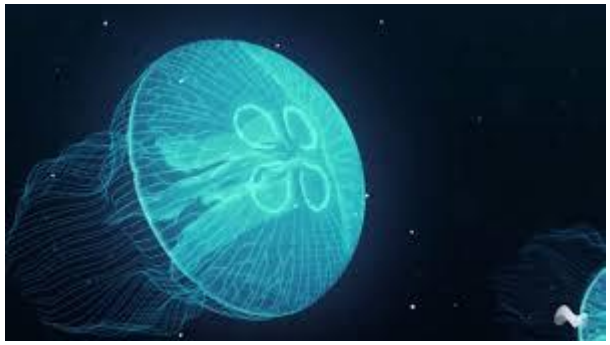
Electrochemistry

Electrochemistry is a discipline that deals with chemical reactions that involve an exchange of electrons between two substances.

A branch of chemistry to study the interrelation between electrical and chemical effects.

Many natural phenomena are based on electrochemical processes, such as the corrosion of metals, the ability of some sea creatures to generate electrical fields, and the workings of the nervous systems of humans and other animals.



Electrochemical reactions

- Chemical changes generate electric currents
- Chemical reactions triggered by the passage of electricity

Electrochemistry

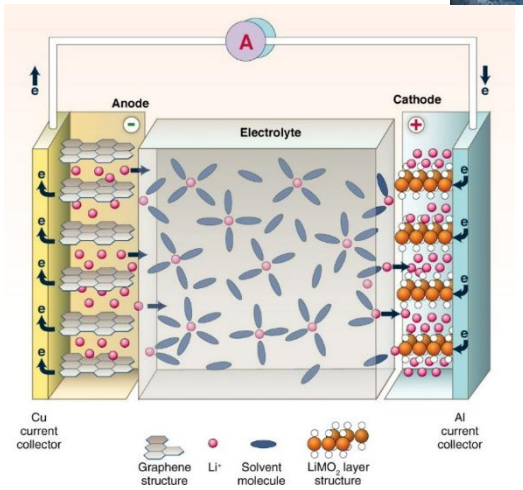
Fireflies, anglerfish, luminous shrimp, squid, jellyfish, and even bacteria give off energy in the form of light as a result of redox reactions. You will discover that the transfer of electrons in a redox reaction produces energy.

Many physiological processes in our body depend on electrified interfaces and electrochemical processes. Neurons use electrochemical processes to transmit information through the nervous system, allowing the nervous system to communicate with itself and with the rest of the body.

Electrochemistry has an ever increasing impact in everybody's daily life.
Applications - They play an important role in modern technology,
Batteries, Fuel cells, Solar cells
Electrophoresis
Corrosion, Electroplating
Electrochemical sensor

Electrochemistry

Electrochemical energy conversion and storage are directly at work in batteries (like in notebooks, smart phones and car batteries) and, increasingly, in fuel cells.



Mining

Space Applications

Consumer Electronics

Power Invertors

Energy Storage System

Lithium Ion Batteries

Electric Vehicles (EV, HEV, PHEV)

Defence /Military Applications

Marines and Submarines

Telecom Towers

Solar and Wind Energy Storage

Railways

Electrochemistry

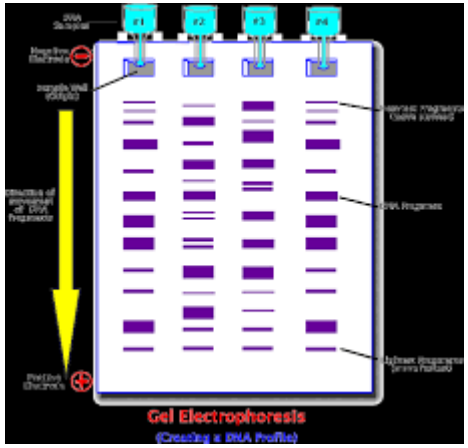
Many appliances of daily life, like screws, nuts, electrical connectors have been surface finished by electroplating processes, to protect them from corrosion (an electrochemical process as well) or to improve functional properties like electronic conductivity.

Even more, the manufacturing of all printed circuit boards in electronic devices contains electrochemical steps for the plating of the interconnects.

Electrochemical Cells

Electrochemical sensor - Handheld Electrochemical Sensor Detects Diseases, Measures Biomarkers, explosives

Electrophoresis



Redox Reactions

Reactions where electrons are transferred from one atom to another are called oxidation–reduction reactions.
When oxidation occurs, an element loses electrons.
An element gains electrons during reduction.

$$2\ Na(s) + Cl_2(g) \rightarrow 2\ Na^+Cl^-(s)$$

Oxidation

$Na \rightarrow Na^+ + 1\ e^-$

Reduction

$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Oxidation

$Zn \rightarrow Zn^{2+} + 2\ e^-$

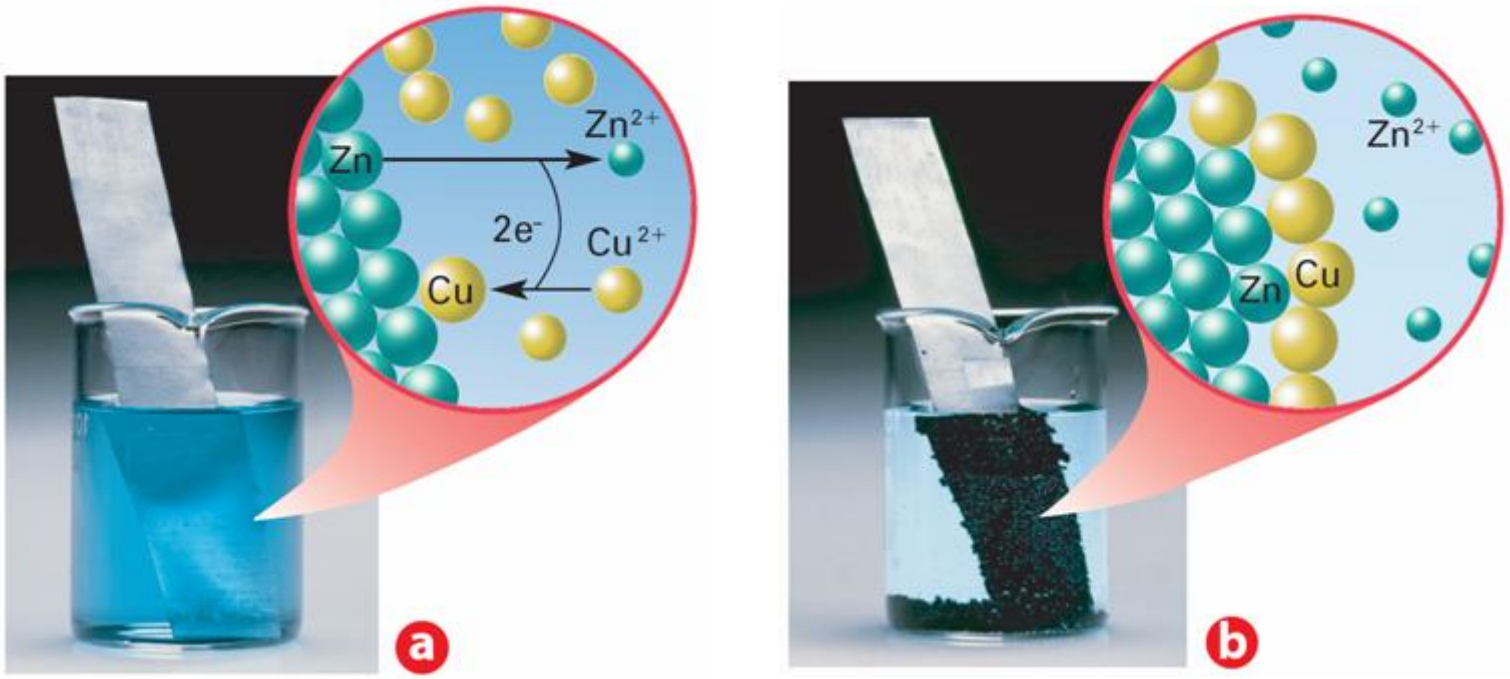
Reduction

$Cu^{2+} + 2\ e^- \rightarrow Cu$

Redox Reactions

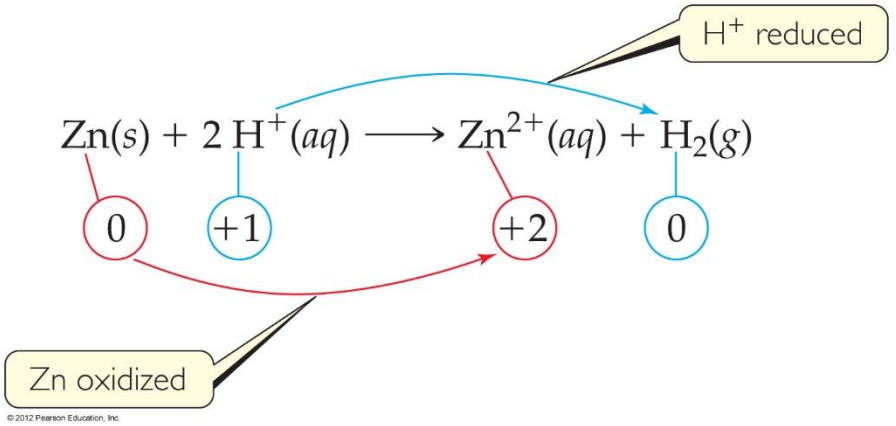
Redox reactions involve the transfer of electrons from one substance to another.

Redox reactions have the potential to generate an electric current.



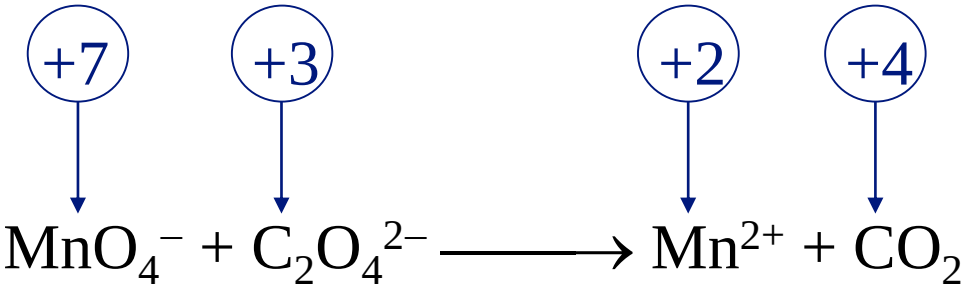
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Redox Reactions



Consider the reaction between MnO_4^- and $C_2O_4^{2-}$:

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq)$$

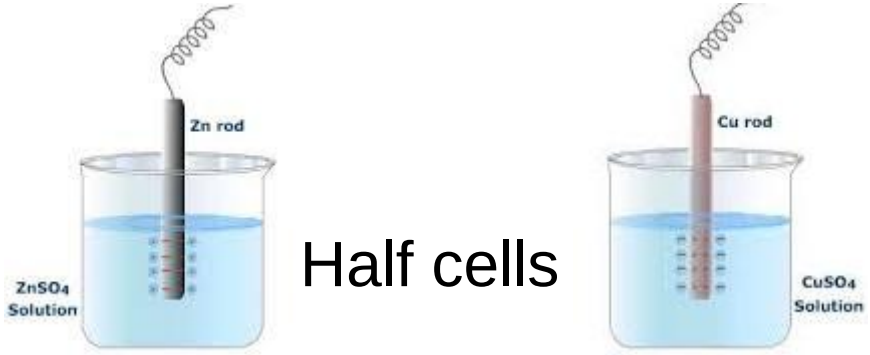


Since the manganese goes from +7 to +2, it is reduced.

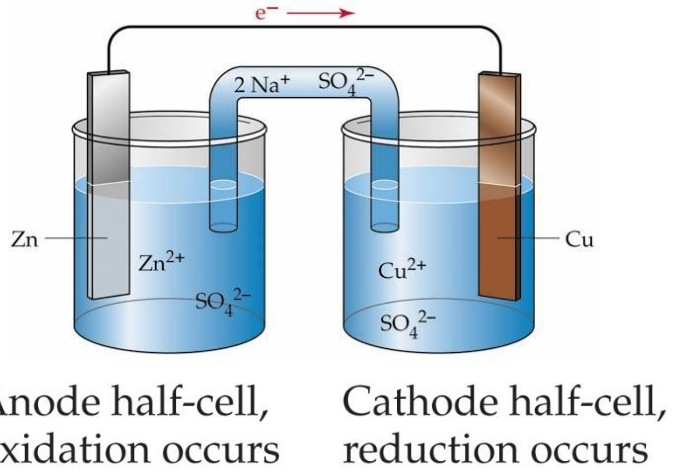
Since the carbon goes from +3 to +4, it is oxidized.

Electrochemical Cells

Placing a piece of electrode in an electrolyte solution makes a half cell. The two half cells combined to make an electrochemical cell. Unless a half cell is connected to another half cell via an electric conductor and salt bridge, no reaction will take place in a half cell.



Half cells



Half cell reactions of a Daniell cell:

At Anode, $Zn \rightarrow Zn^{2+} + 2\ e^-$

At cathode, $Cu^{2+} + 2\ e^- \rightarrow Cu$

overall reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Electrochemical Cells

There are two types of electrochemical cells:

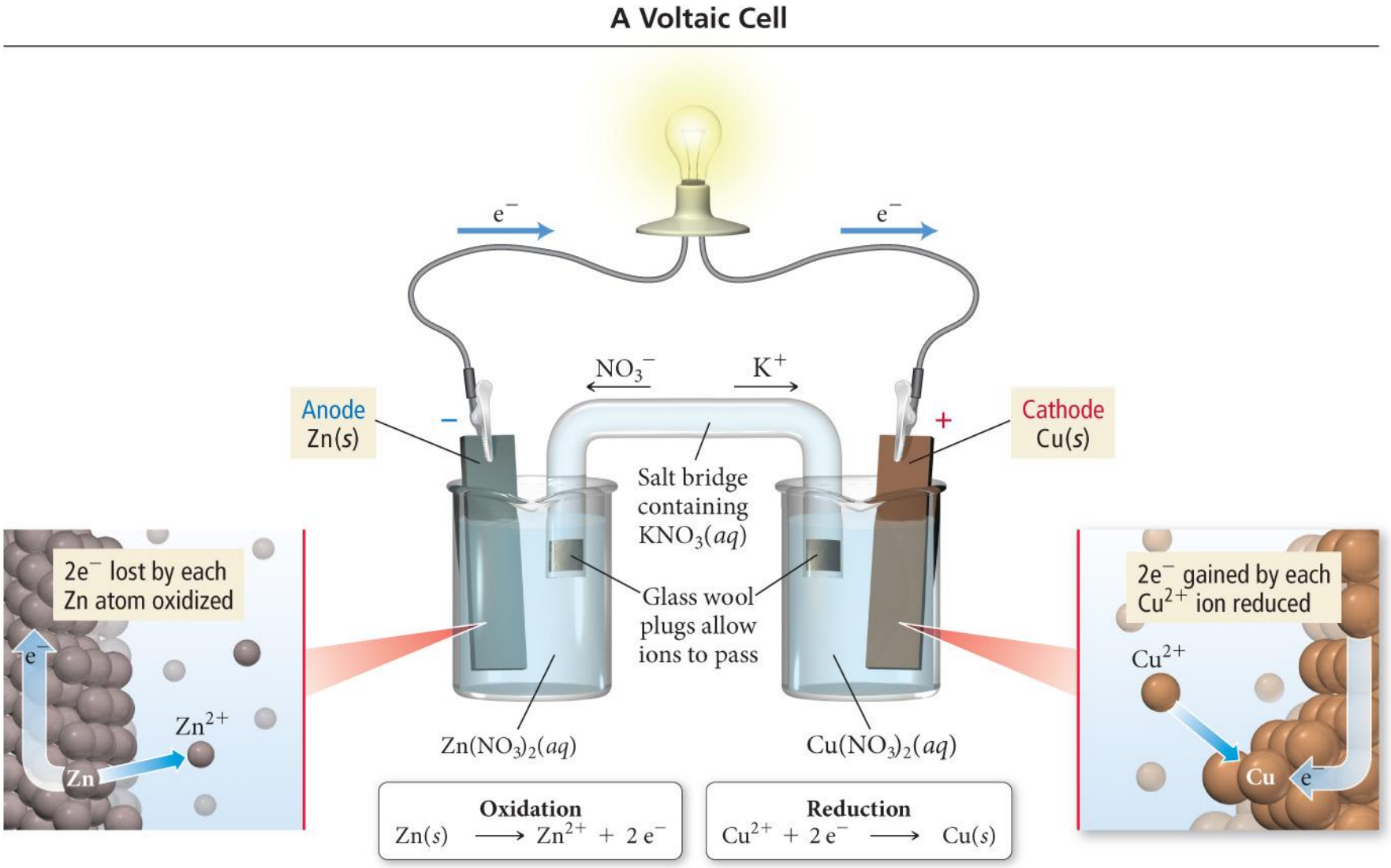
1. Galvanic cells
    - converts chemical energy into electrical energy
    - spontaneous redox reactions take place to produce electrical energy

        Fuell cell, Battery

2. Electrolytic cells
    - converts electrical energy into chemical energy
    - Non-spontaneous redox reactions occurred by the supply of electrical energy

        Electroplating

Galvanic Cell



overall reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Galvanic Cell

- Due to the potential difference between two electrodes, redox reactions occur spontaneously.
- The oxidation occurs at the **anode**.
- The reduction occurs at the **cathode**.
- When one electron flows from the anode to the cathode, the charges in each beaker would not be balanced and the flow of electrons would stop. Therefore, we use a salt bridge, usually a U-shaped tube that contains a salt solution, to keep the charges balanced. The salt bridge is required to complete the circuit and maintain charge balance.
- Cations move toward the cathode - Anions move toward the anode.
- Electrons leave the anode and flow through the wire to the cathode. As the electrons leave the anode, the cations formed dissolve into the solution in the anode compartment.
- As the electrons reach the cathode, cations in the cathode are attracted to the negative cathode. The electrons are taken by the cation, and the neutral metal is deposited on the cathode.

Galvanic Cell

Electrode materials

Solid metals (Pt, Au, Ag, …)

Liquid metals (Hg, amalgam, …)

Carbons (graphite, diamond, …)

Semiconductors (ITO, Si, …)

Electrolyte

Liquid solutions containing ionic species

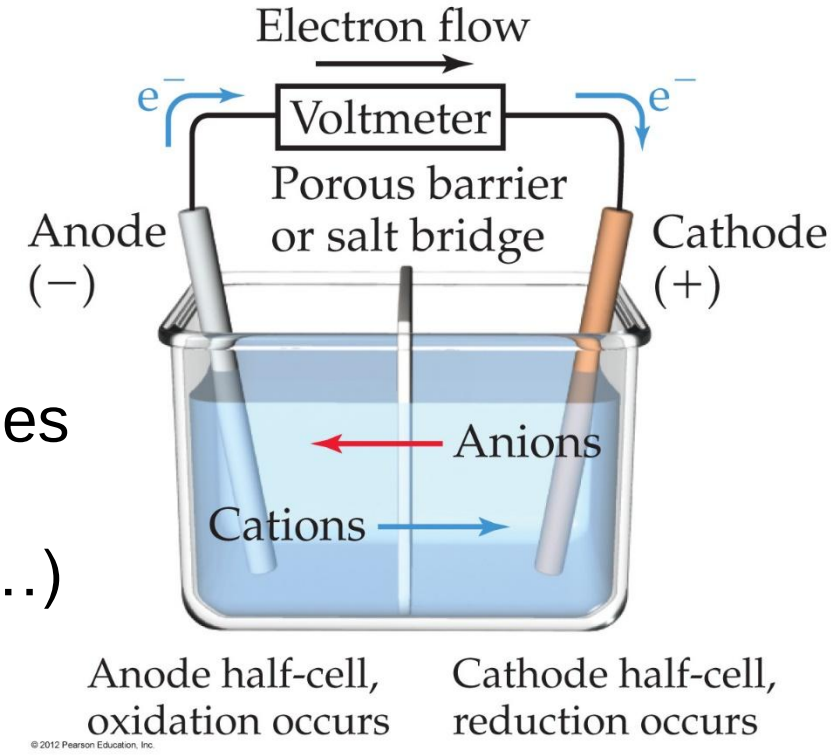
Ionic liquids

Ionically conductive polymer (Nafion,…)

Semipermeable membrane

or

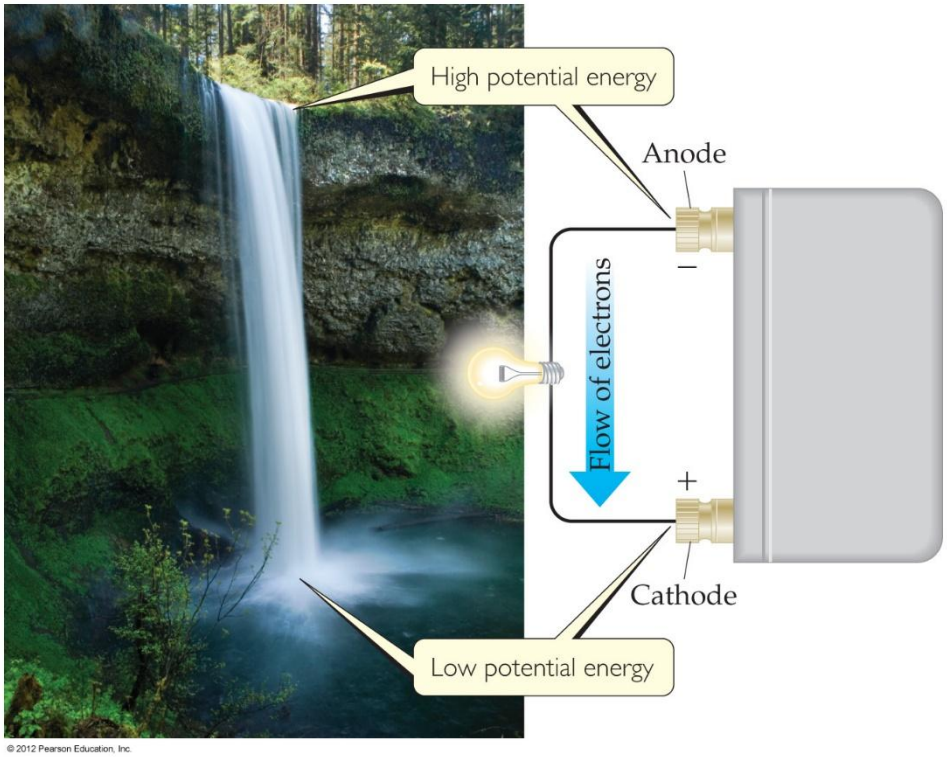
Salt bridge – aq. KNO_3, NaCl, $NaNO_3$, KCl with agar-agar or cotton



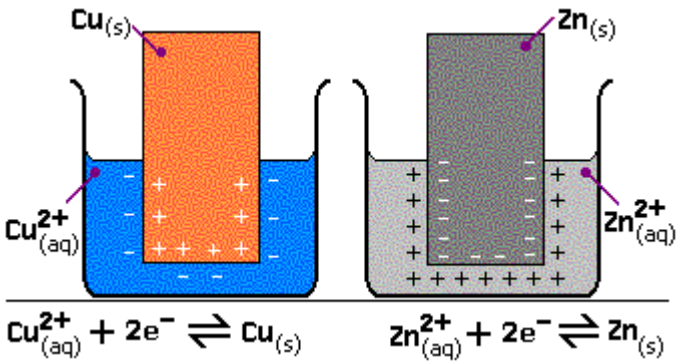
Electromotive Force (emf)

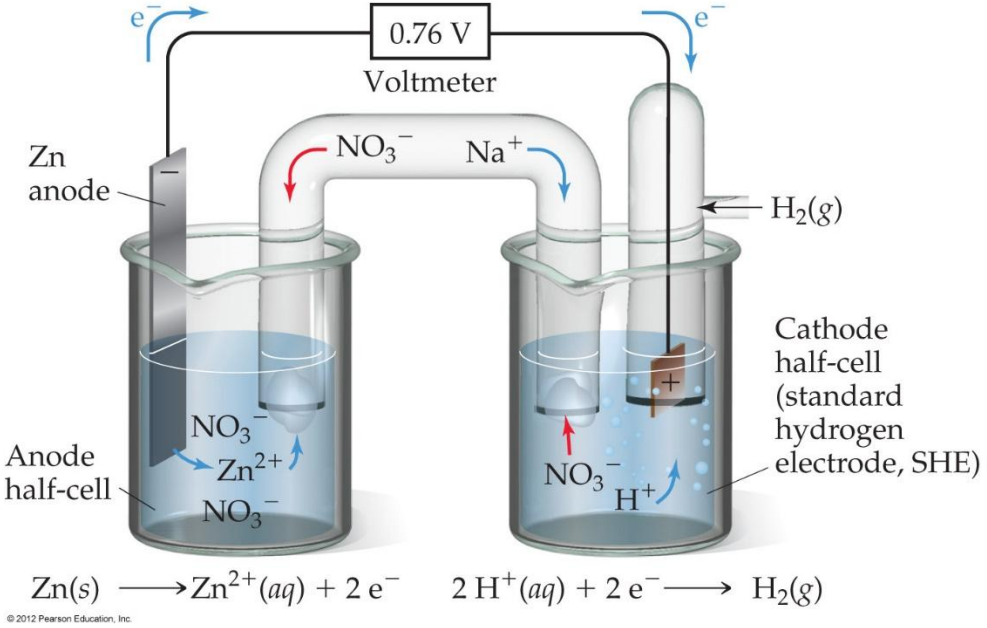
Electrons spontaneously flow one way in a redox reaction from higher to lower potential energy.

The potential difference between the anode and cathode in a cell is called **cell potential.** The cell potential under standard conditions is called the **electromotive force (emf)** and is designated as E_{cell}.



Single Electrode Potential





The electrode potential of any other electrode is obtained by coupling it with a standard hydrogen electrode (SHE, reference electrode). The electrode potential depends upon,

- The nature of the metal and its ions
- Concentration of the ions in the solution
- Temperature

Standard Reduction Potentials

Reduction potentials for many electrodes have been measured and tabulated. Their values are referenced to a standard hydrogen electrode (SHE). A standard hydrogen electrode has been assigned as an electrode potential of 0.0 volt and is used as a primary reference electrode

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

E°_{red} (V)	Reduction Half-Reaction
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+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

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$$2\,H^+(aq, 1M) + 2e^- \longrightarrow H_2(g, 1\ atm)$$

Cell Potential

The cell potential at standard conditions can be found through this equation:

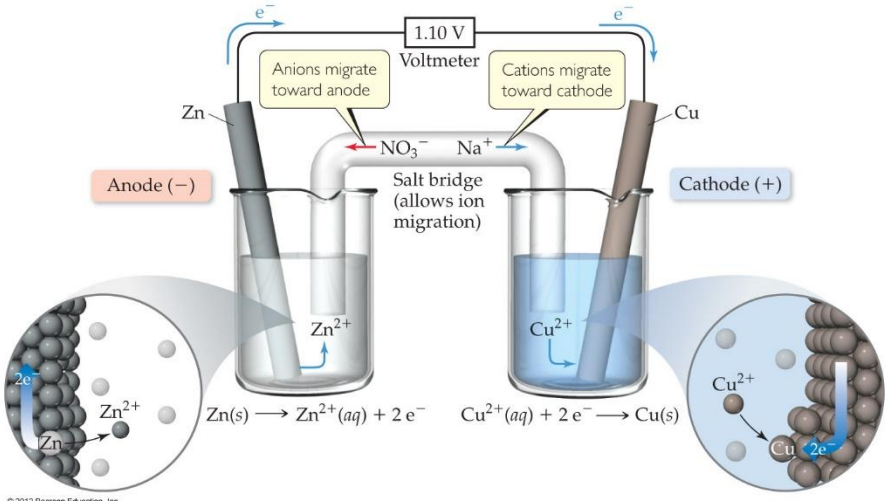
$$E^\circ_{cell} = E^\circ_{red}\,(cathode) - E^\circ_{red}\,(anode)$$

For the oxidation in this cell,

$E_{red} = -0.76$ V

For the reduction,

$E_{red} = +0.34$ V



$$E^\circ_{cell} = E^\circ_{red}\,(cathode) - E^\circ_{red}\,(anode)$$

$$= +0.34\text{ V} - (-0.76\text{ V})$$

$$= +1.10\text{ V}$$

Cell Potential

Predicting Spontaneity of Redox Reactions

- A spontaneous reaction will take place when a reduction half-reaction is paired with an oxidation half-reaction lower on the table.
- If paired the other way, the reverse reaction is non-spontaneous.

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ $\quad E°_{red} = +0.34$ V

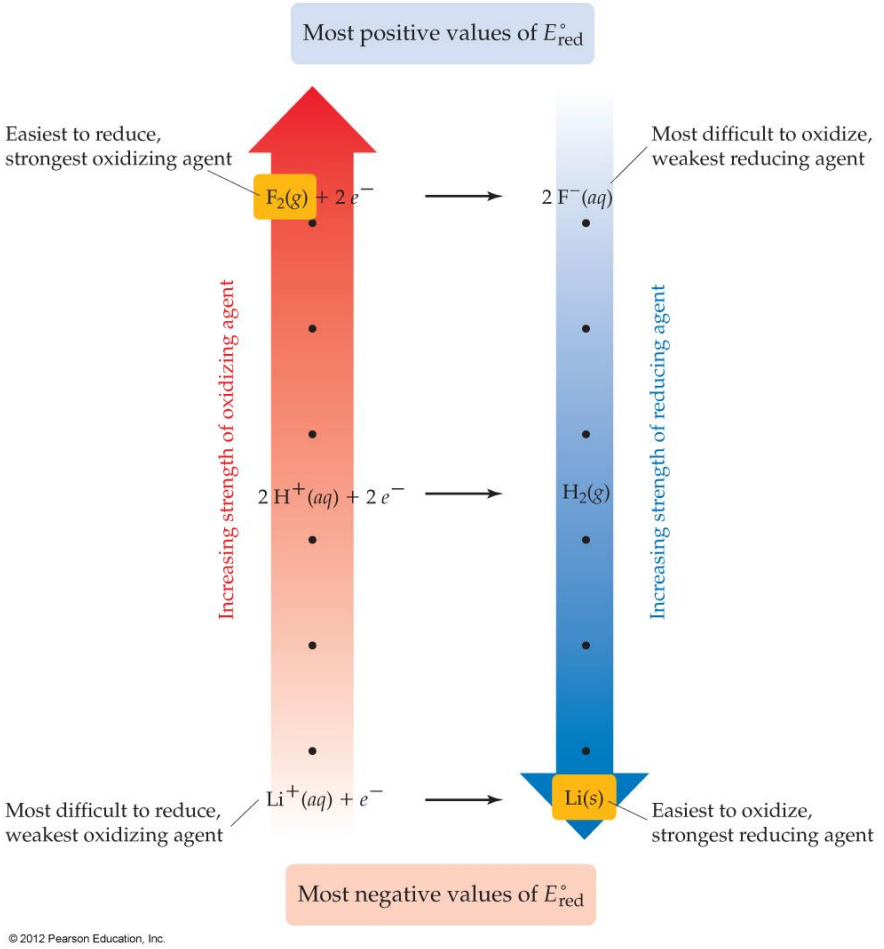
$Zn^{2+}(aq) + 2\ e^- \rightarrow Zn(s)$ $\quad E°_{red} = -0.76$ V

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ **spontaneous**

$Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)$ **nonspontaneous**

Cell Potential

- The strongest oxidizers have the most positive reduction potentials.
- The strongest reducers have the most negative reduction potentials.



Cell Potential

Predicting whether a metal will dissolve in an acid

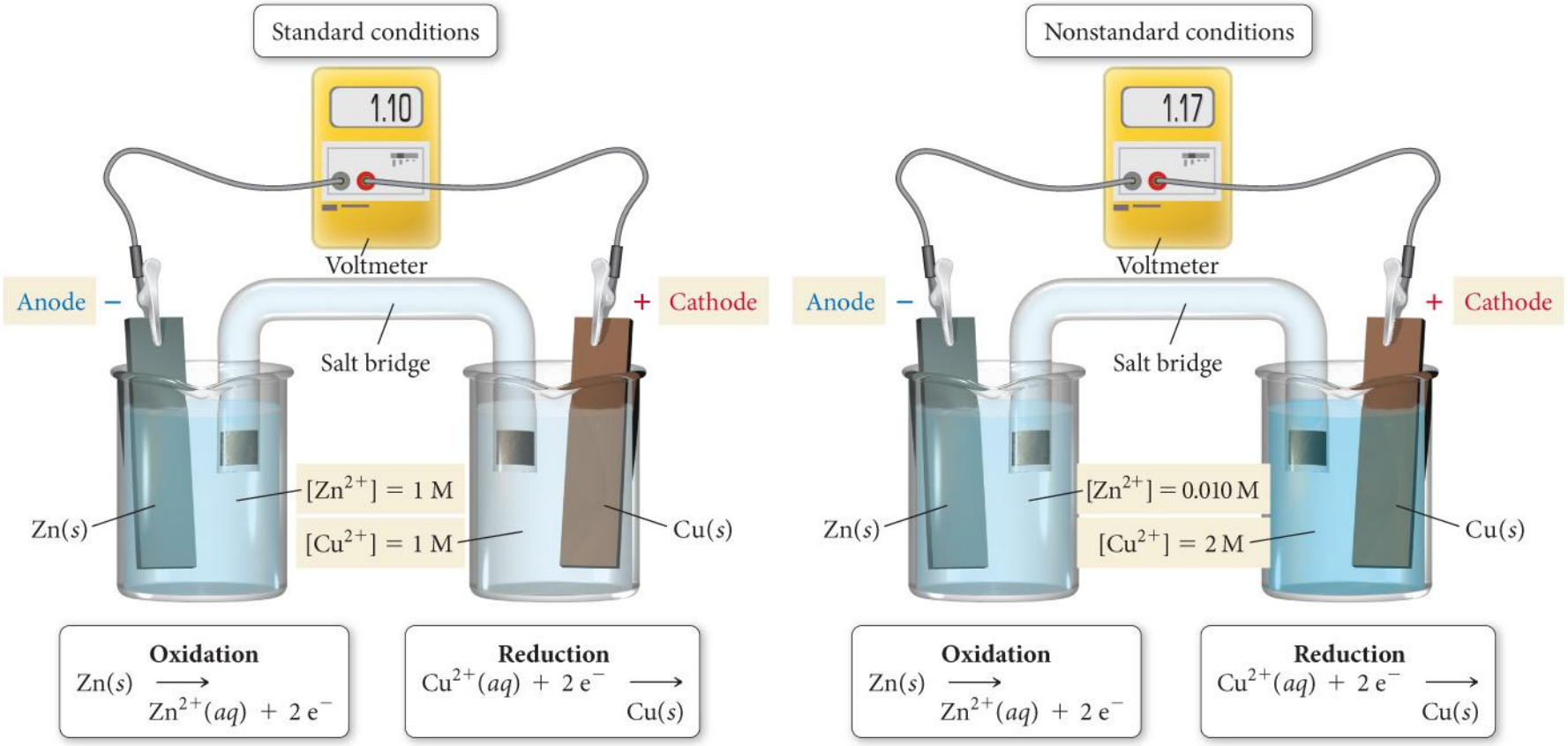
- Metals dissolve in acids.
  - If their ion reduction reaction lies below H^+ reduction on the table

$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

- Almost all metals will dissolve in HNO_3.
  - Au and Pt dissolve in HNO_3 + HCl

Cell Potential

When ion concentrations are not 1 M



Nernst Equation

ΔG for a redox reaction can be found by using the equation

$$\Delta G = -nFE$$

where n is the number of moles of electrons transferred, and F is a constant, the Faraday: 1 F = 96,485 C/mol

Under standard conditions,

$$\Delta G^\circ = -nFE^\circ$$

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

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

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

$$E = E^\circ - \frac{2.303RT}{nF} \log Q$$

Nernst Equation

$$aA + bB \longrightarrow cC + dD$$

For the general cell reaction occurring at 298 K, the Nernst equation can be written as

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$$E = E^\circ - \frac{0.059}{n} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

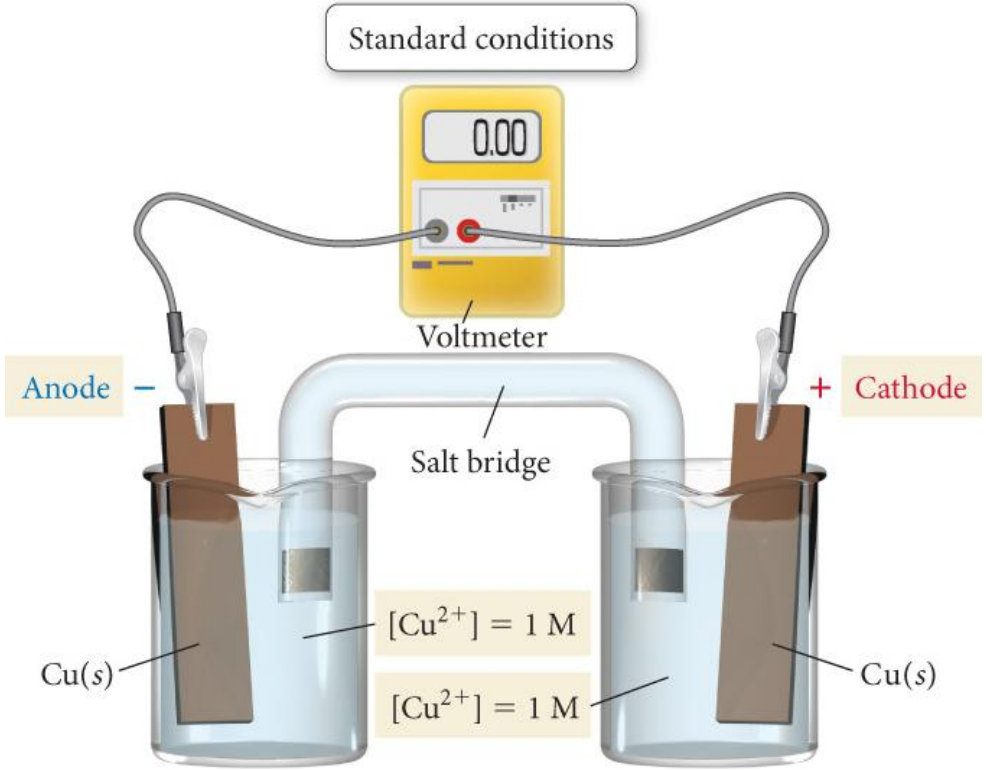
At equilibrium, E=0 and $Q=K_{eq}$

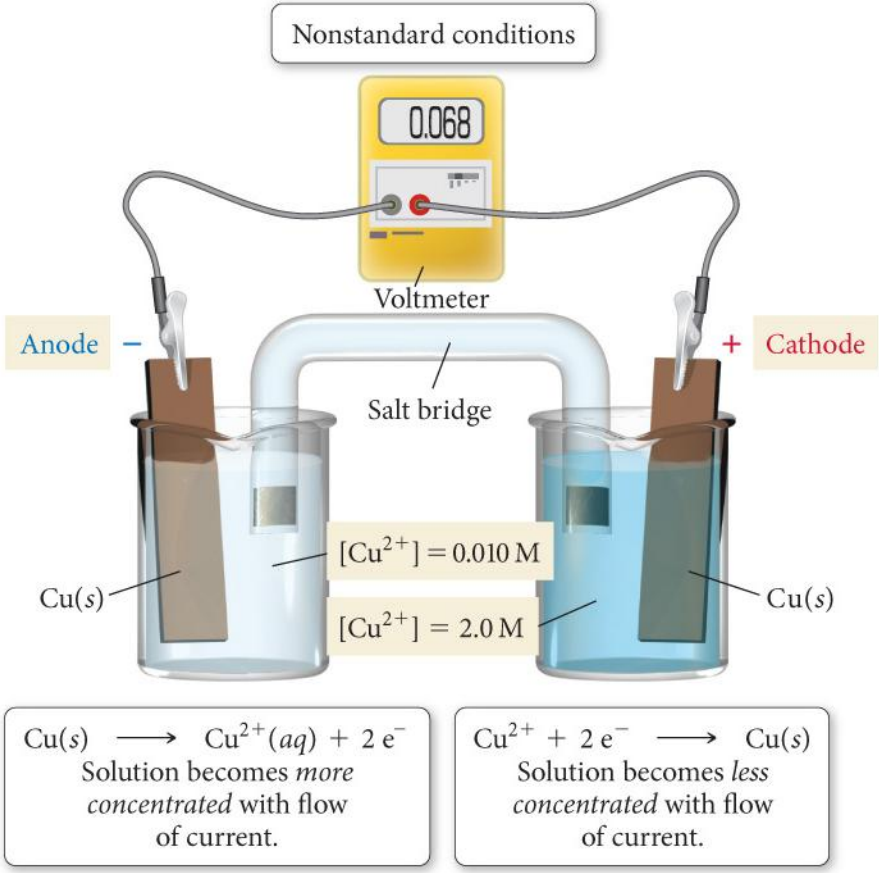
$$0 = E^\circ - \frac{0.059}{n} \log K_{eq}$$

$$\log K_{eq} = \frac{nE^\circ}{0.059}$$

Concentration cells

Based on Nernst equation, an electrochemical cell can be built simply by using the same electrode for both half cells, but by using different concentrations of electrolyte. Cells of this type are called **concentration cells**.





Concentration cells

- It is possible to get a spontaneous reaction when the oxidation and reduction reactions are the same, as long as the electrolyte concentrations are different.
- The difference in energy is due to the entropic difference in the solutions.
  - The more concentrated solution has lower entropy than the less concentrated solution.
- Electrons will flow from the electrode in the less concentrated solution to the electrode in the more concentrated solution.
  - Oxidation of the electrode in the less concentrated solution will increase the ion concentration in the solution; the less concentrated solution has the anode.
  - Reduction of the solution ions at the electrode in the more concentrated solution reduces the ion concentration; the more concentrated solution has the cathode.

Corrosion

Corrosion is a spontaneous and irreversible electrochemical process, which results in the degradation of a metallic material upon interaction with the environment mainly O_2.

The global cost of corrosion is US$2.5 trillion estimated by IMPACT (The Worldwide Corrosion Authority) and within India, it estimates that the cost of corrosion to the Indian economy is 4.2% of the GDP.

Metals are often used for their strength and malleability, but these properties are lost when metal corrodes. For many metals, the product of corrosion also does not adhere to the metal, and as it flakes off more metal can corrode.

Corrosion

TABLE 20.1 • Standard Reduction Potentials in Water at 25 °C

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+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
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−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

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Corrosion

- O_2 is very easy to reduce in moist conditions.

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 2\ OH^-(aq)$ $E^o = 0.40$ V

- O_2 is even easier to reduce under acidic conditions.

$O_2(g) + 4\ H+ + 4\ e^- \rightarrow 2\ H_2O(l)$ $E^o = 1.23$ V

- Because the reduction of most metal ions lies below O_2 on the table of standard reduction potentials, the oxidation of those metals by O_2 is spontaneous.

Corrosion

Mechanism:

1. Dry or Chemical Corrosion

2. Wet or Electrochemical Corrosion

Dry or Chemical Corrosion

1) Oxidation Corrosion (Reaction With Oxygen)

Mechanism i) Formation of metal ions $M \rightarrow M^{2+} + 2e^-$

ii) Oxygen changes to ionic form $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

iii) Metal – Oxide film formation $M + \frac{1}{2} O_2 \rightarrow MO$

a) Protective and non porous oxide film: Metals such as Al, Cr, Cu &W develop nonporous, stable oxide film on the surface.

b) Unstable oxide film: Au & pt develop unstable oxide film which instantaneously decomposes to form metal &oxygen.

c) Volatile oxide film: Molybdenum develops an oxide which immediately vaporizes. As a result metal surface easily undergoes further corrosion.

d) Porous and non protective film: Alkali and alkaline earth metals form porous oxide layer which further facilitates corrosion of the metal due to porous nature. Oxide layer cannot protect the metal from corrosion.

Pilling Bedworth rule

Vol of MO > Vol of metal - Protective film

Vol of MO < Vol of metal - Porous film

Dry Corrosion

2) Corrosion By Other Gases:

gases like Cl_2, SO_2, H_2S, NO_x

$2\,Ag + Cl_2 \rightarrow 2AgCl$ (protective),

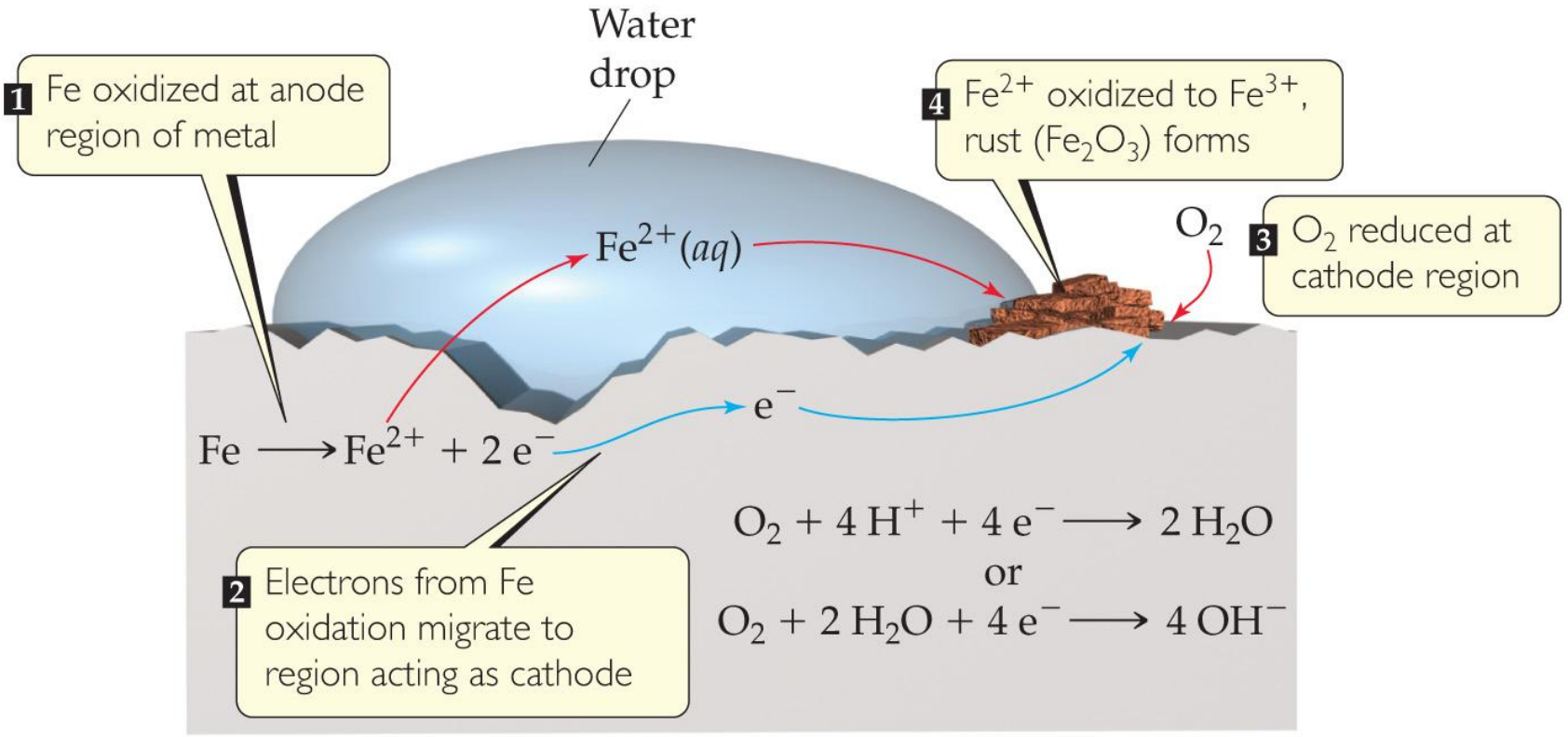
$Sn + 2Cl_2 \rightarrow SnCl_4$ volatile

Formation of cracks and blisters on metal surface due to high pressure of H_2 gas.

$Fe + H_2S \rightarrow FeS + H_2$

3) Liquid Metal Corrosion : Liquid metal mercury dissolves most metals by forming amalgams, there by corroding them.

Electrochemical Corrosion



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Corrosion

- At the anodic regions, Fe(*s*) is oxidized to Fe^{2+}.
- The electrons travel through the metal to a cathodic region where O_2 is reduced.
-
- The Fe^{2+} ions migrate through the moisture to the cathodic region where they are further oxidized to Fe^{3+}, which combines with the oxygen and water to form rust.
  - Rust is hydrated iron(III) oxide, $Fe_2O_3 \cdot nH_2O$.
- Electrolytes promote rusting.
  - Enhances current flow
- Acids promote rusting.
  - Lowering pH will lower $E°_{red}$ of O_2.

Electrochemical Corrosion

Anodic Reaction:

$M \rightarrow M^{n+} + ne^-$

Cathodic Reaction:

a) Evolution of Hydrogen type:

$2H^+ + 2e^- \longrightarrow H_2$

$2H_2O + 2e^- \rightarrow 2OH^- + H_2$

b) Absorption of oxygen:

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$

$2Fe(OH)_2 + O_2 + 2H_2O \rightarrow 2(Fe_2O_3.3H_2O)$

Corrosion

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+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

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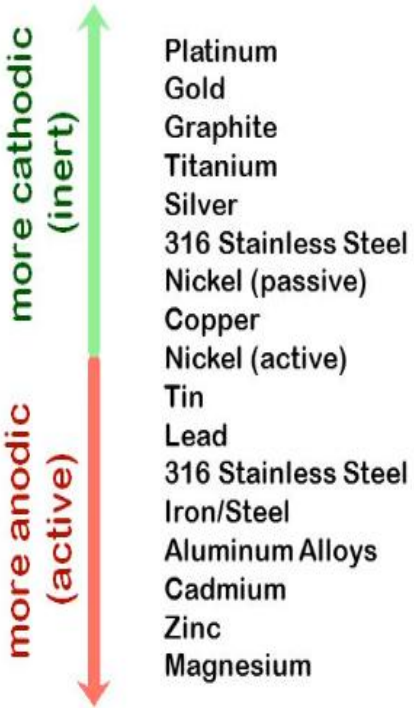
GALVANIC SERIES

- Ranks the reactivity of metals/alloys in seawater



Rate of Corrosion

Nature of metal

1. Position of metal in galvanic series
2. Ratio of anodic area to cathodic area
3. Passivity
4. Purity of the metal

Metal	% purity	Corrosion rate
Zinc	99.999	1
Zinc	99.99	2650
Zinc	99.95	5000

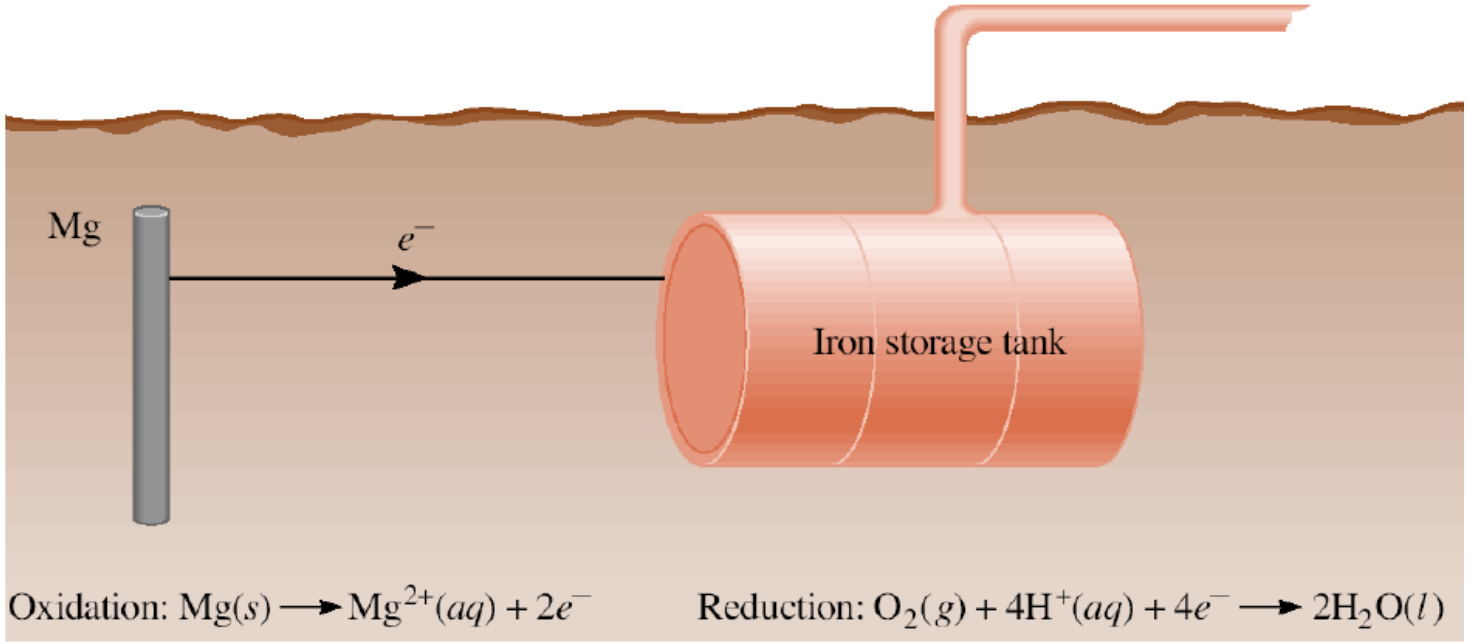
Nature of Environment

1. Temperature
2. Humidity of air
3. Effect of pH
4. Nature of corrosion product
5. Nature of atmosphere

Prevention methods

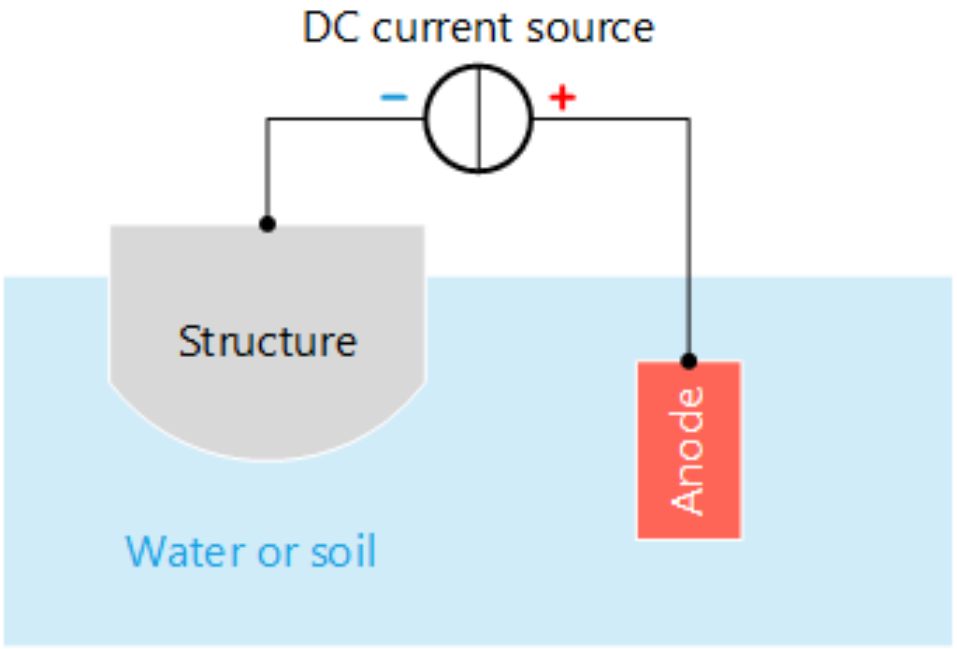
1. Cathodic Protection Technique

a. Sacrificial Anodic protection

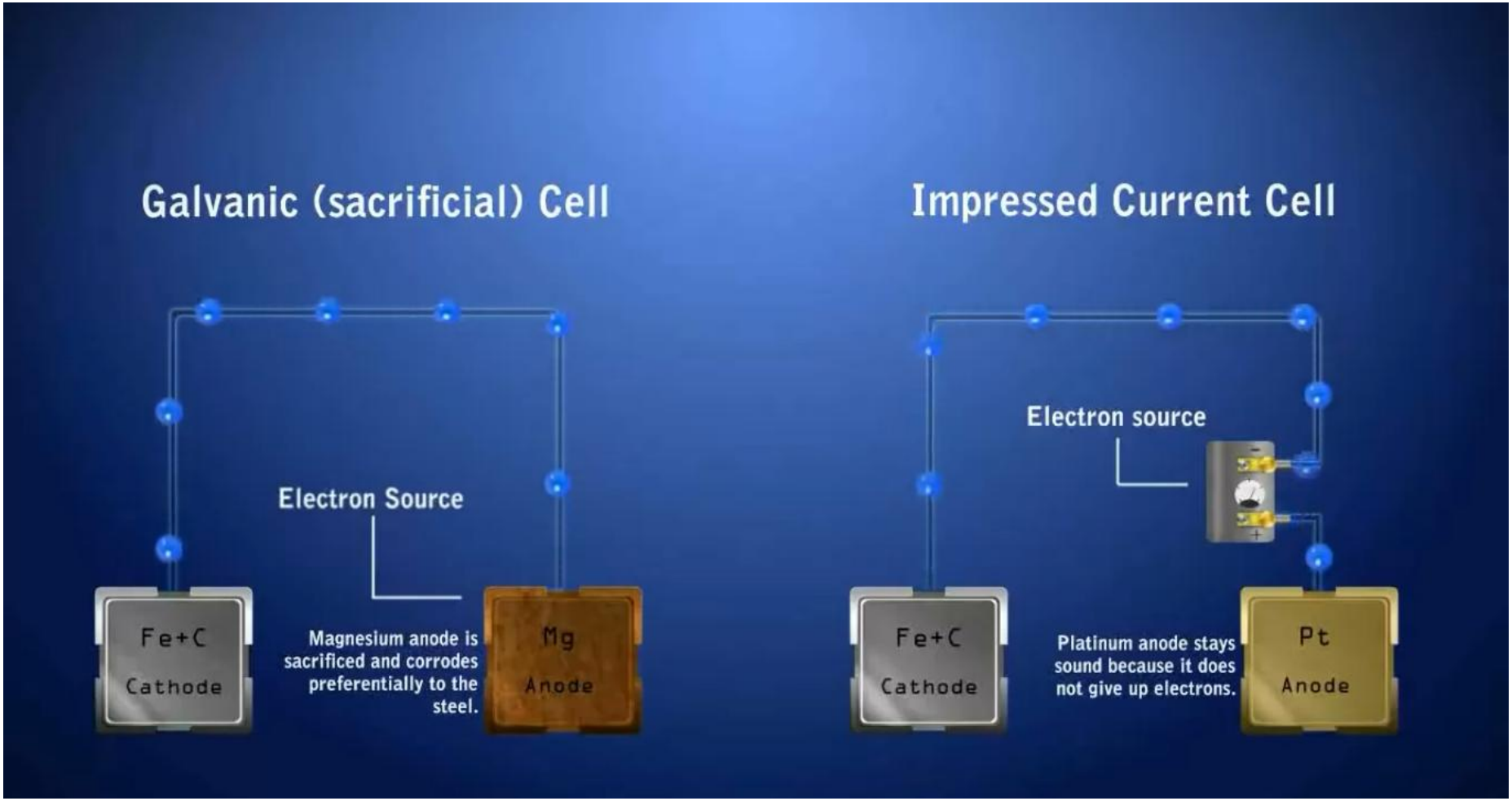


Prevention methods

b. Impressed Current Cathodic Protection

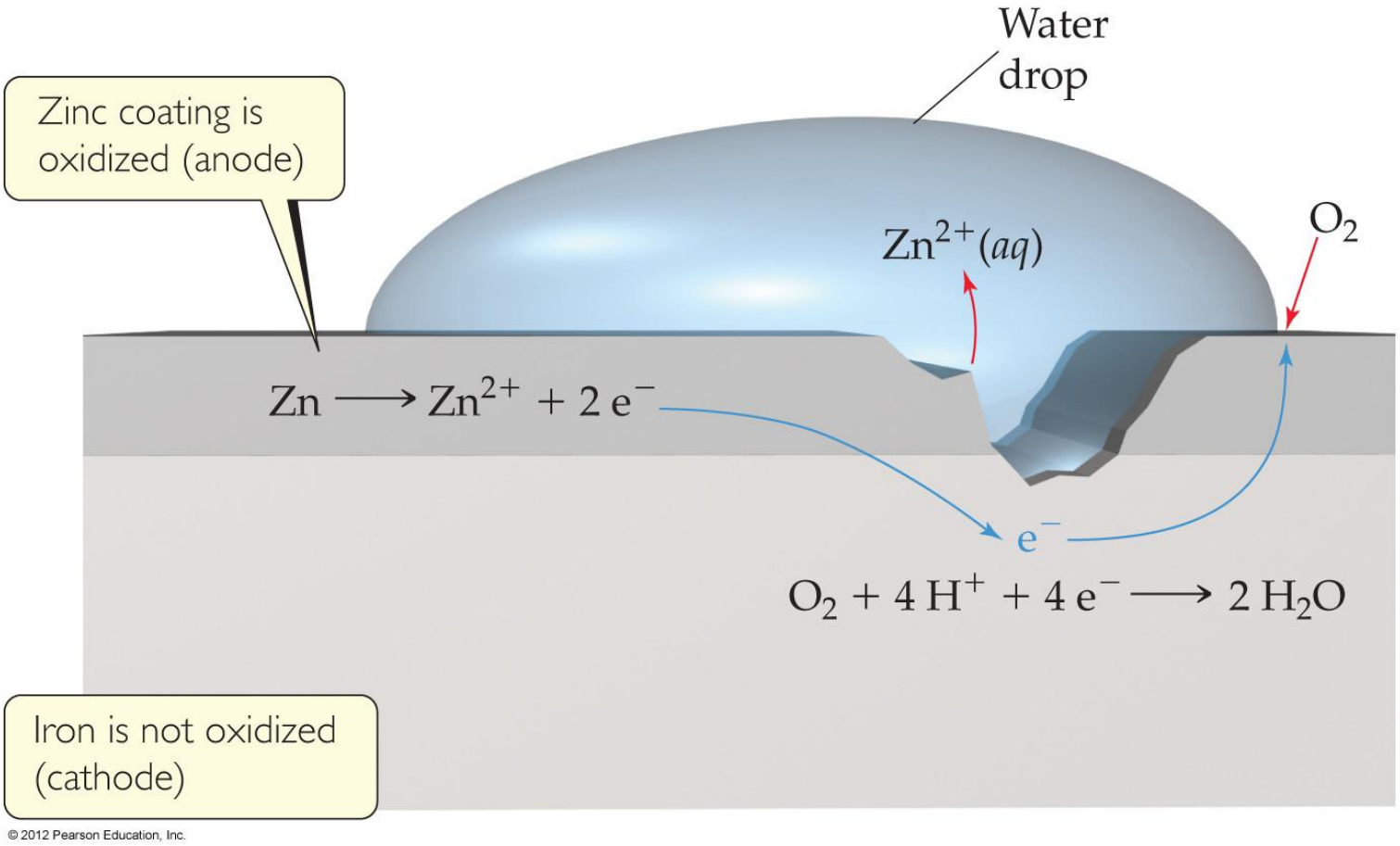


Prevention methods



Prevention methods

- Protection with metallic films – galvanized nails



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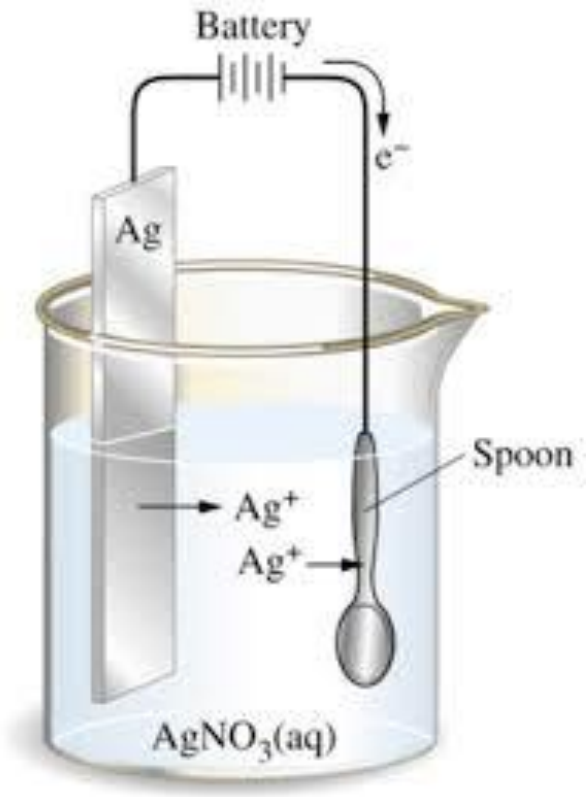
ELECTROPLATING



Solvent cleaning - Trichloro ethylene and methylene chloride
Alkali cleaning - detergents, sodium carbonate, sodium hydroxide
Mechanical cleaning
Pickling – dipping in dil. acids
Rinsing with water

Electroplating With Silver:

Cathode: Article to be electroplated (Spoon)
Anode: Block of Silver metal
Electrolyte: Aqueous solution of $AgNO_3$