# Electrochemistry

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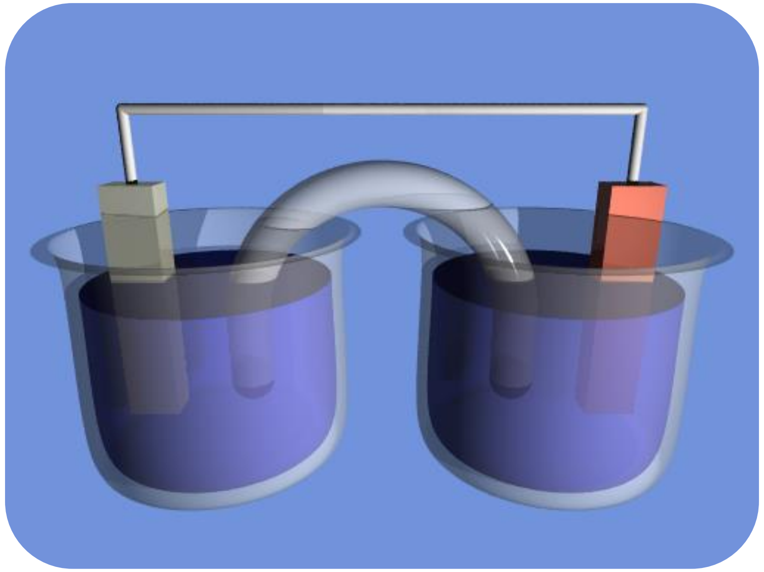


The contents of this presentation is prepared to provide a brief idea about the topics, details will be discussed in the classes.
Contents have been collected from multiple textbooks and internet.

# What is Electrochemistry

- *Electrochemistry* is the branch of chemistry that deals with the interconversion of electrical energy and chemical energy.

- Electrochemical processes are *redox* (oxidation-reduction) reactions -
  - in which the *energy released* by a *spontaneous* reaction is converted to electricity, or
  - in which *electrical energy* is used to cause a *nonspontaneous* reaction to occur.

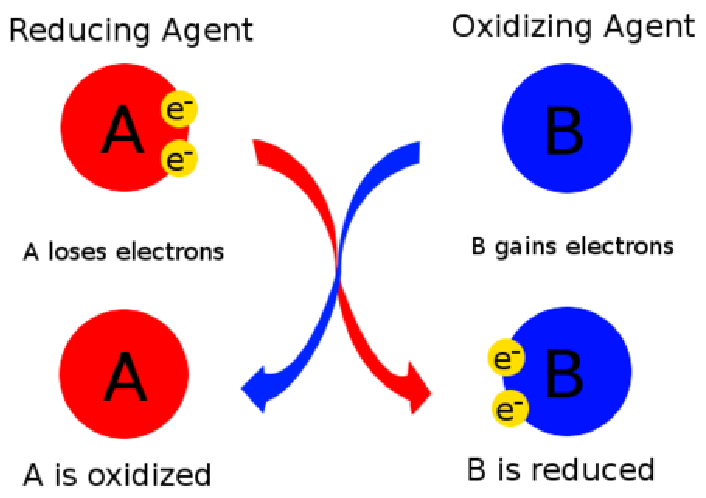
# Redox Reactions

- *Oxidation is the loss of electrons and reduction is the gain of electrons. These processes occur simultaneously.*

- *Oxidation results in an increase in oxidation number (O.N.) while reduction results in a decrease in O.N.*

- *The oxidizing agent takes electrons from the substance being oxidized. The oxidizing agent is therefore reduced.*

- *The reducing agent gives electrons to the substance being reduced. The reducing agent is therefore oxidized.*



# Balancing Redox Reactions

$$Cr_2O_7^{2-}(aq) + I^{-}(aq) \rightarrow Cr^{3+}(aq) + I_2(s)$$

***Step 1: Divide the reaction into half-reactions.***

$$Cr_2O_7^{2} \rightarrow Cr^{3+}$$

$$I \quad \rightarrow \quad I_2$$

***Step 2: Balance the atoms and charges in each half-reaction.***

For the $Cr_2O_7^{2-}/Cr^{3+}$ half-reaction:

Balance atoms other than O and H:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

Balance O atoms by adding $H_2O$ molecules:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

# Balancing Redox Reactions

*Balance H atoms by adding $H^+$ ions:*

$$14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

*Balance charges by adding electrons:*

$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

*This is the reduction half-reaction. $Cr_2O_7^{2-}$ is reduced, and is the oxidizing agent. The O.N. of Cr decreases from +6 to +3.*

*For the $I^-/I_2$ half-reaction:*

*Balance atoms other than O and H:*

$$2I^- \rightarrow I_2$$

*There are no O or H atoms, so we balance charges by adding electrons:*

$$2I^- \rightarrow I_2 + 2e^-$$

*This is the oxidation half-reaction. $I^-$ is oxidized and is the reducing agent. The O.N. of I increases from –1 to 0.*

# Balancing Redox Reactions

*Step 3: Multiply each half-reaction, if necessary, by an integer so that the number of $e^-$ lost in the oxidation equals the number of $e^-$ gained in the reduction.*

*The reduction half-reaction shows that $6e^-$ are gained; the oxidation half-reaction shows only $2e^-$ being lost and must be multiplied by 3:*

$$3(2I^- \rightarrow I_2 + 2e^-)$$
$$6I^- \rightarrow 3I_2 + 6e^-$$

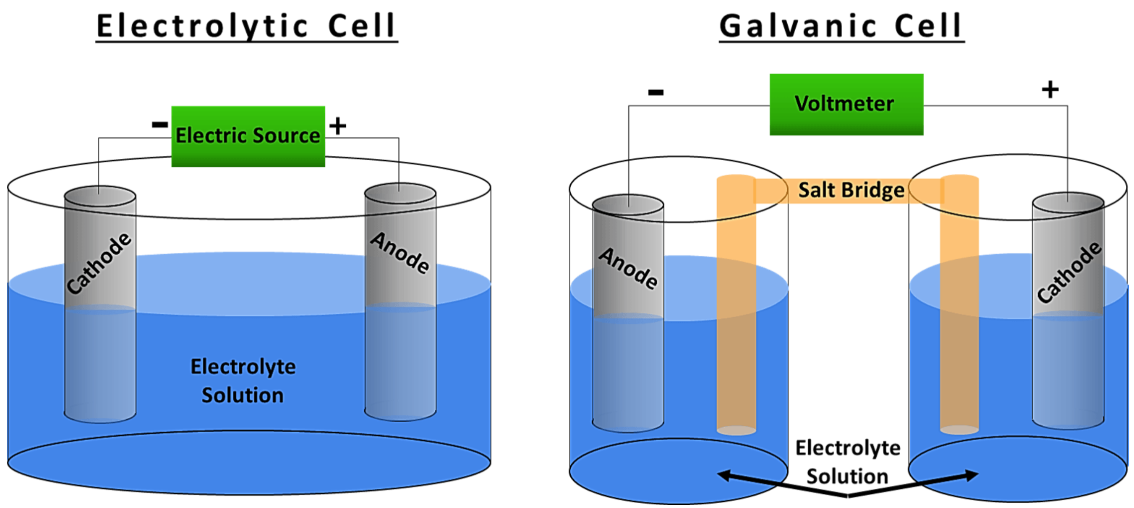
*Step 4: Add the half-reactions, canceling substances that appear on both sides, and include states of matter. Electrons must always cancel.*

$$\cancel{6e^-} + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
$$6I^- \rightarrow 3I_2 + \cancel{6e^-}$$

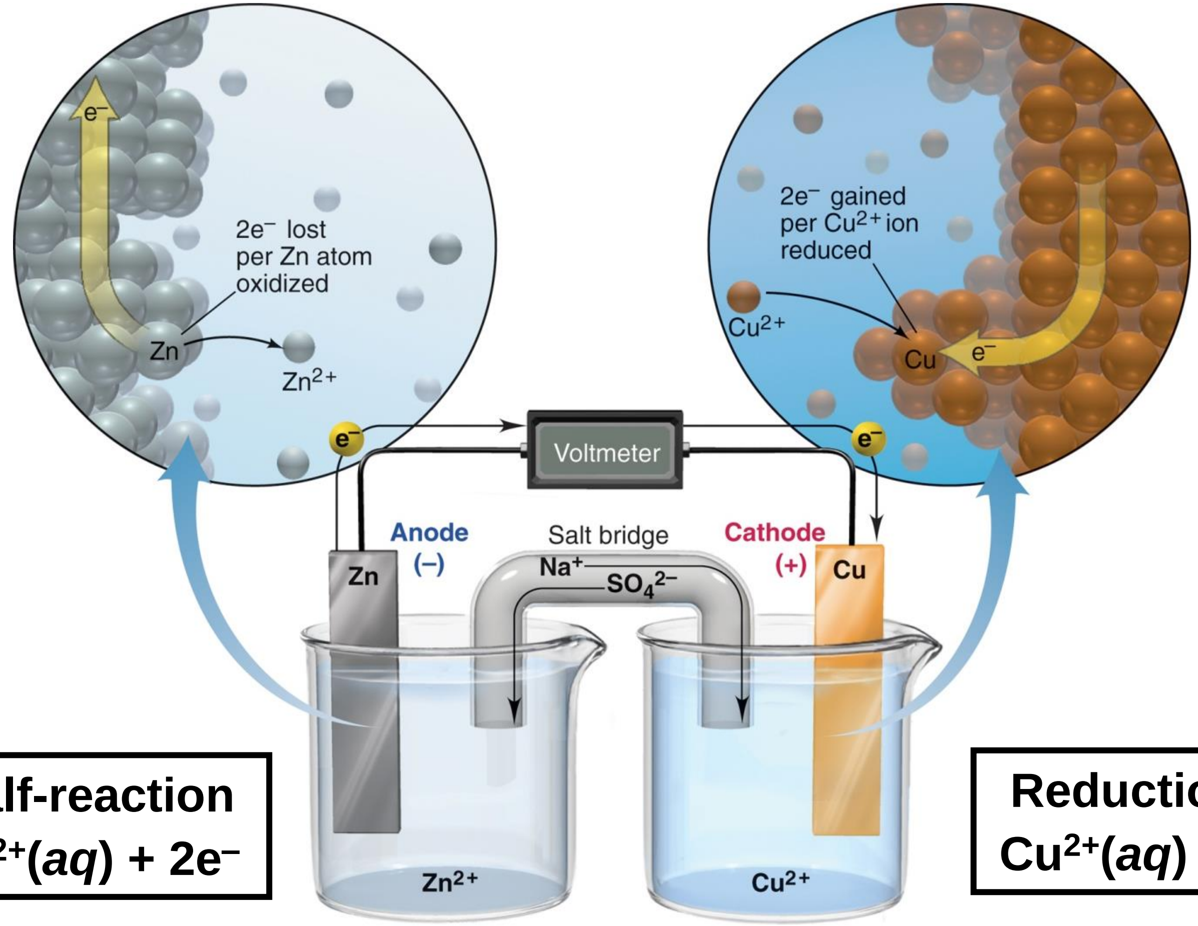
$$6I^-(aq) + 14H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3I_2(s) + 7H_2O(l) + 2Cr^{3+}(aq)$$

# Electrochemical Cells

- An *electrochemical cell* is a device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions.
- A *voltaic or galvanic cell* uses a *spontaneous* redox reaction ($\Delta G < 0$) to generate electrical energy.
- An *electrolytic cell* uses electrical energy to drive a *nonspontaneous* reaction ($\Delta G > 0$).
- Both types of cell are constructed using *two electrodes* placed in an electrolyte solution.
- The *anode* is the electrode at which *oxidation* occurs.
- The *cathode* is the electrode at which *reduction* occurs.



# Voltaic or Galvanic Cell




**Oxidation half-reaction**

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

**Reduction half-reaction**

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

**Overall (cell) reaction**

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

# Voltaic or Galvanic Cell

- *Oxidation (loss of $e^-$) occurs at the anode, which is therefore the source of $e^-$.*

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

- *Over time, the Zn(s) anode decreases in mass and the $[Zn^{2+}]$ in the electrolyte solution increases.*

- *Reduction (gain of $e^-$) occurs at the cathode, where the $e^-$ are used up.*

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

- *Over time, the $[Cu^{2+}]$ in this half-cell decreases and the mass of the Cu(s) cathode increases.*

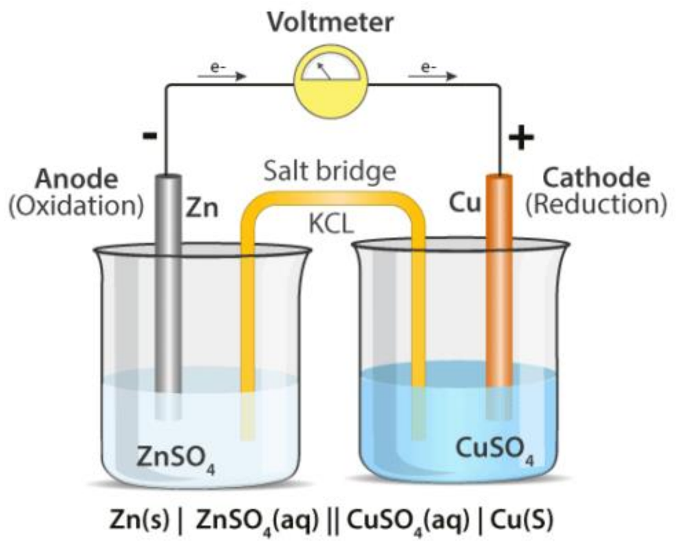
- *The anode produces $e^-$ by the oxidation is the negative electrode and the cathode is the positive electrode in a voltaic cell.*

# Voltaic or Galvanic Cell

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

The anode components are written on the *left*.

The cathode components are written on the *right*.




- *Electrons flow through the external wire from the anode to the cathode.*
- *The salt bridge completes the electrical circuit and allows ions to flow through both half-cells.*

# Cell Potential

- *Also known as the Voltage or Electromotive Force (emf) of the cell.*
- *Standard reduction potential ($E^0$) is the potential associated with a reduction reaction at an electrode when all solutes are 1M and all gases are at 1 atm.*
- *By convention, all standard electrode potentials refer to the half-reaction written as a reduction.*
- *The cell potential depends on the difference of electrical potential between two electrodes.*

$$\boxed{E_{cell} = E_{cathode} - E_{anode}}$$

- For $Zn(s)|Zn^{2+}(aq)\|Cu^{2+}(aq)|Cu(s)$

$$E\ cell = E_{Cu2+/Cu} - E_{Zn2+/Zn}$$

# Standard Electrode Potentials ($E^0$)

| Half-Reaction | $E^o$(V) |
|---|---|
| $F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$ | +2.87 |
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ | +1.36 |
| $MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$ | +1.23 |
| $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$ | +0.96 |
| $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ | +0.80 |
| $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ | +0.77 |
| $O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$ | +0.40 |
| $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ | +0.34 |
| **$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$** | **0.00** |
| $N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$ | −0.23 |
| $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ | −0.44 |
| $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ | −076 |
| $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ | −0.83 |
| $Na^+(aq) + e^- \rightleftharpoons Na(s)$ | −2.71 |
| $Li^+(aq) + e^- \rightleftharpoons Li(s)$ | −3.05 |

strength of oxidizing agent

strength of reducing agent

# Problems

Predict what will happen if molecular bromine ($Br_2$) is added to a solution containing NaCl and NaI at 25°C. Assume all species are in their standard states.

$$Cl_2(1\ \text{atm}) + 2e^- \longrightarrow 2Cl^-(1\ M) \qquad E° = 1.36\ \text{V}$$
$$Br_2(l) + 2e^- \longrightarrow 2Br^-(1\ M) \qquad E° = 1.07\ \text{V}$$
$$I_2(s) + 2e^- \longrightarrow 2I^-(1\ M) \qquad E° = 0.53\ \text{V}$$

***Looking at the standard reduction potentials, $Br_2$ will oxidize $I^-$ but will not be able to oxidize $Cl^-$***

$$\begin{array}{ll} \text{Oxidation:} & 2I^-(1\ M) \longrightarrow I_2(s) + 2e^- \\ \text{Reduction:} & Br_2(l) + 2e^- \longrightarrow 2Br^-(1\ M) \\ \hline \text{Overall:} & 2I^-(1\ M) + Br_2(l) \longrightarrow I_2(s) + 2Br^-(1\ M) \end{array}$$

# Problems

A galvanic cell consists of a Mg electrode in a 1.0 *M* $Mg(NO_3)_2$ solution and a Ag electrode in a 1.0 *M* $AgNO_3$ solution. Calculate the standard emf of this cell at 25°C.

The standard reduction potentials are

$$\begin{array}{lll} Ag^{+}(1.0\,M) + e^{-} \longrightarrow Ag(s) & & E^\circ = 0.80\text{ V} \\ Mg^{2+}(1.0\,M) + 2e^{-} \longrightarrow Mg(s) & & E^\circ = -2.37\text{ V} \end{array}$$

$$\begin{array}{rl} \text{Anode (oxidation):} & Mg(s) \longrightarrow Mg^{2+}(1.0\,M) + 2e^{-} \\ \text{Cathode (reduction):} & 2Ag^{+}(1.0\,M) + 2e^{-} \longrightarrow 2Ag(s) \\ \hline \text{Overall:} & Mg(s) + 2Ag^{+}(1.0\,M) \longrightarrow Mg^{2+}(1.0\,M) + 2Ag(s) \end{array}$$

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{Ag^{+}/Ag} - E^\circ_{Mg^{2+}/Mg} \\ &= 0.80\text{ V} - (-2.37\text{ V}) \\ &= \boxed{3.17\text{ V}} \end{aligned}$$

# The Nernst Equation – Effect of concentration on emf

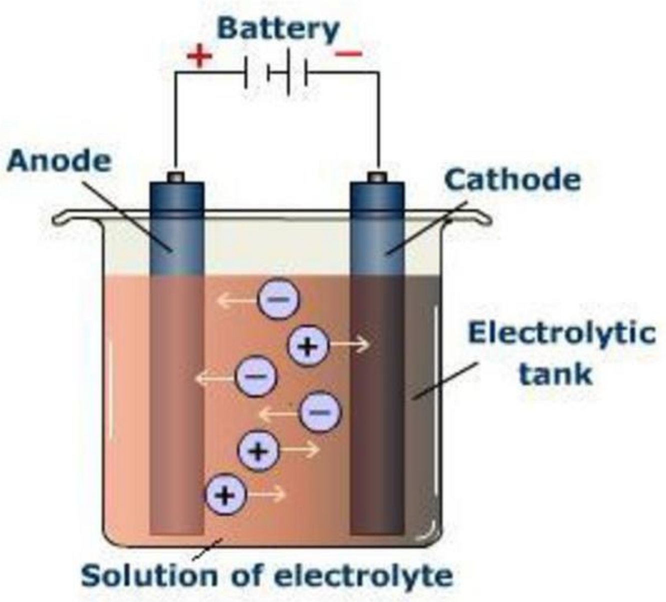
Nernst Equation:

$$\boxed{E_{cell} = E^{o}_{cell} - \frac{RT}{nF} \ln Q}$$

$E^o$ = standard potential
R = gas constant
T = temperature
F = Faraday's constant
n = moles of electrons
Q = reaction quotient

# Electrolysis

- *The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed as Electrolysis.*
- *Electrolytes are electrovalent substances that forms ions in solution which conduct an electric current.*
- *The process of electrolysis is carried out in an apparatus called Electrolytic Cell.*



# Faraday's Laws of Electrolysis

- *1st Law:* *'The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution.'*

$$m \propto Q; \quad or,\ m = Z \times Q; \ or\ m = Z \times I \times t$$

*If, I = 1 ampere and t = 1 s; then, m = Z*

*Z is the electrochemical equivalent, which is the amount of substance deposited by 1 ampere of current passing for 1s.*

- *2nd Law:* *'When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.'*

$$w \propto E$$

$$or,\ w_1/w_2 = E_1/E_2$$

# Thank You