

## Chapter 5

# Electrochemistry

Galvanic/Electrolytic Cells

Nernst Equation

} Part 1

Part 2

Corrosion

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## Electrochemistry

- Deals with studying **interchange** of **chemical** and **electrical** energy.
- Studies chemical reactions involving **electron transfer** in **solutions** at the **interface** of an **electron conductor** (a metal or a semiconductor) and an **ionic conductor** (the electrolyte).
- Is primarily concerned with two opposite processes involving **oxidation–reduction** reactions.
- The reactor in electrochemistry is called **Cell**.
- **Applications**
  - ✓ **Batteries** , **Corrosion**, **Electrolysis** (aluminum, and  $\text{Cl}_2$  production), **Analysis** (ion selective electrodes)

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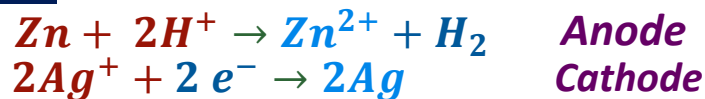
## Reversible electrochemical Cells

- Reversible cells are those whose cell reactions can be get reversed when an external emf ( $E_{ext}$ ) greater than its capacity ( $E_{cell}$ ) is applied. E.g., Metal/metal ion electrodes.

## Irreversible electrochemical Cells

- Cells whose cell reactions can not be reversed when an external emf ( $E_{ext}$ ) greater than its capacity ( $E_{cell}$ ) is applied.

**Example** The Zn/H<sup>+</sup>/Ag cell



$\text{H}_2$  is escaped from the system

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## Reversible Cells/ Example Daniel cell

**Anode** Zn  $\text{Zn}^{2+}$  **Cathode** Cu  $\text{Cu}^{2+}$

$\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$        $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

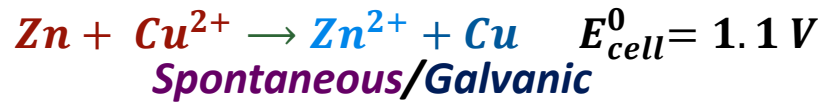
$\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \quad E_{cell}^0 = 1.1 \text{ V}$

**Cell representation**  
 $\text{Zn(s)} | \text{ZnSO}_4(\text{aq}) // \text{CuSO}_4(\text{aq}) | \text{Cu(s)}$

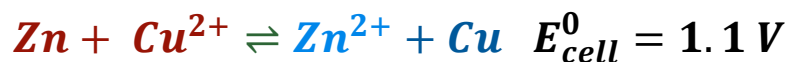
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### Daniel cell, $E^0 = 1.1 \text{ V}$

- If an external emf **less than 1.1 V** is applied, current will flow from the cell according to



- If an external emf of 1.1 V is applied, the cell reaction stops and **no current flows** ( $I = 0$ ).



- If an external emf **higher than 1.1 V** is applied, the cell reaction will be **reversed** and current will flow in **opposite direction**. **Non-Spontaneous/Electrolytic**



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### Galvanic/Electrolytic

- A **galvanic (voltaic) process**: generation of an electric current from a spontaneous chemical reaction.
- An **electrolytic processes**: uses a current to produce chemical change.

**Spontaneous/Galvanic**

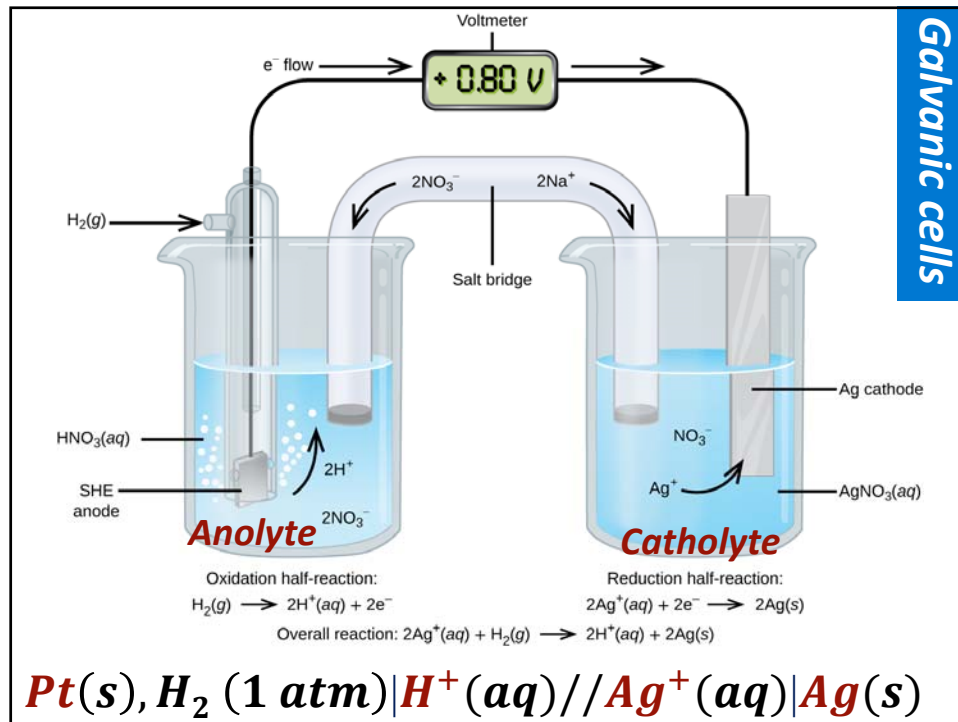


**Reactants**  $\rightleftharpoons$  **Products** + **Electrical Energy**

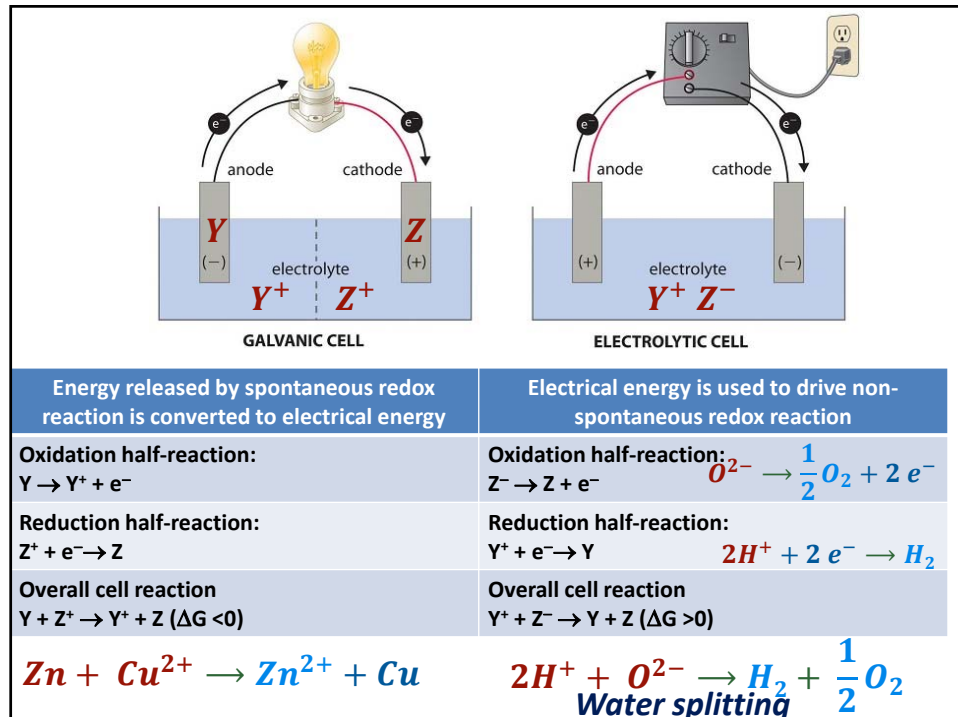


**Non-Spontaneous/Electrolytic**

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<b>Galvanic Cell</b>	<b>Electrolytic cell</b>
<i>converts chemical energy into electrical energy.</i>	<i>converts electrical energy into chemical energy.</i>
<i>Spontaneous redox reaction</i>	<i>non-spontaneous redox reaction</i>
<i>The two half-cells are set up in different containers, being connected through the salt bridge or porous partition.</i>	<i>Both electrodes can be placed in the same container with the electrolyte.</i>
<i>The anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction.</i>	<i>The anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.</i>
<i>Electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit.</i>	<i>The external battery supplies the electrons. They enter through the cathode and come out through the anode.</i>

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<b>Electrodes/Electrolyte</b>
<ul style="list-style-type: none"> <li>▪ <i>The electrode (<b>Pole</b>) at which <b>oxidation</b> occurs is called the <b>anode</b>; the electrode at which <b>reduction</b> occurs is called the <b>cathode</b>.</i></li> <li>▪ <i>The cathode and anode are <b>usually</b> made of <b>metals</b> or <b>carbon</b> (i.e., first class conductors) and they <b>may</b> be or <b>may not</b> be involved in the reactions.</i></li> <li>▪ <i>The solution between electrodes is composed of a <b>polar solvent</b> (mostly water) and at least one chemical (called <b>Electrolyte</b>) that ionizes to produce ions in solution.</i></li> </ul>

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## Electricity

- **Electricity** is conducted through the cell by
  - **Electrons** in the electrodes and wires, and
  - **Ions** in solution.
- Species undergoing **oxidation** at the anode is called **Anolyte**
- Species undergoing **reduction** at the cathode is the **Catholyte**.

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## Cell potential, $E_{\text{cell}}$

- The **electromotive force (emf)** pulling electrons from the anodic to the cathodic compartments.
- The unit of electrical potential is the **volt** (abbreviated **V**), which is defined as **1 joule of work per coulomb of charge transferred**.

## Standard Cell potential, $E^0$

- The **emf** of the cell if **unit activities** (concentrations = **1 M**, **P= 1 atm**) are employed for the existing ions and gases in the cell.

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**STANDARD REDUCTION POTENTIALS AT 25°C (298 K)**

Reduction Half-reaction	$E^\circ$ (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
<b><math>2H^+ + 2e^- \longrightarrow H_2</math></b>	<b>0.00</b>
$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	-0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.76
$H_2 + 2e^- \longrightarrow 2H^-$	-2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.37
$Na^+ + e^- \longrightarrow Na$	-2.71
$Li^+ + e^- \longrightarrow Li$	-3.05

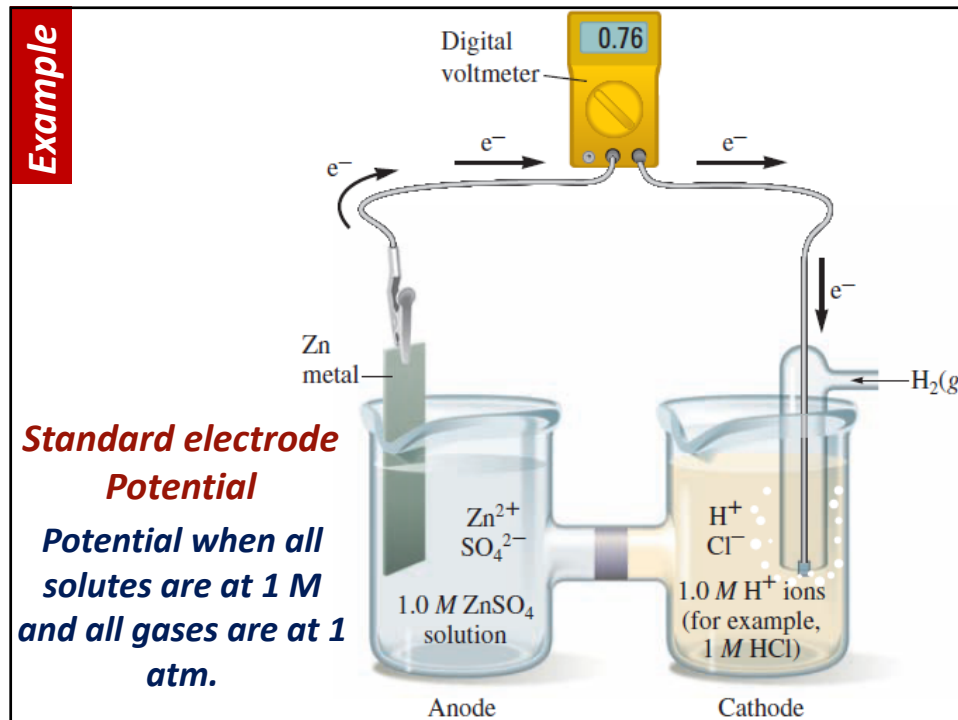
Stonger oxidizing agent (top), Weaker oxidizing agent (bottom), Stronger reducing agent (bottom), Weaker reducing agent (top)

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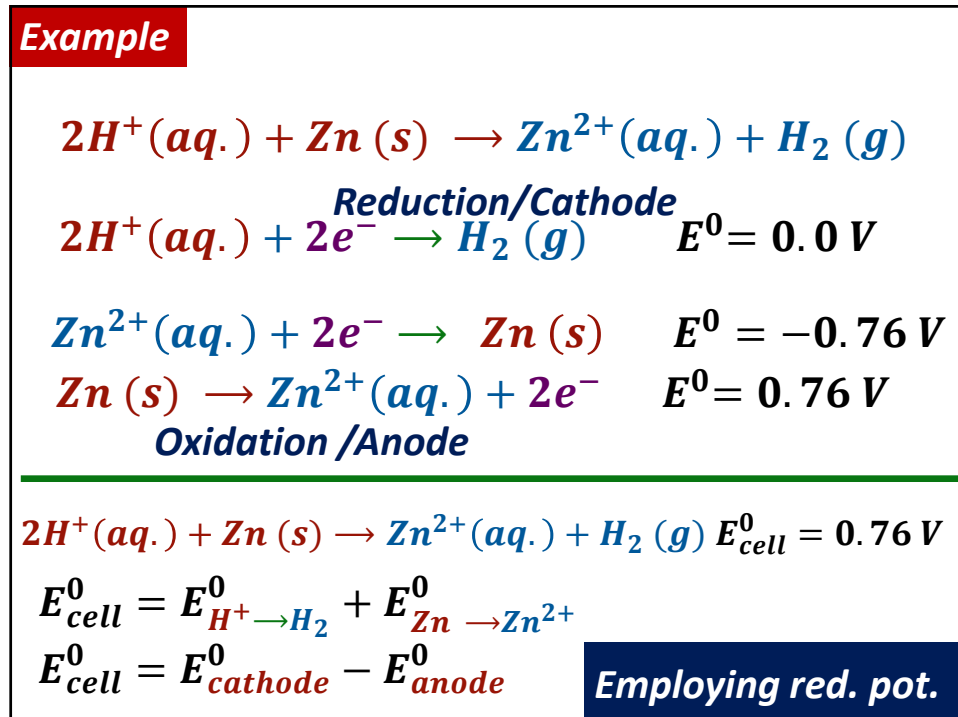
**TABLE 18.1 > Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions**

Half-Reaction	$E^\circ$ (V)	Half-Reaction	$E^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	<b><math>2H^+ + 2e^- \rightarrow H_2</math></b>	<b>0.00</b>
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.41
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

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## The Nernst Equation

- ✚ It represents the dependence of the cell potential ( $E$ ) on concentration.
- ✚ In fact, the potential of a single electrode or half-cell varies with the concentration of ions in the cell according to Nernst equation

**For this half cell reaction**  $M^{n+}(aq) + n e^{-} \rightarrow M(s)$

$$E = E^0 + \frac{RT}{nF} \ln[M^{n+}]$$

$$E = E^0 + \frac{2.303RT}{nF} \log[M^{n+}]$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad F = 96500 \text{ C/mol e}^{-}$$

**At 25°C**

$$E = E^0 + \frac{0.059}{n} \log[M^{n+}]$$

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**Example**

- ✚ Calculate the electrode potential and the electromotive force of the following cell knowing that  $E_{Zn}^0 = -0.76 \text{ V}$ , and  $E_{Cu}^0 = +0.34 \text{ V}$



**Solution**  $Zn^{2+}(aq) + 2 e^{-} \rightarrow Zn(s), \quad E_{Zn}^0 = -0.76 \text{ V}$

$Cu^{2+}(aq) + 2 e^{-} \rightarrow Cu(s), \quad E_{Cu}^0 = +0.34 \text{ V}$

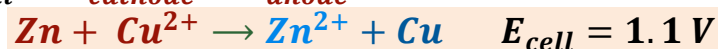
**Calculate E**

$$E = E^0 + \frac{0.059}{n} \log[M^{n+}]$$

$$E_{Zn} = E_{Zn}^0 + \frac{0.059}{2} \log[0.1] = -0.7895 \quad \text{Anode}$$

$$E_{Cu} = E_{Cu}^0 + \frac{0.059}{2} \log[0.1] = +0.3105 \quad \text{Cathode}$$

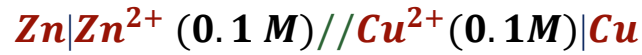
$$E_{cell} = E_{cathode} - E_{anode} = 0.3105 + 0.7895 = 1.1 \text{ V}$$



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**Example**

Calculate the electrode potential and the electromotive force of the following cell knowing that  $E_{Zn}^0 = -0.76 V$ , and  $E_{Cu}^0 = +0.34 V$

**Solution****Calculate E**

$$E = E^0 + \frac{0.059}{n} \log[M^{n+}]$$

$$E_{Zn} = E_{Zn}^0 + \frac{0.059}{2} \log[0.1] = -0.7895$$

$$E_{Zn} = E_{Zn}^0 + \frac{0.059}{2} \log[0.1] = -0.7895$$



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