

## Module 3

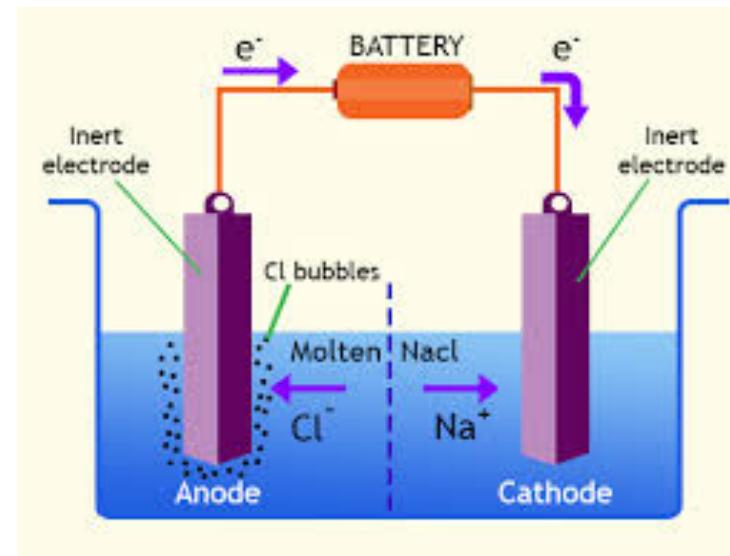
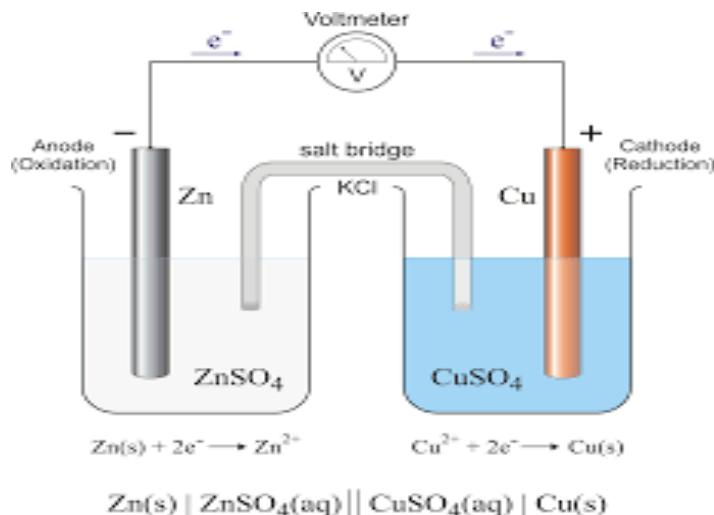
# Electrochemistry - Corrosion

# Electrochemistry

Deals with the **production** of electric current through **chemical reactions**

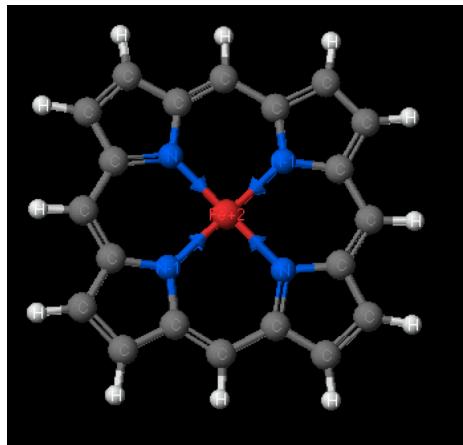
or

the **chemical reactions produced by passing electric current**



# Electrochemistry

- Batteries
- Corrosion
- Industrial production of chemicals such as  $\text{Cl}_2$ ,  $\text{NaOH}$ ,  $\text{F}_2$  and  $\text{Al}$
- Biological redox reactions



The heme group

# Electrochemistry

**Study of redox reactions at an electrode.**

- Obtaining electricity directly from a spontaneous ( $\Delta G < 0$ ) reaction.
- Using an electric current to drive a non-spontaneous ( $\Delta G > 0$ ) reaction.

**Electrochemical cells:**

- systems utilizing a redox reaction to produce or use electrical energy

# Oxidation Number

Hypothetical charges called **oxidation numbers** to atoms with polar covalent bonds.

The general idea is to assign the shared electrons in each bond to the more electronegative element.

H

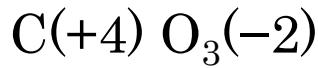
(+1)

O

(-2)

H

(+1)



- Oxidation numbers are assigned to each element in a chemical reaction to help us learn which element is oxidized and which is reduced.
- If, in a reaction, the oxidation number of an element **increases** (becomes more positive), the element is being **oxidized**. On the other hand, if the oxidation number of an element **decreases**, the element is being **reduced**.
- The oxidizing agent is reduced, whereas the reducing agent is oxidized.
- Oxidation: loss of electrons (**OIL**)
- Reduction: gain of electrons (**RIG**)
- Oxidizing agent: accepts electrons (reduced)
- Reducing agent: donates electrons (oxidized)

# Oxidation – Reduction Reaction

Consider metallic zinc reacting with chlorine gas to form zinc chloride:

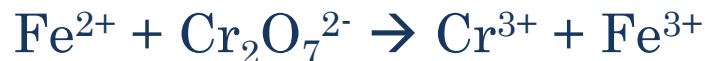


The oxidizing agent that gains electrons is chlorine, and the reducing agent that loses electrons is zinc.

**Use Oxidation numbers for balancing reactions.** The goal is to keep the total number of electrons lost in the oxidation equal to the total number gained in the reduction.

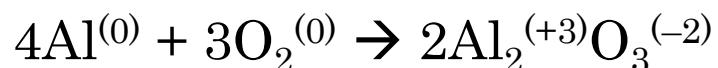
**Assignment:**

Balance the following reaction in both basic and acidic medium:



# Redox Reactions

- The energy producing reactions in industry as well as in the body.
- The core of a redox reaction is the passing of one or more electrons from one species to another.
- Oxidation and reduction occur **simultaneously**.



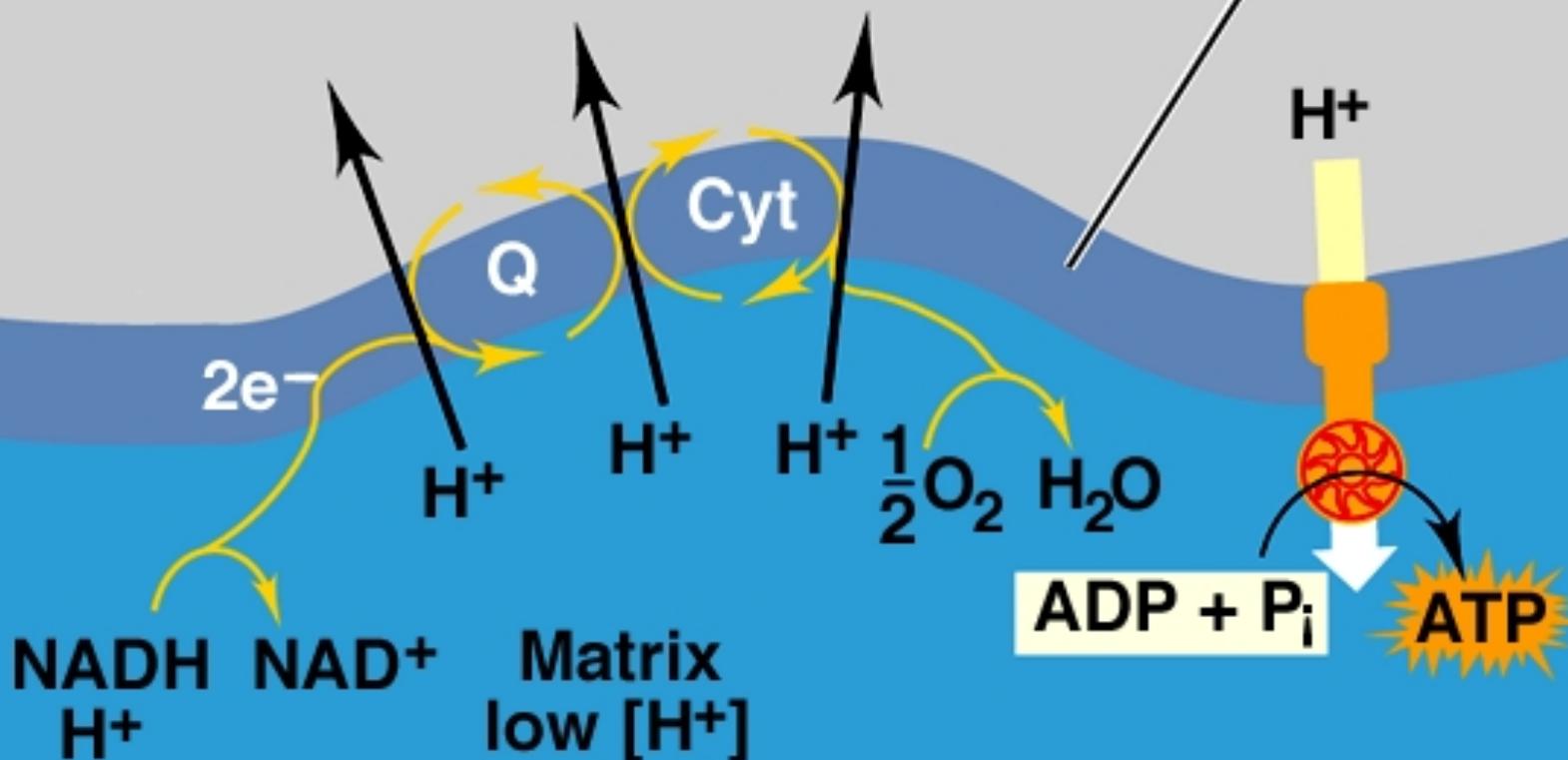
# ATP Synthesis

Outside mitochondrion

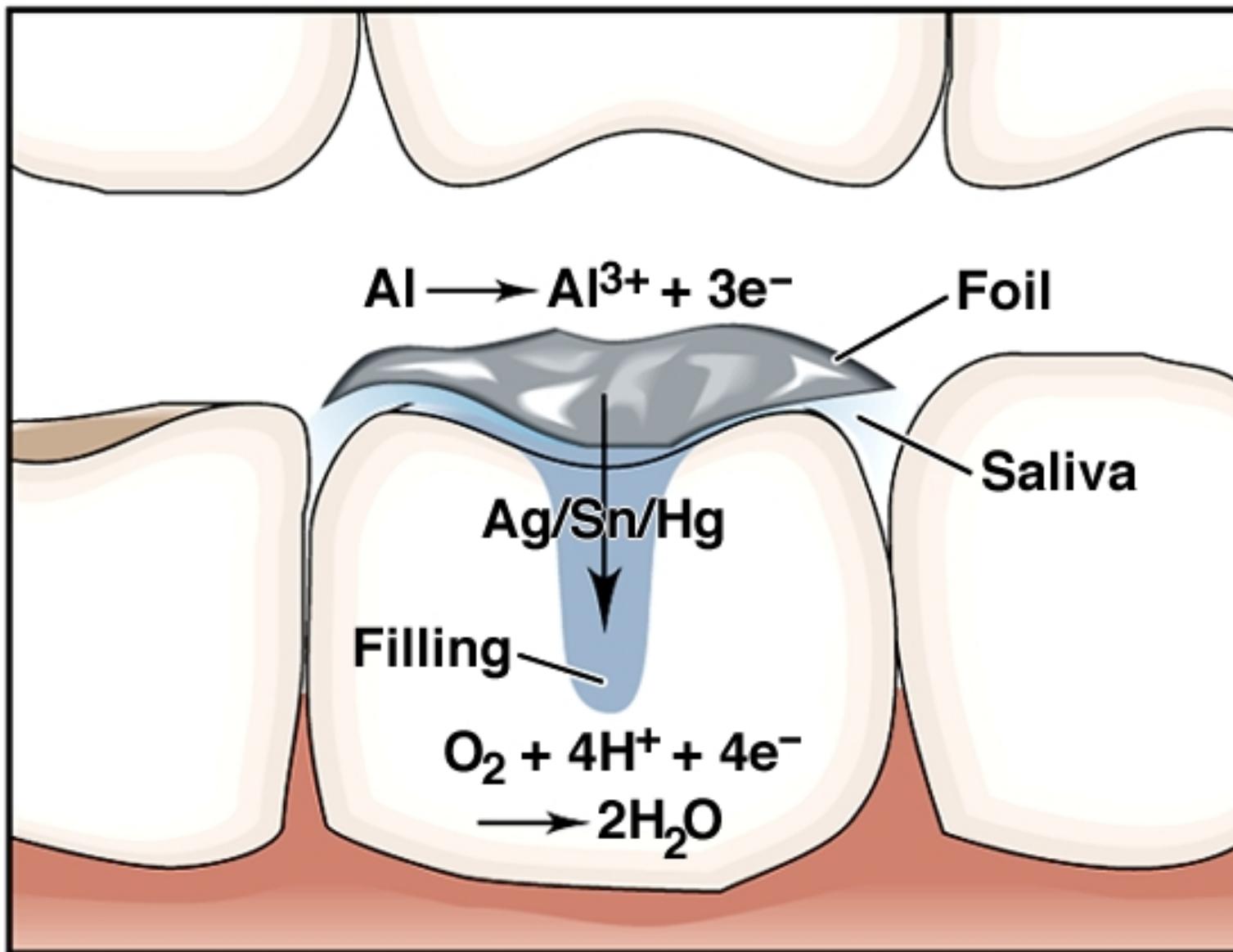
Outer membrane

Intermembrane space  
high [H<sup>+</sup>]

Inner  
membrane

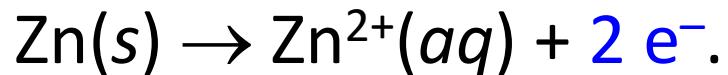


# The Pain of a Dental Voltaic Cell

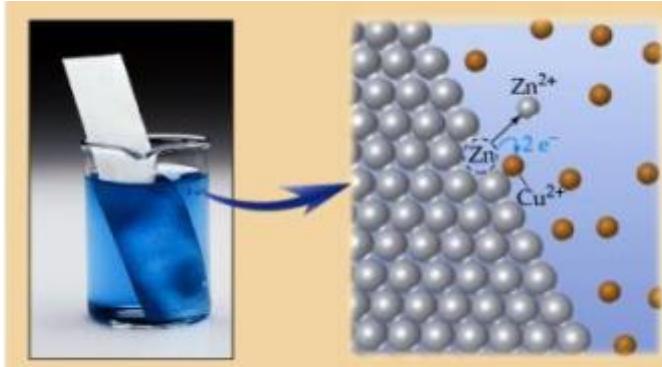


# Redox Reactions

## Oxidation Half-Reaction:



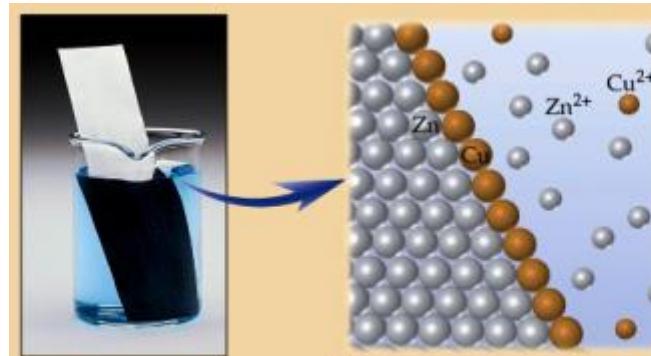
The Zn loses two electrons to form  $\text{Zn}^{2+}$ .



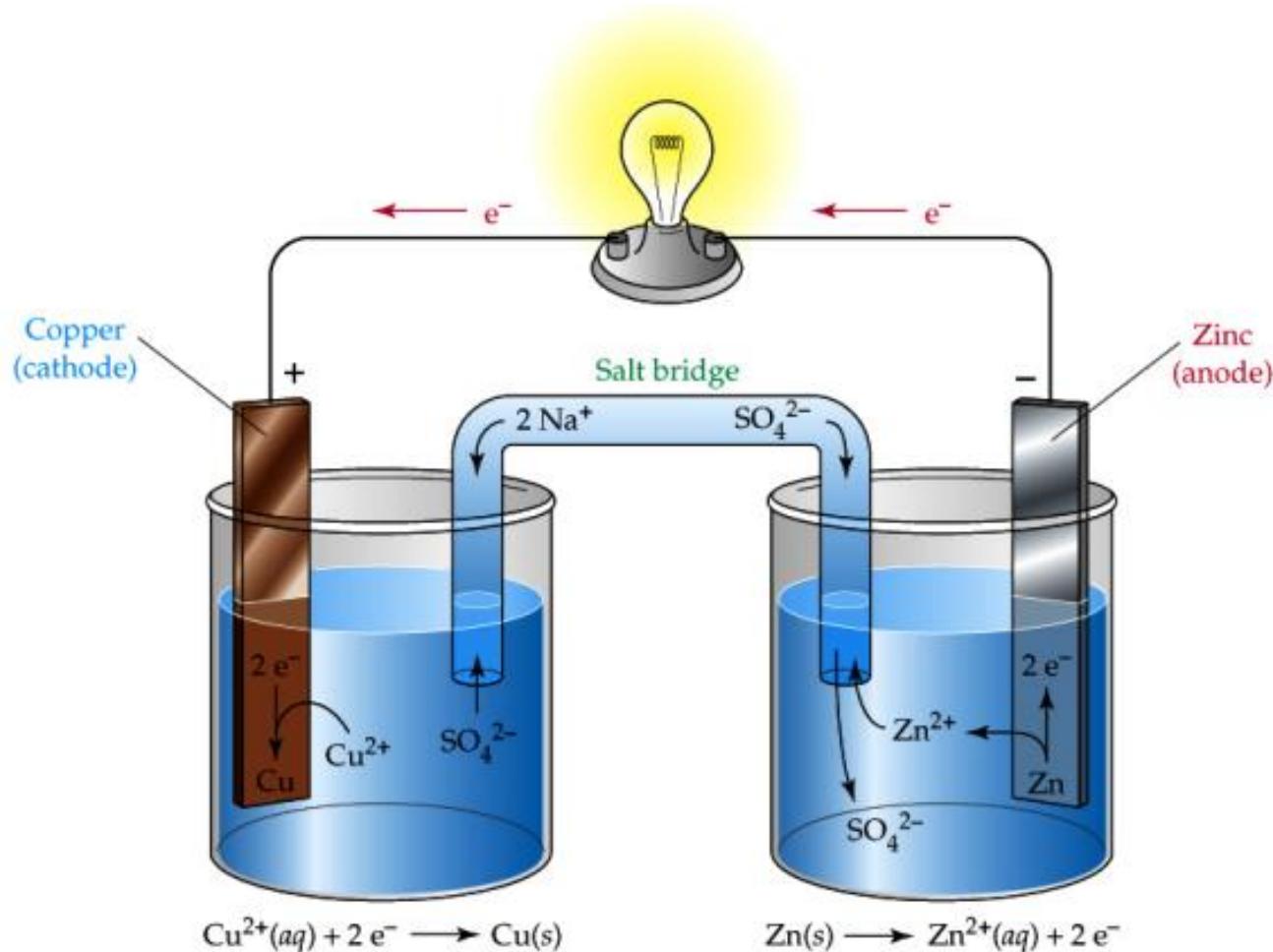
## Reduction Half-Reaction:

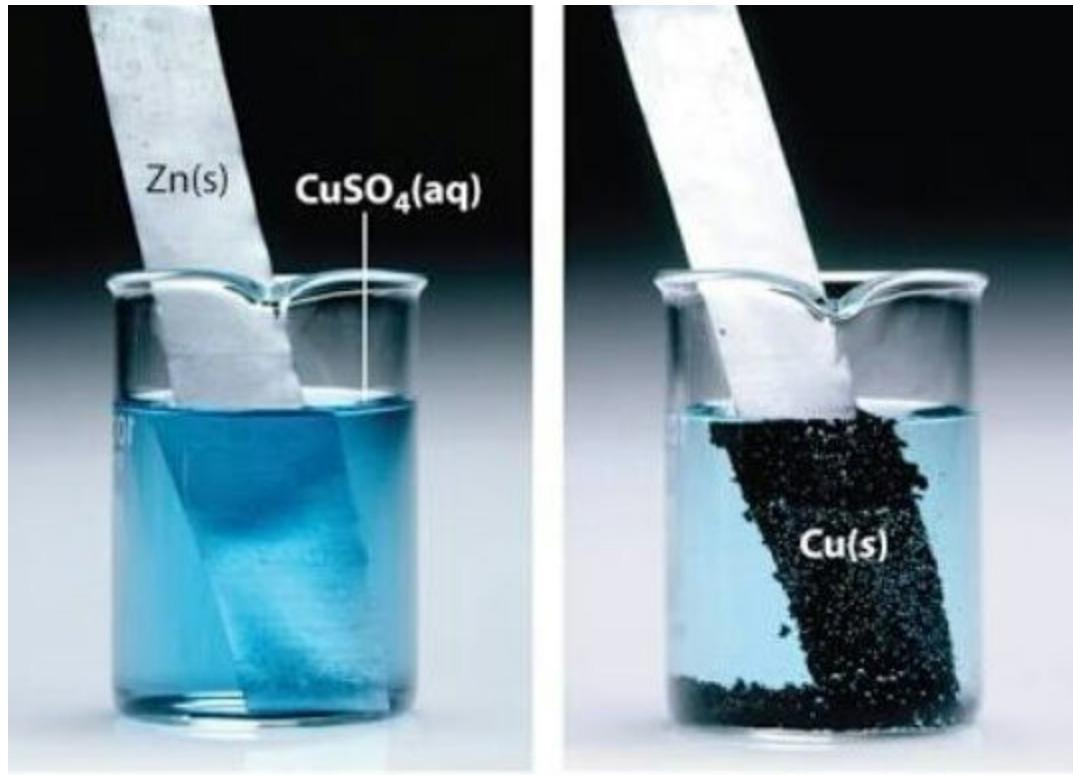


The  $\text{Cu}^{2+}$  gains two electrons to form copper.



# Redox Reactions





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Short-circuit, no electric current. → need to separate → electrochemical cell.

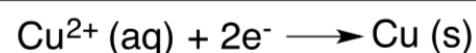
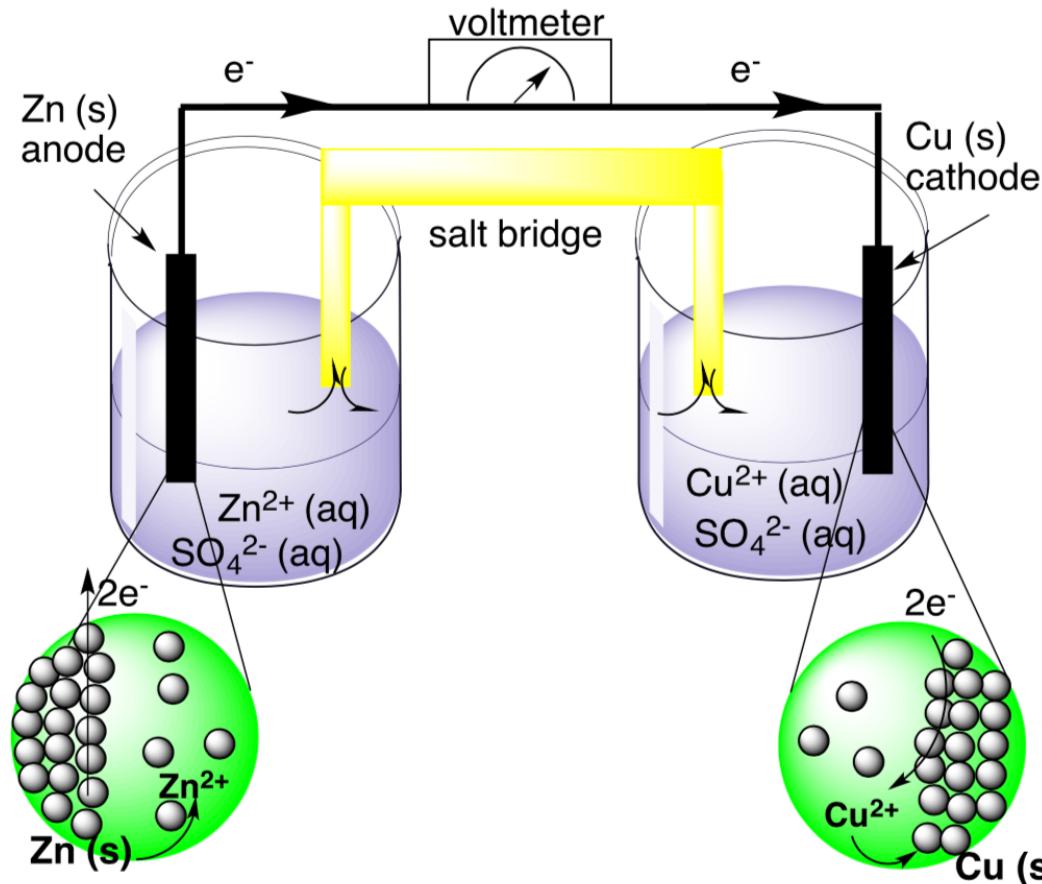
# Electrochemical Cells

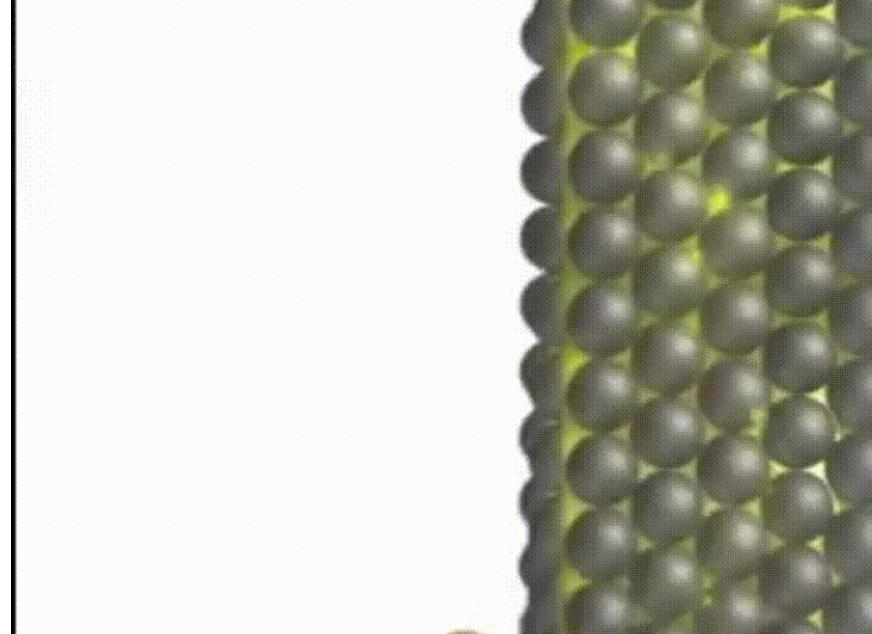
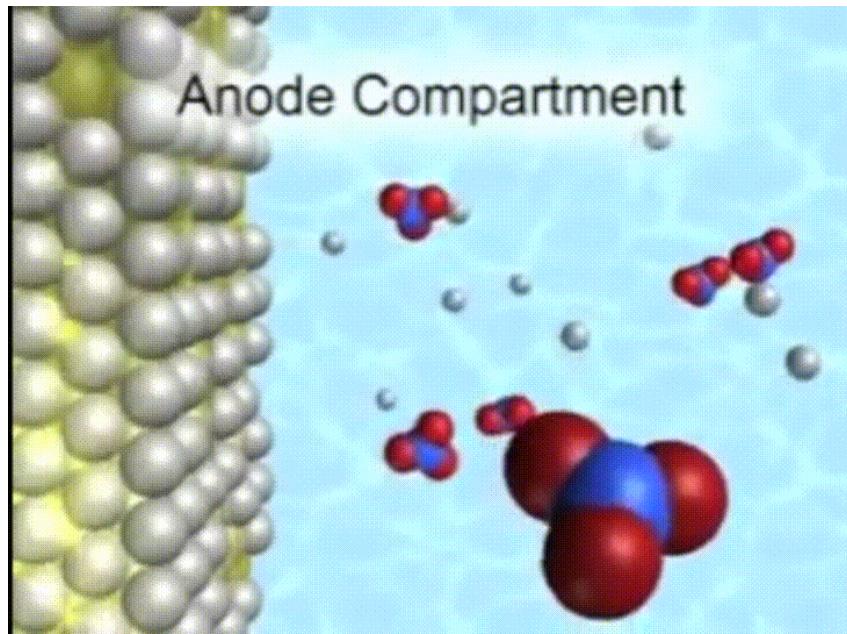
The basic experimental setup which realizes electron transfer in redox reactions is called an electrochemical cell.

Devices in which an electric current (a flow of electrons through a circuit) is either

- produced by a spontaneous chemical reaction (**Galvanic** cell)
- used to bring about a non-spontaneous reaction (**Electrolytic** cell)

# Electrochemical Cell



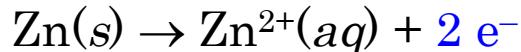


# Components

- **Electrodes:**

Any solid on whose surface oxidation-reduction reactions occur.

**Anode:** oxidation half-reaction takes place;



Oxidation of metal releases metal ions into the solution, leaving behind the electron at the surface of the metal electrode.

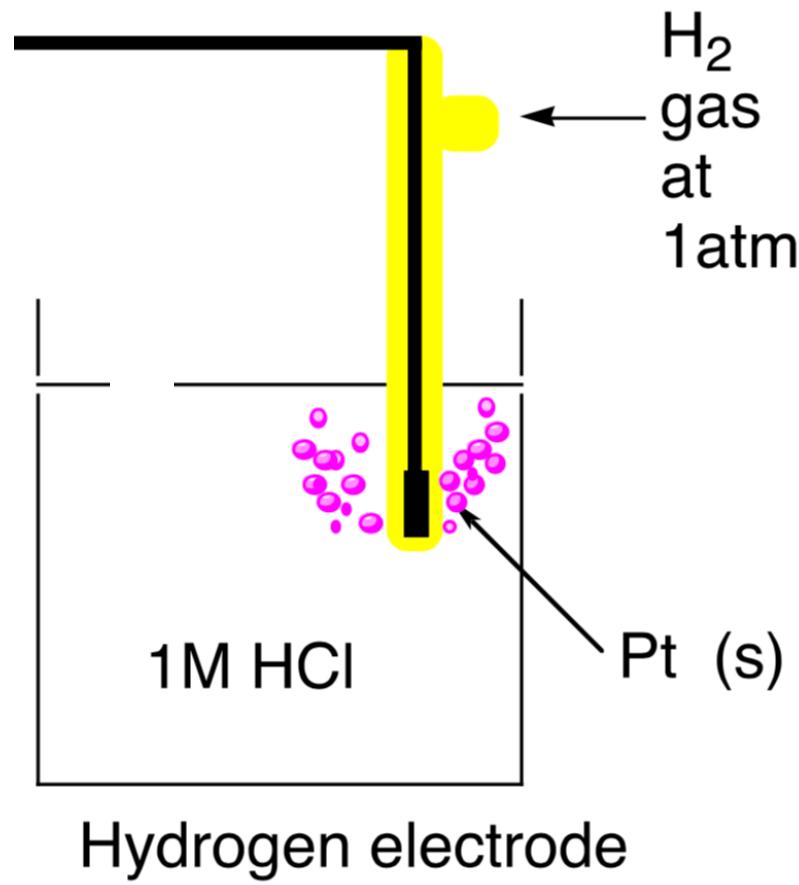
**Cathode:** reduction half-reaction occurs;



Movement of metal ions from the solution to the electrode leads to accumulation of positive charge at the surface of the electrode.

- **Active electrodes:** participate in redox
- **Inactive:** sites of oxidation and reduction.

# Types of Electrodes



# Components

- **Electrolyte:**

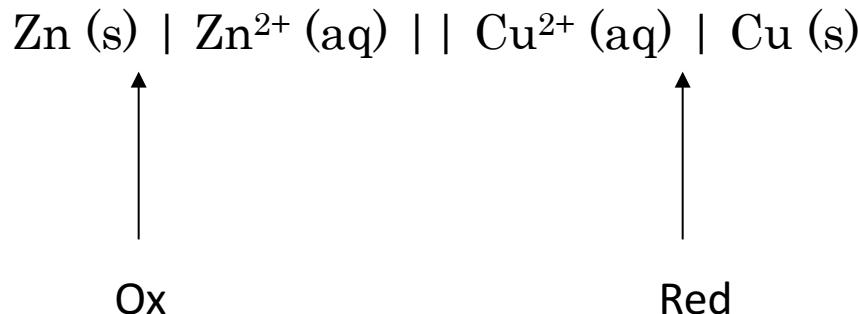
mixture of ions involved in reaction or carrying charge. Internal conducting environment that allows ions to migrate between both half cells so as to preserve electro neutrality.

- **Salt bridge:**

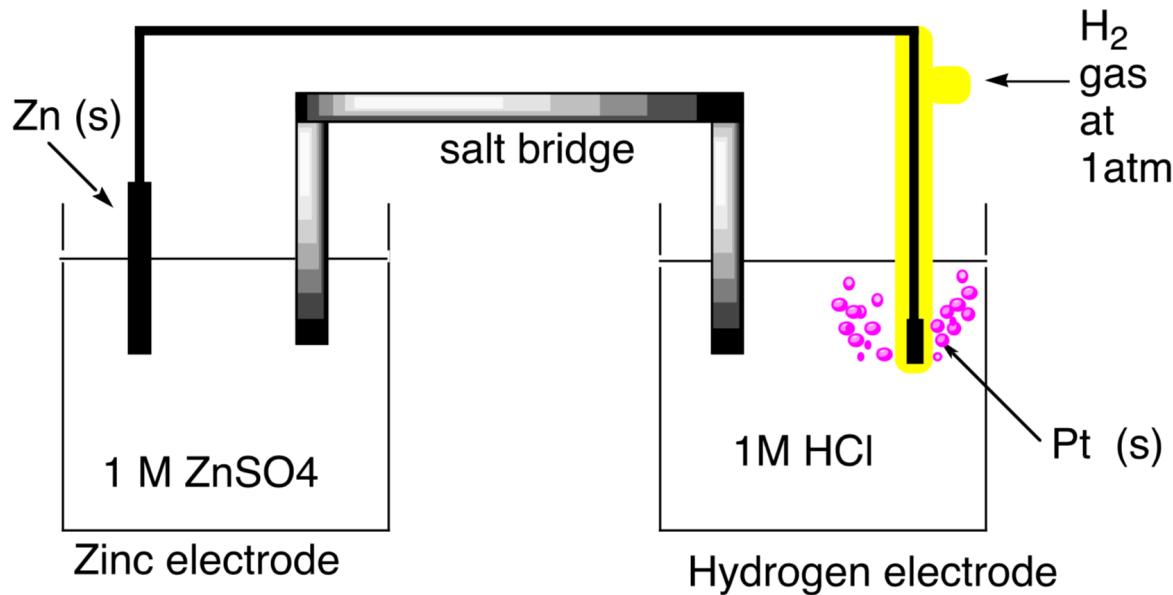
completes circuit (provides charge balance). Serves as a bridge to complete the electric circuit and maintain electro neutrality in the electrolyte.

# Cell Representation

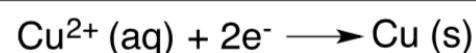
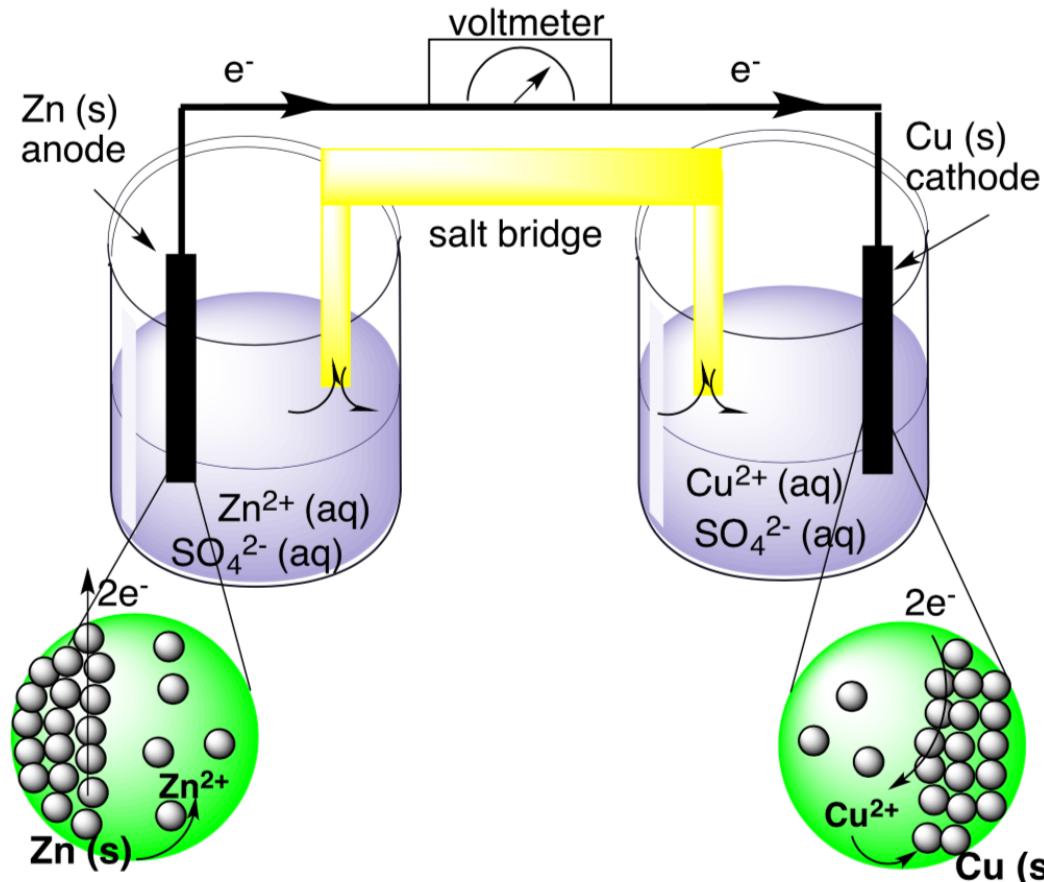
- Phase boundaries are represented by “ | ”, and salt bridge is represented by “ || ”.
- No phase boundary, then use “ , ”.
- Anode Half-Cell | | Cathode Half-Cell
- Electrode | Anode Soln | | Cathode Soln | Electrode



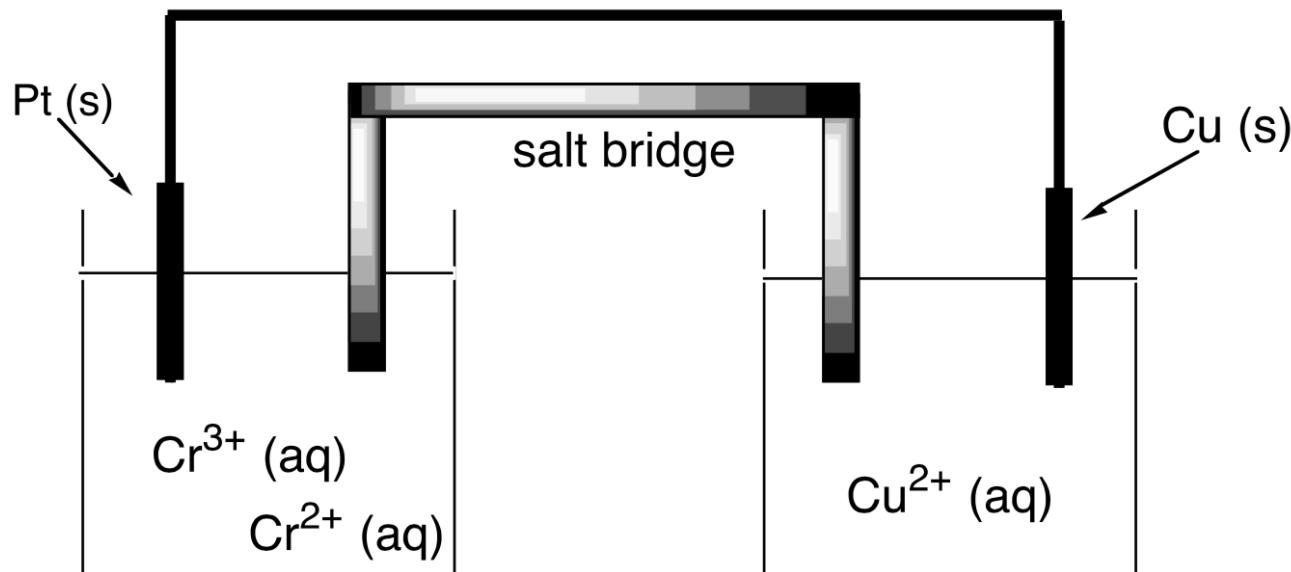
# Cell Representation



# Galvanic/Voltaic Cells



# Electrochemical Cells



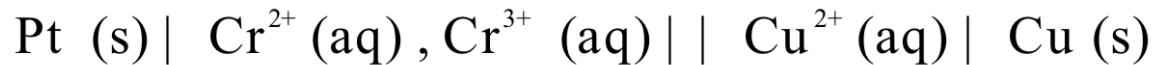
Anode (oxidation)



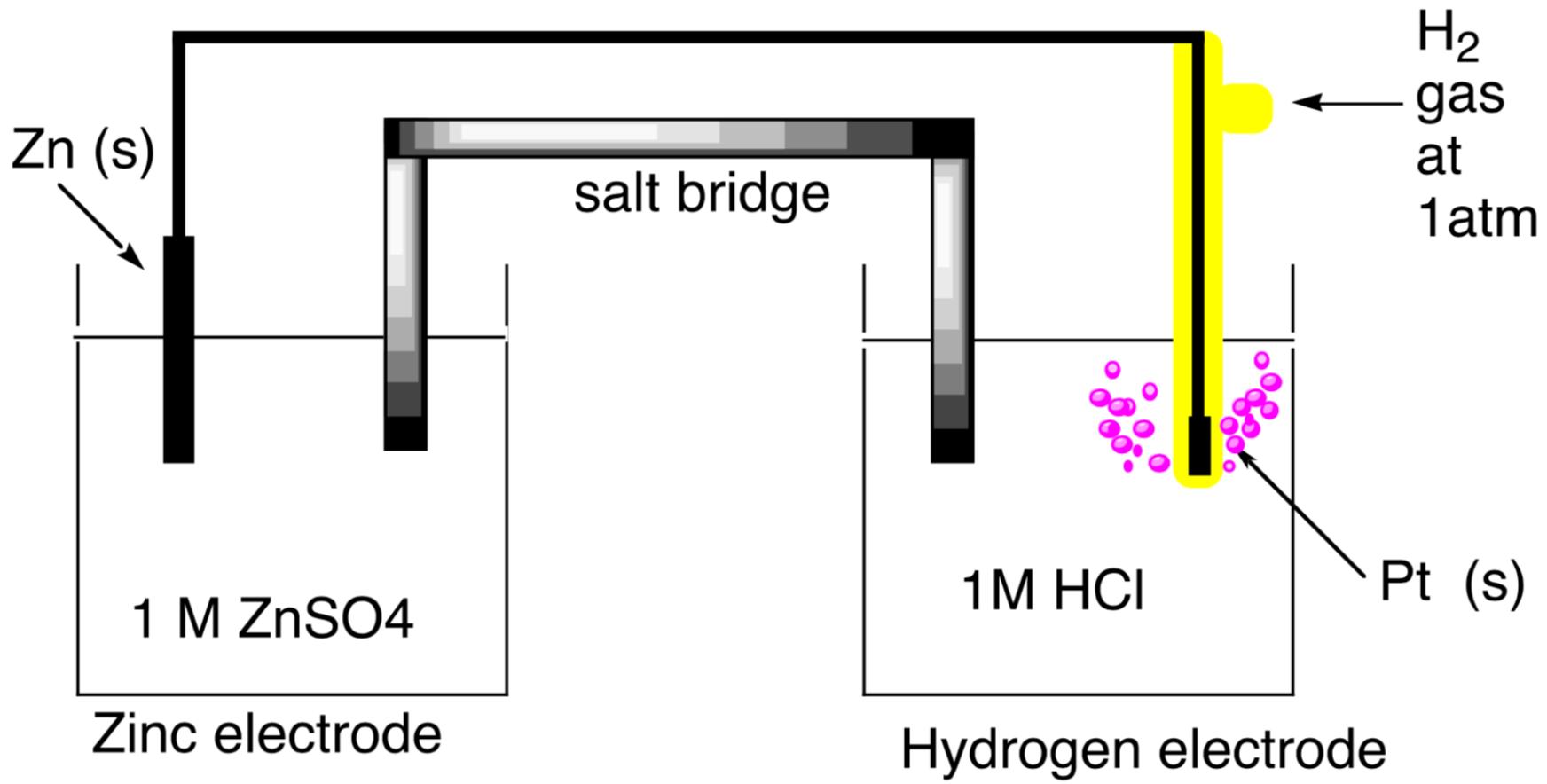
Cathode (reduction)



Notation for this type of cell is:

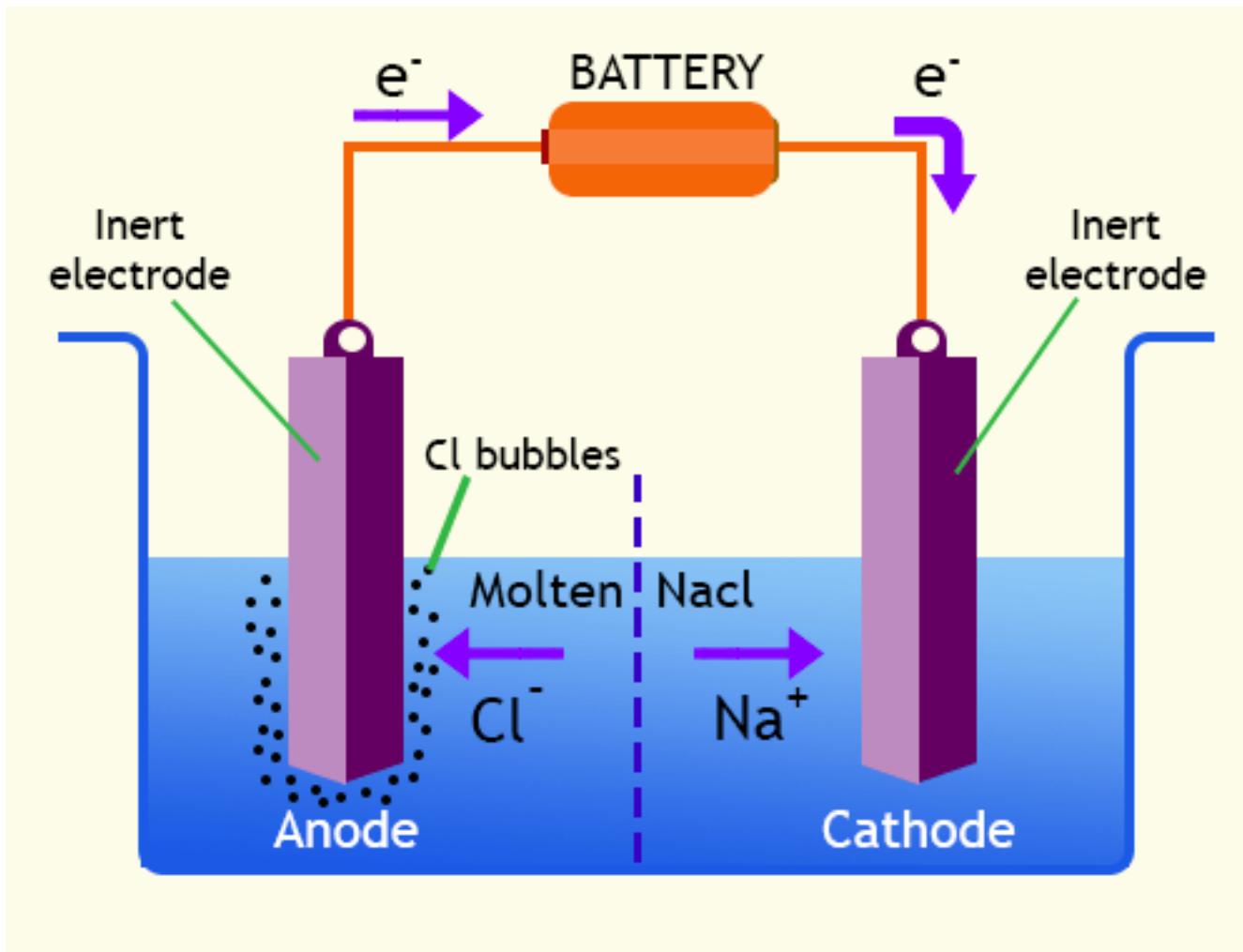


# Electrochemical Cells



Standard Hydrogen Electrode

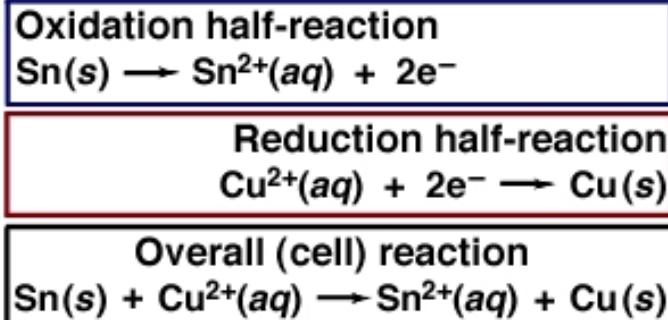
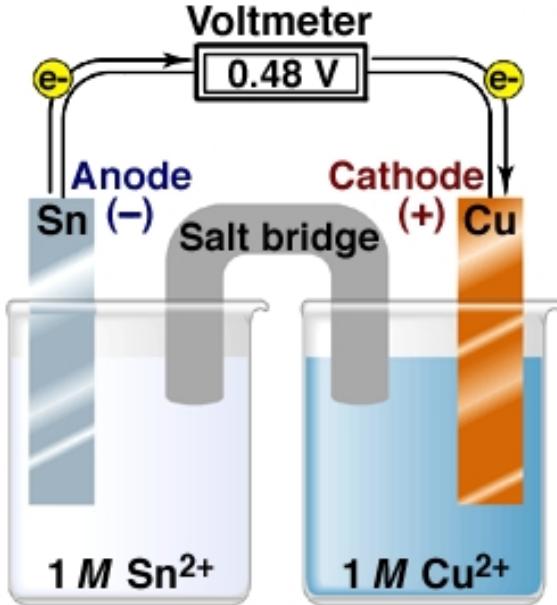
# Electrolytic Cells



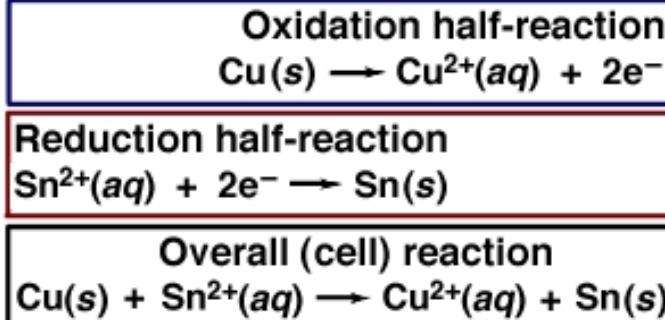
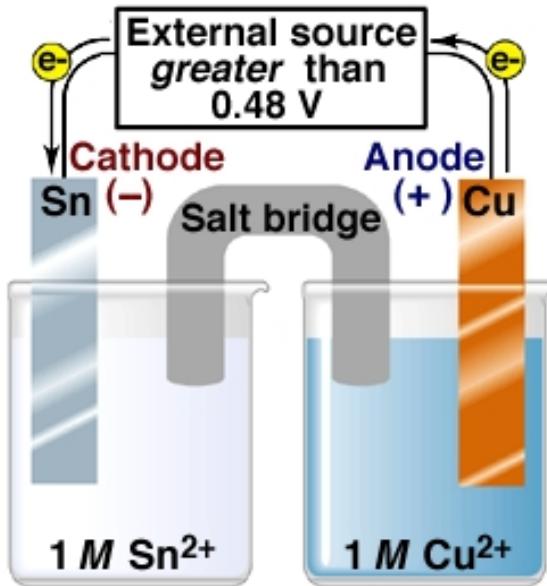
# Electrolytic Cells

Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, 2<sup>nd</sup> Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

## The Basis of a Voltaic and an Electrolytic Cell

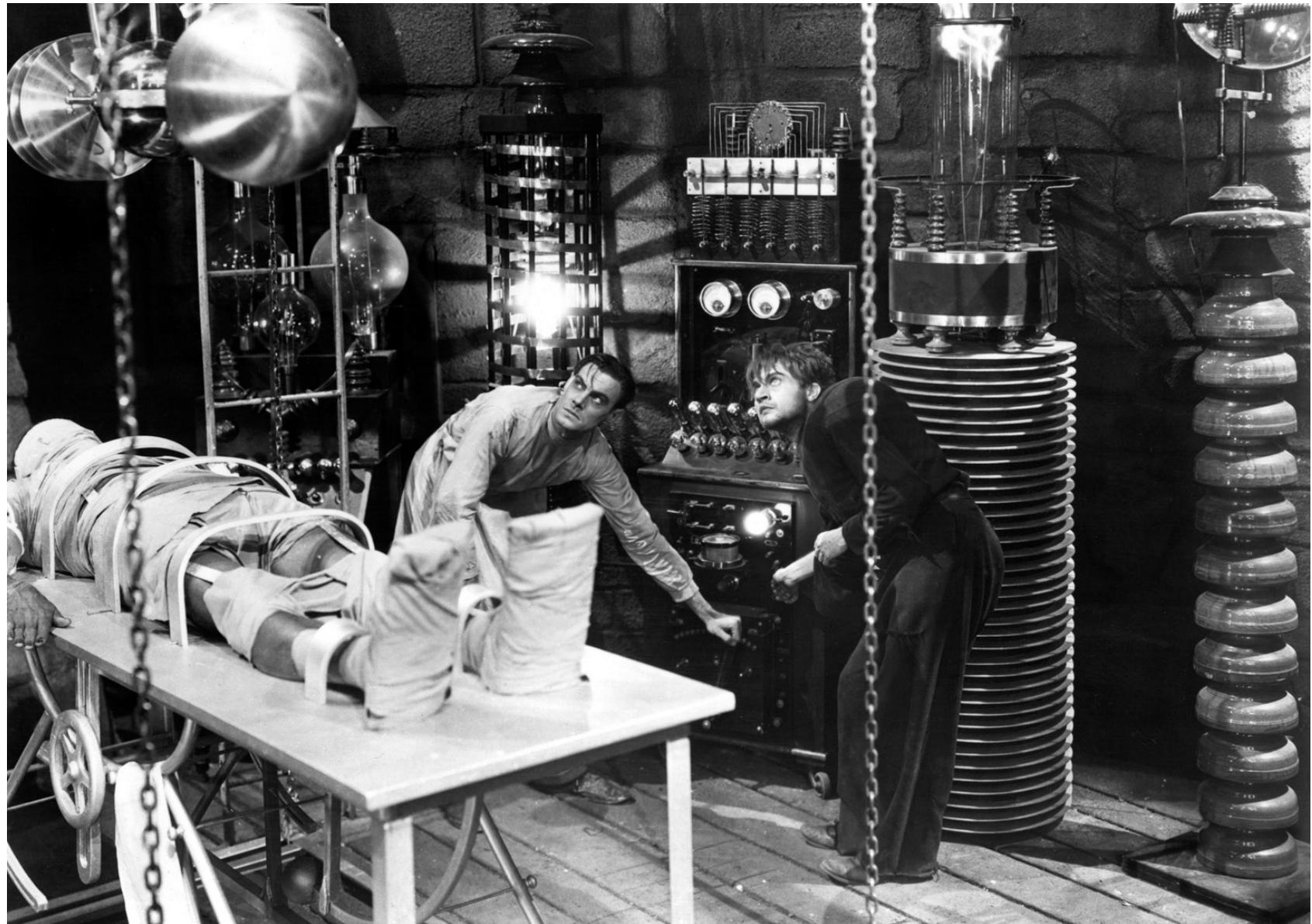


A Voltaic cell



B Electrolytic cell

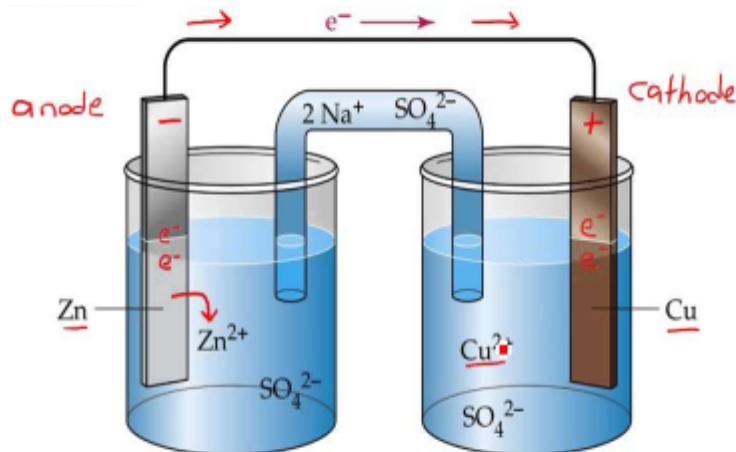
# Frankenstein



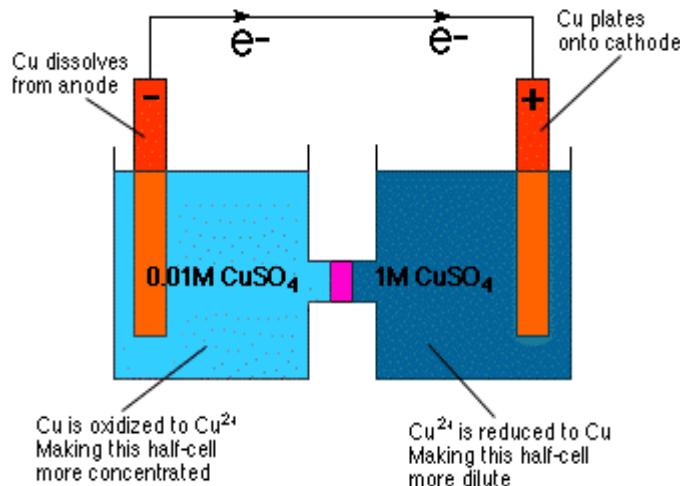
# Electrology



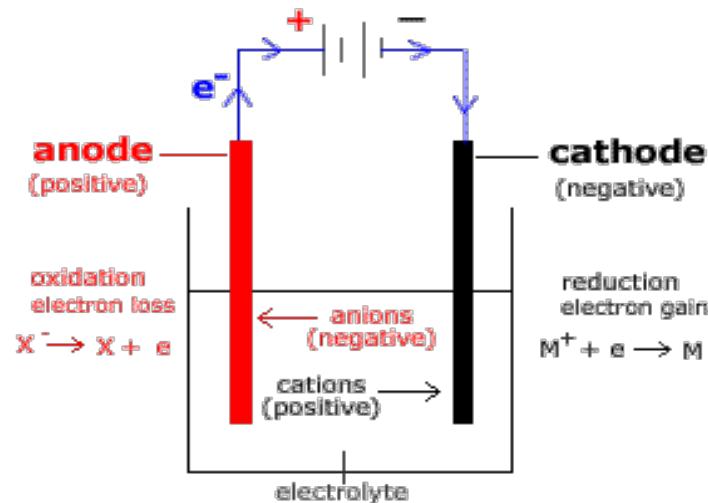
# Electrochemical Cells



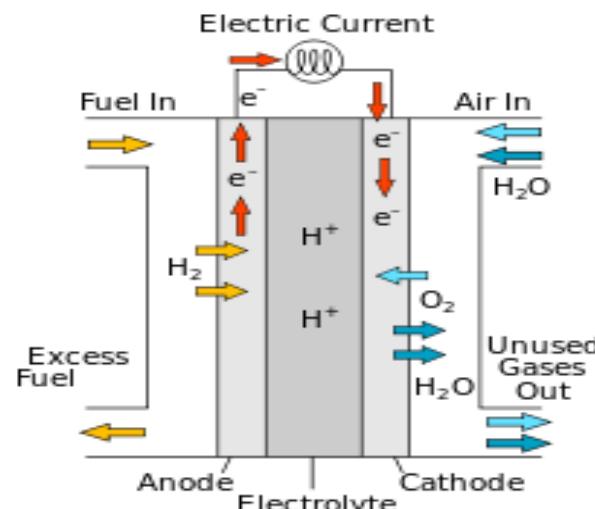
Galvanic cell



Concentration cell



Electrolytic cell



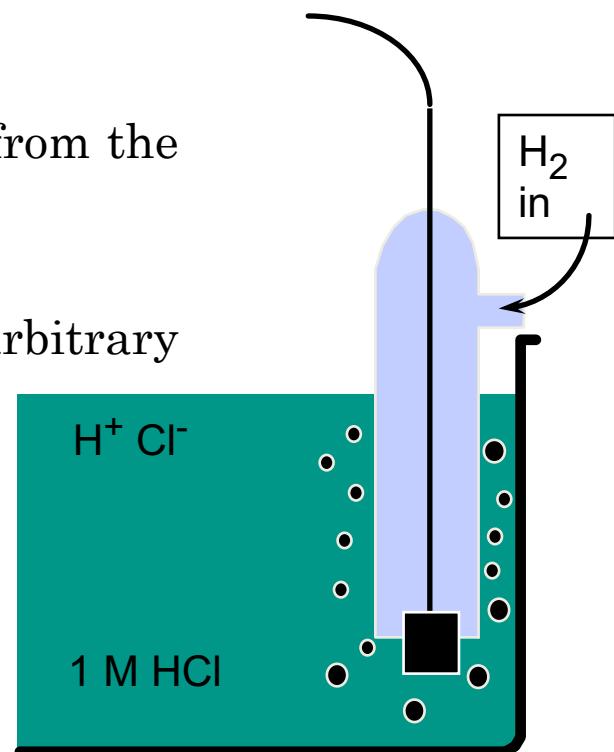
Fuel cell

# Electrode Potential

- Oxidation at one electrode and reduction at the other electrode.
- Can think of the cell as consisting of two **half-cells** joined together by an external circuit for flow of electrons and an internal pathway for migration of ions to maintain electroneutrality.
- Each half-cell has a potential difference depending on the electrode reaction, **Electrode Potential (E)**.
- **Oxidation potential:** tendency to lose electron
- **Reduction potential:** tendency to gain electron

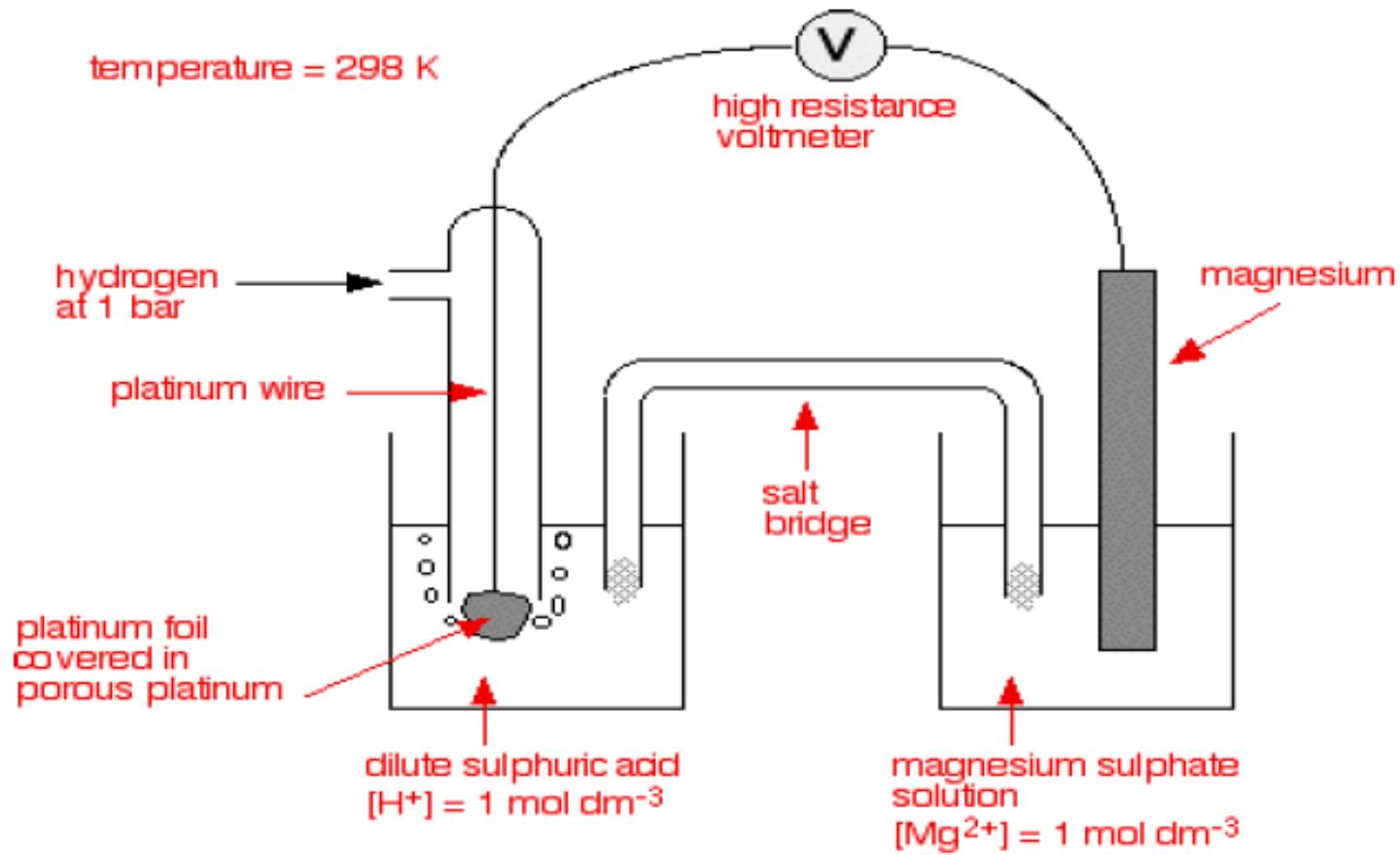
# Electrode Potential

- Individual half-cell potential are not directly measurable, so we use **reference** half-cell potential.
- Usually measured w.r.t. a standard hydrogen electrode (SHE) as anode.
- Defined as Standard Electrode Potential,  $E^\circ$ : **unit molar concentration (1 atm for gases) at  $25^0\text{ C}$ .**
- The standard half-cell potentials are determined from the difference between the two electrodes.
- The standard hydrogen electrode is assigned an arbitrary value of exactly **0.00 V**.



# Electrode Potential

$Mg^{2+} | Mg$  is -2.37V



# Electrochemical Series

|                                 | Reduction Half-Reaction   | $E^\circ$ (V) |                                |
|---------------------------------|---|---------------|--------------------------------|
| <b>Stronger oxidizing agent</b> | $F_2(g) + 2 e^- \rightarrow 2 F^-(aq)$  | 2.87          | <b>Weaker reducing agent</b>   |
|                                 | $H_2O_2(aq) + 2 H^+(aq) + 2 e^- \rightarrow 2 H_2O(l)$                        | 1.78          |                                |
|                                 | $MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O(l)$         | 1.51          |                                |
|                                 | $Cl_2(g) + 2 e^- \rightarrow 2 Cl^-(aq)$                                      | 1.36          |                                |
|                                 | $Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^- \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$ | 1.33          |                                |
|                                 | $O_2(g) + 4 H^+(aq) + 4 e^- \rightarrow 2 H_2O(l)$                            | 1.23          |                                |
|                                 | $Br_2(aq) + 2 e^- \rightarrow 2 Br^-(aq)$                                     | 1.09          |                                |
|                                 | $Ag^+(aq) + e^- \rightarrow Ag(s)$  | 0.80          |                                |
|                                 | $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$                                   | 0.77          |                                |
|                                 | $O_2(g) + 2 H^+(aq) + 2 e^- \rightarrow H_2O_2(aq)$                           | 0.70          |                                |
|                                 | $I_2(s) + 2 e^- \rightarrow 2 I^-(aq)$  | 0.54          |                                |
|                                 | $O_2(g) + 2 H_2O(l) + 4 e^- \rightarrow 4 OH^-(aq)$                           | 0.40          |                                |
|                                 | $Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$                                       | 0.34          |                                |
|                                 | $Sn^{4+}(aq) + 2 e^- \rightarrow Sn^{2+}(aq)$                                 | 0.15          |                                |
|                                 | $2 H^+(aq) + 2 e^- \rightarrow H_2(g)$  | 0             |                                |
| <b>Weaker oxidizing agent</b>   | $Pb^{2+}(aq) + 2 e^- \rightarrow Pb(s)$                                       | - 0.13        | <b>Stronger reducing agent</b> |
|                                 | $Ni^{2+}(aq) + 2 e^- \rightarrow Ni(s)$                                       | - 0.26        |                                |
|                                 | $Cd^{2+}(aq) + 2 e^- \rightarrow Cd(s)$                                       | - 0.40        |                                |
|                                 | $Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$                                       | - 0.45        |                                |
|                                 | $Zn^{2+}(aq) + 2 e^- \rightarrow Zn(s)$                                       | - 0.76        |                                |
|                                 | $2 H_2O(l) + 2 e^- \rightarrow H_2(g) + 2 OH^-(aq)$                           | - 0.83        |                                |
|                                 | $Al^{3+}(aq) + 3 e^- \rightarrow Al(s)$                                       | - 1.66        |                                |
|                                 | $Mg^{2+}(aq) + 2 e^- \rightarrow Mg(s)$                                       | - 2.37        |                                |
|                                 | $Na^+(aq) + e^- \rightarrow Na(s)$  | - 2.71        |                                |
|                                 | $Li^+(aq) + e^- \rightarrow Li(s)$  | - 3.04        |                                |

To maintain uniformity, convention is that half-cell potentials are always defined for the **reduction** direction.

# Electrochemical Series

- When selecting two half-cell reactions the **more negative value** will form the **oxidation half-cell**.
- Consider the reaction between zinc and silver:



- Therefore, zinc forms the oxidation half-cell:



# Cell Potential

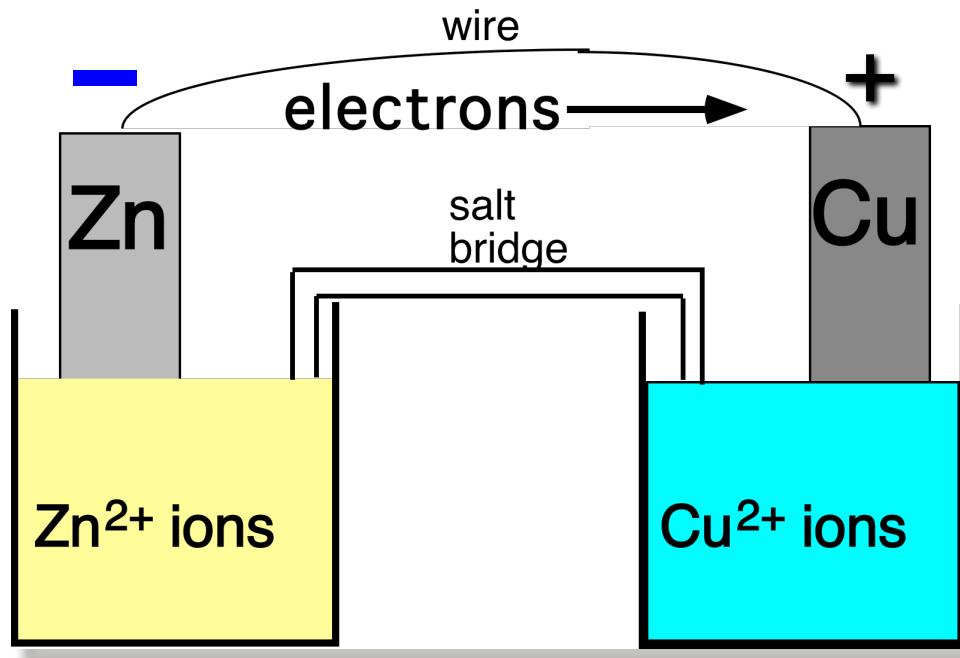
- Cell potential  $E_{\text{Cell}} = E_{\text{Right}} - E_{\text{left}}$  Reduction on the Right
  - At Anode:  $M \rightarrow M^{n+} + n e^-$
  - At Cathode:  $M^{n+} + n e^- \rightarrow M$
- Cell potential = Reduction potential of reduction half-cell + oxidation potential of the oxidation half-cell
- Oxidation potential =  $-1 \times$  Reduction potential

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$



$$E_{\text{Cell}}^{\circ} = 0.337 - 0.222 = 0.115 \text{ V}$$

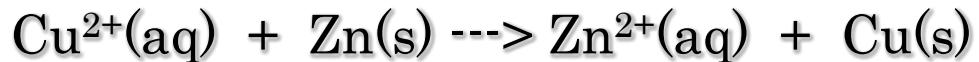
# Zn/Cu Electrochemical Cell



$$E^\circ = +0.76 \text{ V}$$



$$E^\circ = +0.34 \text{ V}$$



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

# Cell Voltage

Assume I<sup>-</sup> ion can reduce water.

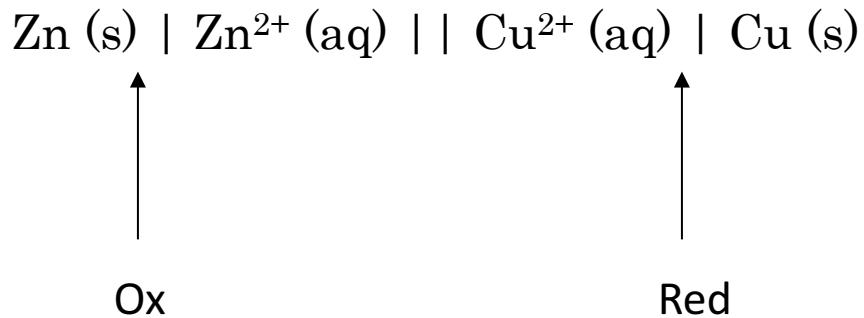


Assuming reaction occurs as written,

$$E^\circ = E^\circ_{\text{cat}} + E^\circ_{\text{an}} = (-0.828 \text{ V}) - (+0.535 \text{ V}) = -1.363 \text{ V}$$

Minus E<sup>°</sup> means rxn. occurs in opposite direction

(the connection is backwards or you are recharging the battery)



- Spontaneous reactions → electrons flow from left to right.
- Cell voltage  $\Delta V = V_R - V_L$
- **Electromotive Force (EMF), E,** of a cell is the potential difference of the cell measured under the condition of **no electric current flow.**

# EMF

- The “pull” or driving force on electrons
- Measured voltage (potential difference)

$$E_{\text{cell}} = \frac{\text{work or electrical potential energy}}{\text{unit of charge moved}} = \frac{J}{C} = V$$

# EMF

- Apply current via potentiometer in either direction of the cell. If EMF changes slightly upon reversing the current direction, cell is reversible.
- In reversible cell, the chemical reaction can process in either direction, depending upon the flow of current.
- If  $E > 0$ , spontaneous reaction and non-spontaneous if  $E < 0$ .
- Can be related to Gibbs free energy,  $G$ .

- Consider a cell in which n moles of electrons are transferred from left to the right electrode.
- Charge magnitude =  $Q_e \times N_A = 96485 \text{ C mol}^{-1}$  (Faraday constant, **F**).
- If  $\Delta V > 0$ , amount of work by electrons =  $n F \Delta V$
- For a reversible cell, this work =  $n F E^0$
- $\Delta G = - w_{\text{non PV}} = - n F E^0$

$$\Delta G^0 = - n F E^0$$

- EMF depends on the concentrations of reactant and products in the cell reaction.

# Problem

- Calculate  $\Delta G^0$  for the following reaction:



- $\text{Fe}^{+2}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}(\text{s}) \quad E^0 = 0.44 \text{ V}$
- $\text{Cu}^{+2}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s}) \quad E^0 = 0.34 \text{ V}$

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

- $E_{\text{cell}}^0 > 0$        $\Delta G^0 < 0$       Spontaneous
- $E_{\text{cell}}^0 < 0$        $\Delta G^0 > 0$       Non-spontaneous
- $E_{\text{cell}}^0 = 0$        $\Delta G^0 = 0$       Equilibrium

**$E_{\text{cell}}^0$ :** cell potential under standard conditions

- elements in standard states (298 K)
  - solutions: 1 M
  - gases: 1 atm

**$E_{\text{cell}}$ :** cell potential under non-standard conditions?

# The Nernst Equation



$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{where } Q = \frac{[M]}{[M^{n+}]}$$

$$\therefore -nFE = -nFE^\circ + RT \ln Q$$

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

$$E = E^\circ - \frac{RT}{nF} \ln \left[ \frac{M}{M^{n+}} \right]$$

$$E = E^\circ - \frac{0.0591}{n} \log \left[ \frac{M}{M^{n+}} \right]$$

Nernst's equation for single electrode

# The Nernst Equation



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

where  $Q = \frac{[M_1^{n+}]}{[M_2^{n+}]}$

$$\therefore -nFE = -nFE^\circ + RT \ln Q$$

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

$$E = E^\circ - \frac{0.0591}{n} \log \left[ \frac{M_1^{n+}}{M_2^{n+}} \right]$$

$$E_{cell}^0 = E_{Cathode}^0 - E_{Anode}^0$$



Write the electrode reactions and calculate the EMF of the cell at 298 K  
(Std. reduction potentials of Ni and Cu are -0.25 and 0.34 V respectively.)

**Solution:**

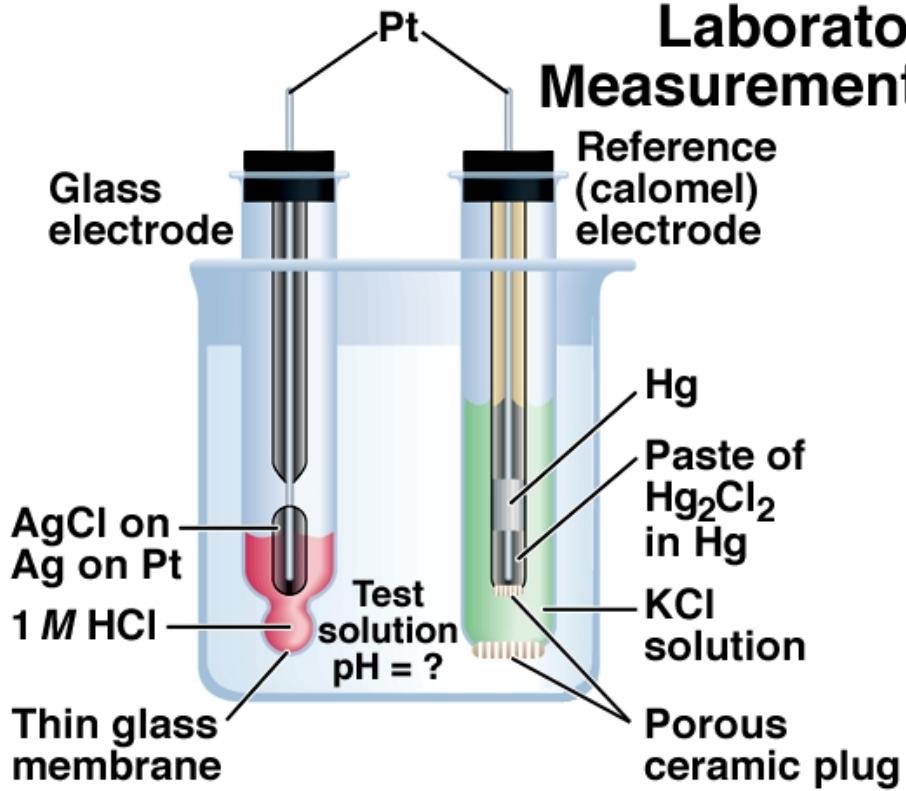
1. Find Anode and Cathode
2. Anode reaction; Cathode reaction; Cell reaction
3. Nernst Equation

$$E = E^o - \frac{0.0591}{2} \log \left[ \frac{\text{Ni}^{2+}}{\text{Cu}^{2+}} \right]$$

$$E = E^o - \frac{0.0591}{2} \log \left[ \frac{0.01}{0.5} \right]$$

$$E = 0.59 + 0.05 = 0.64\text{V}$$

## Laboratory Measurement of pH



$$E_{cell} = E_{\text{Ref}} + E_{\text{Hydrogen}}$$

$$E_{\text{Hydrogen}} = E_{\text{Hydrogen}}^0 - \frac{RT}{nF} \ln Q$$

$$E_{\text{Hydrogen}} = 0 - \frac{0.0591}{2} \log \left[ \frac{[H^+]^2}{P_{H_2}} \right]$$

$$E_{\text{Hydrogen}} = -\frac{0.0591}{2} 2 \log[H^+]$$

$$E_{\text{Hydrogen}} = 0.0591 \text{pH}$$

$$\therefore E_{cell} = E_{\text{Ref}} + 0.0591 \text{pH}$$

$$pH = \frac{E_{cell} - E_{\text{Ref}}}{0.0591}$$

# Calculating $E^0_{\text{cell}}$

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$



Given:  $E^0_{\text{cell}} = +1.39 \text{ V}$

$E^0_{\text{Br2}} = +1.07 \text{ V}$

What is  $E^0_{\text{V}^{3+}}$  and is the reaction spontaneous?

# Problem

Calculate the voltage generated in the following cell at 298 K:



(Std. reduction potentials of Fe and Mn are -0.40 and -1.18 V respectively.)

**Solution:**

1. Find Anode and Cathode
2. Anode reaction; Cathode reaction; Cell reaction
3. Nernst Equation

$$E = E^o - \frac{0.0591}{2} \log \left[ \frac{\text{Mn}^{2+}}{\text{Fe}^{2+}} \right]$$

$$E = E^o - \frac{0.0591}{2} \log \left[ \frac{0.1}{1} \right]$$

$$E = 0.78 + 0.02960 = 0.8096V$$

A cell is constructed by coupling a zinc electrode dipped in 0.5 M ZnSO<sub>4</sub> and a Nickel electrode dipped in 0.05 M NiSO<sub>4</sub>. Write the cell representation and cell reaction. Calculate the EMF of the cell at 298 K.  
(std. red. Potentials of Zn and Ni are -0.76 and -0.25 V resp.)

**Solution:**

1. Find Anode and Cathode
2. Anode reaction; Cathode reaction; Cell reaction
3. Nernst Equation

$$E = E^o - \frac{0.0591}{2} \log \left[ \frac{\text{Zn}^{2+}}{\text{Ni}^{2+}} \right]$$

$$E = E^o - \frac{0.0591}{2} \log \left[ \frac{0.5}{0.05} \right]$$

$$E = 0.59 - 0.02960 = 0.48V$$

# Concentration Cell

Consider the following cell:



calculate the EMF of the cell at 298 K

**Solution:**

$$E = E^\circ - \frac{0.0591}{n} \log \left[ \frac{LC}{HC} \right]$$

$$E = 0 - \frac{0.0591}{n} \log \left[ \frac{LC}{HC} \right]$$

$$E = \frac{0.0591}{n} \log \left[ \frac{HC}{LC} \right]$$

# Charging a Battery

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When you charge a battery, you are forcing the electrons backwards (from the + to the -). To do this, you will need a higher voltage backwards than forwards. This is why the ammeter in your car often goes slightly higher while your battery is charging, and then returns to normal.

