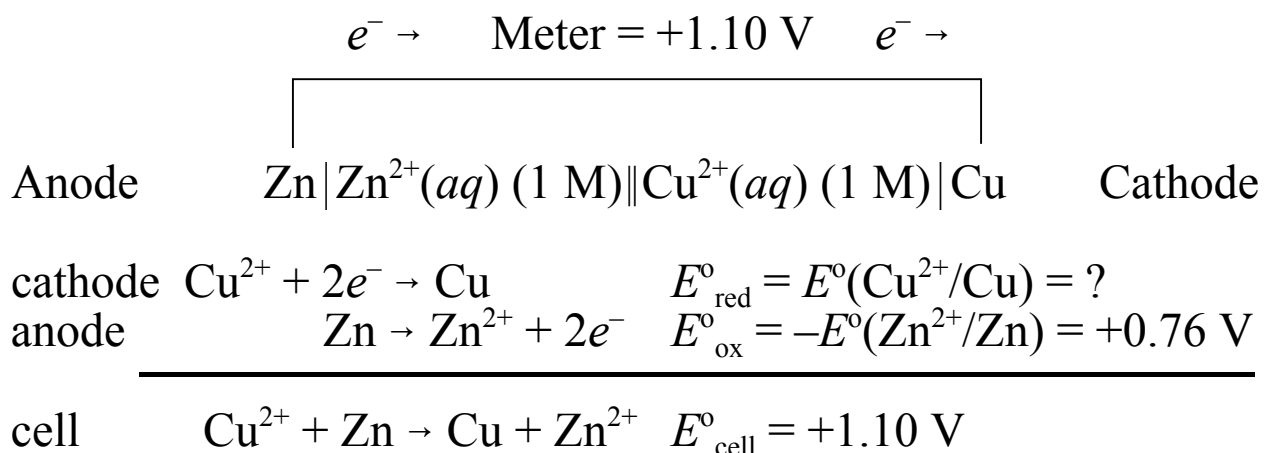
$$E^\circ_{\text{cell}} = +0.76 \text{ V} = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = -E^\circ(\text{Zn}^{2+}/\text{Zn}) + 0.00$$

$$-E^\circ(\text{Zn}^{2+}/\text{Zn}) = E^\circ_{\text{cell}} - 0.00 = +0.76 \text{ V}$$

$$E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$$

## Using an Alternative Couple as a Standard Galvanic Cell to Determine $E^\circ(\text{Cu}^{2+}/\text{Cu})$

- ☞ We are at liberty to use any convenient couple as a standard, once other  $E^\circ$  values have been determined.
- ☞ Knowing that  $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ , we could use that couple in a cell with the  $\text{Cu}^{2+}/\text{Cu}$  couple as a means of determining  $E^\circ(\text{Cu}^{2+}/\text{Cu})$ .



$$E^\circ_{\text{cell}} = +1.10 \text{ V} = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = +0.76 + E^\circ(\text{Cu}^{2+}/\text{Cu})$$

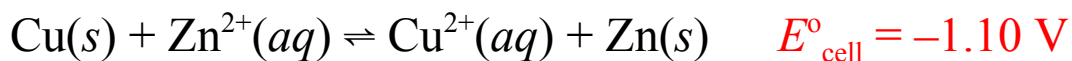
$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = E^\circ_{\text{cell}} - 0.76 \text{ V} = 1.10 \text{ V} - 0.76 \text{ V} = 0.34 \text{ V}$$

$$E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$$

## $E^\circ_{\text{cell}}$ and Spontaneous Redox Under Standard Conditions

- ☞ Spontaneous redox occurs between the stronger oxidant and the stronger reductant; i.e., upper left and lower right on our table.
- ☞ The stronger oxidant has a more positive (or less negative) reduction potential ( $E^\circ$ ), and therefore its couple runs as a reduction.
- ☞ The stronger reductant has a more positive (or less negative) oxidation potential ( $-E^\circ$ ), and therefore its couple runs as an oxidation.
- ☞ Together, the two couples add to give a positive  $E^\circ_{\text{cell}}$  for a spontaneous redox reaction.
- ☞ If  $E^\circ_{\text{cell}}$  is negative for a redox reaction, the reaction will not go spontaneously in the written direction.
  - ☞ To make it run in that direction would require applying at least the calculated emf to force *electrolysis*.
  - ☞ The reaction is spontaneous in the reverse direction; i.e., right to left as written.

Non-spontaneous →



← Spontaneous

## Nernst Equation

Walther Nernst, 1889

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{n\mathcal{F}} \ln Q$$

$E_{\text{cell}}$  = cell potential under given conditions

$E^{\circ}_{\text{cell}}$  = cell potential under standard conditions

$R$  = gas law constant

$T$  = temperature in Kelvin (K)

$n$  = number of electrons transferred in the balanced redox equation

$\mathcal{F}$  = Faraday =  $96,489 \pm 2$  Coulombs  $\approx 96,500$  C  
= charge of one mole of electrons

$Q$  = reaction quotient (form like equilibrium constant,  $K$ , but concentrations not usually at equilibrium)

☞ At 25° C, using base 10 logarithms:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

## $E^\circ_{\text{cell}}$ and $K$

- ✓ As a spontaneous redox reaction runs, products increase and reactants decrease, making  $Q$  become progressively larger.
- ✓ As  $Q$  gets bigger, the logarithmic term in the Nernst equation becomes more negative, and  $E_{\text{cell}}$  becomes less positive.
- ✓ When equilibrium is reached,  $E^\circ_{\text{cell}} = -(RT/n\mathcal{F})\ln Q$ , at which point  $E_{\text{cell}} = 0$  and  $Q \equiv K$ .
- ✓ At 25 °C, at equilibrium:

$$E_{\text{cell}} = 0 = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log K$$



$$\log K = \frac{nE^\circ_{\text{cell}}}{0.0592}$$