CHAPTER- 2
ELECTROCHEMISTRY

Electrochemical Cells

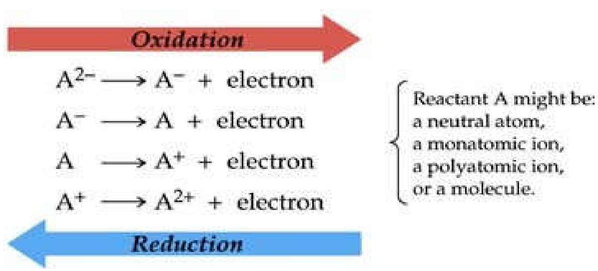
- A cell in which oxidation- reduction reaction occurs.
- Transform energy from chemical reaction to electrical energy or vice versa.

Oxidation- reduction reaction

- Deals with movement of electrons during a chemical reaction.
- Reactions in which electrons are transferred from one substance to another
- Describe all chemical reactions in which atoms have oxidation number change.
- Not all reaction are redox reaction

Oxidation–Reduction Reactions

- The transfer of electrons between or among reactants is called the **oxidation** or **reduction** of species depending on which way the electrons are flowing.



- Oxidation and reduction ***must*** occur together. They cannot exist alone.
- Therefore, a redox reaction can be broken into two half- reactions, one a reduction and the other an oxidation
- **Half–reaction:** the oxidation or the reduction part of the chemical reaction.

Oxidation: loss of one or more electrons.

Reduction: gain of one or more electrons

Oxidizing Agent: substance reduced or Gains electrons

Reducing Agent: substance oxidized or Loses electrons

The "Agent" is the "opposite"

- ***Oxidation number***" is a positive or negative number assigned to an atom to indicate its degree of oxidation or reduction.
- Generally, a bonded atom's oxidation number is the charge it would have if the electrons in the bond were assigned to the atom of the more electronegative element

Rules for Assigning Oxidation Numbers

1) The oxidation number of any uncombined element is zero.
2) The oxidation number of a monatomic ion equals its charge. $2\overset{0}{Na} + \overset{0}{Cl_2} \rightarrow 2\overset{+1}{Na}\overset{-1}{Cl}$
3) The oxidation number of oxygen in compounds is -2, except in peroxides, such as H_2O_2 where it is -1. $\overset{+1}{H}_2\overset{-2}{O}$
4) The oxidation number of hydrogen in compounds is +1, except in metal hydrides, like NaH, where it is -1.
5) The sum of the oxidation numbers of the atoms in the compound must equal 0.

$\overset{+1}{H}_2\overset{-2}{O}$ $\quad \underset{H}{2(+1)} + \underset{O}{(-2)} = 0$

$\overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2$ $\quad \underset{Ca}{(+2)} + \underset{O}{2(-2)} + \underset{H}{2(+1)} = 0$

6) The sum of the oxidation numbers in the formula of a polyatomic ion is equal to its ionic charge.

$\overset{?}{N}\overset{-2}{O_3}{}^{-}$

$\underset{N}{X} + \underset{O}{3(-2)} = -1$

thus $X = +5$

$\overset{?}{S}\overset{-2}{O_4}{}^{2-}$

$\underset{S}{X} + \underset{O}{4(-2)} = -2$

thus $X = +6$

Oxidation–Reduction Reactions

For each of the following, write and balance the two half-reactions. For each, identify which species is the reducing agent and which is the oxidizing agent:

i. $Ca(s) + 2\ H^{+}(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

ii. $2\ Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2\ Fe^{3+}(aq) + 2\ Cl^{-}(aq)$

iii. $SnO_2(s) + 2\ C(s) \rightarrow Sn(s) + 2\ CO(g)$

iv. $Sn^{2+}(aq) + 2\ Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2\ Fe^{2+}(aq)$

Determine oxidation state for each atom in the following reaction

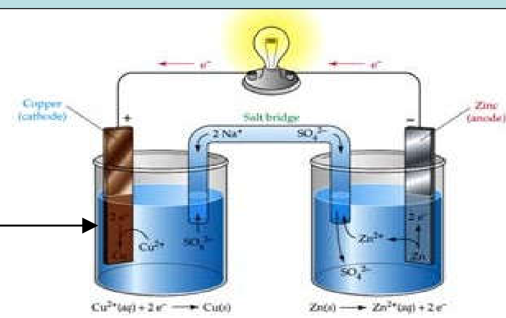
v. $Mg + CuSO_4 \longrightarrow MgSO_4 + Cu$

vi. $2K + Br_2 \longrightarrow 2KBr$

vii. $Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag$

Electrochemical Cells –Terms/components

1. **Electrodes**: are usually metal strips/wires connected by an electrically conducting wire (the **anode** and the **cathode**).



Anode: Is where oxidation occurs; Is where electrons are produced; Is what anions migrate toward; Has a negative sign

Cathode: Is where reduction occurs; Is where electrons are consumed; Is what cations migrate toward; Has a positive sign

Electrodes: is electronic conductor

- Conduct electricity between cell and surroundings
- Are electron carrier and on which half redox reaction occurs.

➢ **Anode electrode:** On w/c oxidation half-rxn(in which oxidation number of atoms increase) occur.

➢ On which reducing agent exist.

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

▪ Metal loses electrons and dissolves (enters solution)

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

$$Ag(s) \rightarrow Ag^+ + e^-$$

➢ **Cathode electrode :** An electrode on which reduction half-reaction(in which oxidation number of atoms decrease) occur:

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

✓ At which oxidizing agent exist

✓ Positively charged metal ion gains electrons

✓ Neutral atoms are deposited on the electrode

✓ The process is called electro deposition

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

$$Ag^+ + e^- \rightarrow Ag(s)$$

- Sum of oxidation and reduction half-reactions gives the ***net redox reaction or the overall reaction***

The overall reaction

- Both an oxidation and a reduction coexist.
- No electrons appear in the overall reaction

2. Electrolyte solution:

➢ Are electro active species

➢ Mixture of ions involved in reaction or carrying charge (ion carrier).

3. External connections between two electrodes (wire)

4. **Salt bridge:**

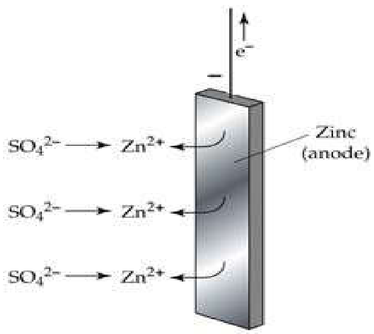
➢ Usually consists of tube filled with saturated KCl.

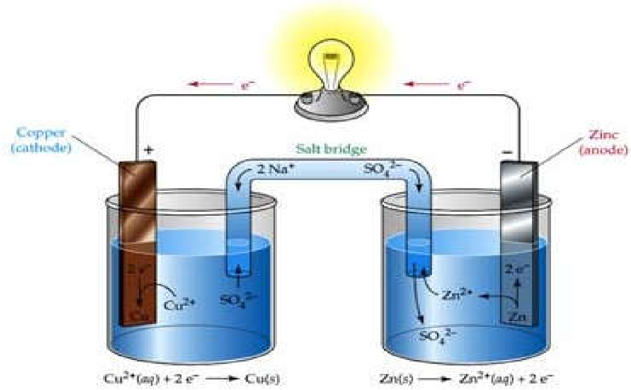
➢ Separates species to prevent direct chemical reactions.

➢ Completes the circuits (provides charge balance).

Electrochemical Cells -Terms

- **<u>Salt Bridge</u>**: is a U-shaped tube that contains a gel permeated with a solution of an inert
- These ions do not react with the other ions and they are not reduced or oxidized
- The salt bridge completes the electrical circuit by neutralizing any growing charge in the solutions. Anions flow into the anode and cations flow to the cathode



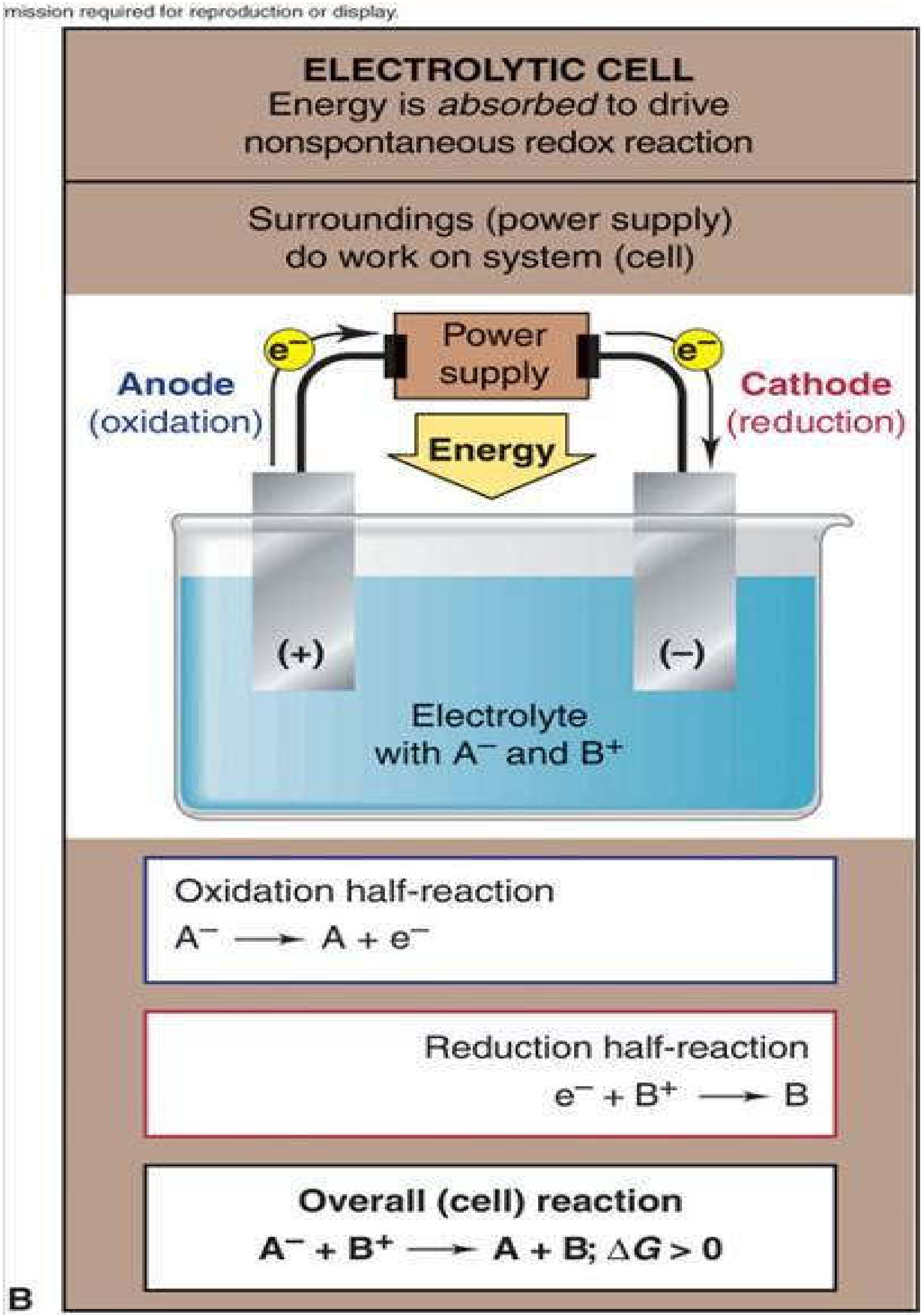


Electrochemical Cells are of two basic types:
ELECTROLYTIC CELLS: - An electric current drives a *non- spontaneous* reaction
A device in which electrical energy is converted to chemical energy.

- Non-spontaneous reaction takes place.
- Requires electrical energy to occur
- Consumes electricity from an external source

- **Anode** (oxidation occurs) is positive sign from the cell.
- **Cathode** (reduction occurs) is negative sign from the cell by convention.

Schematic representation of electrolytic cell



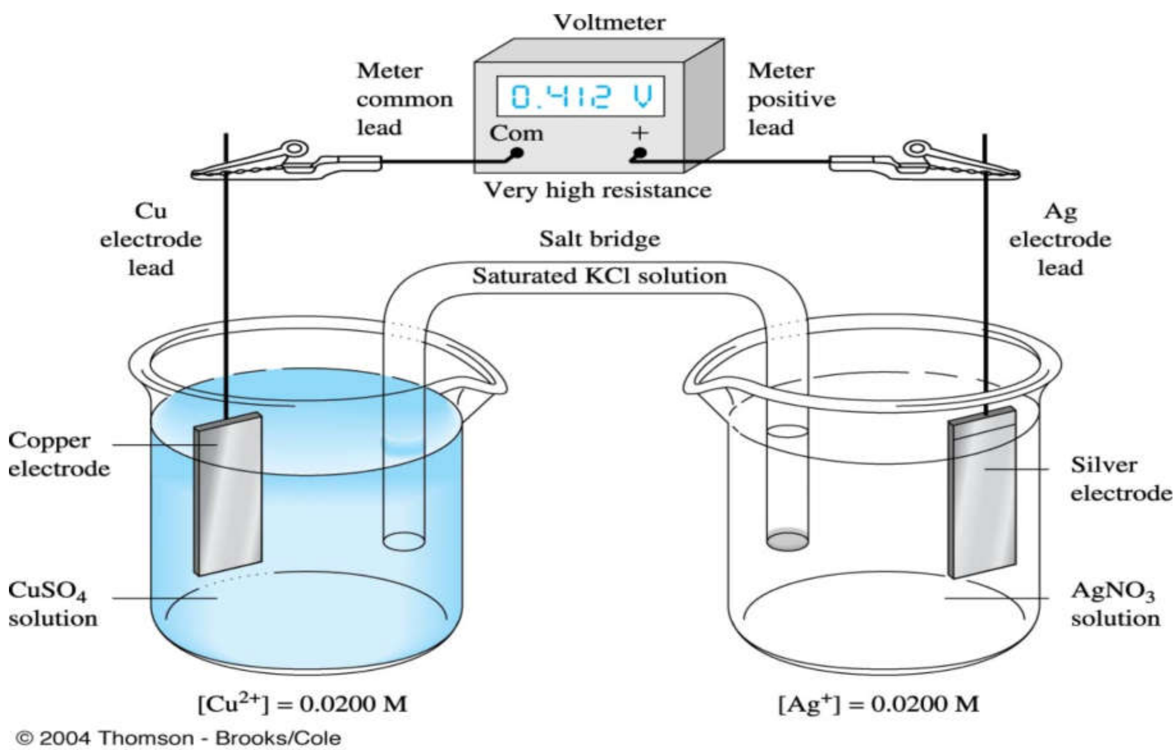
GALVANIC CELLS (voltaic cell):- a *spontaneous* chemical reaction generates an electric current

A device in which chemical energy is converted to electrical energy is called **galvanic** cells. It uses a spontaneous redox reaction to produce a current that can be used to generate energy or to do work.

- Redox reaction can be reversed electrolytically for reversible cells
- We will be focused on the Galvanic cells for this Chapter.
- The spontaneous reaction that drives these cells is a redox reaction!

Example: Rechargeable batteries

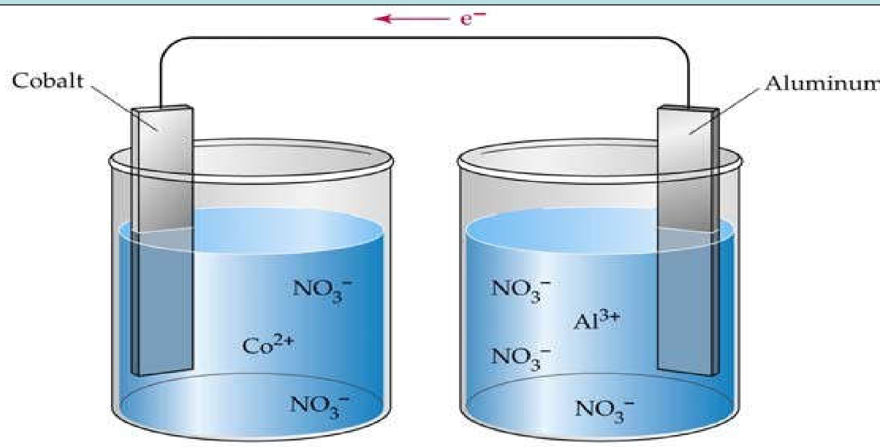
Schematic representation of galvanic cell between copper and silver



In Galvanic Cell:

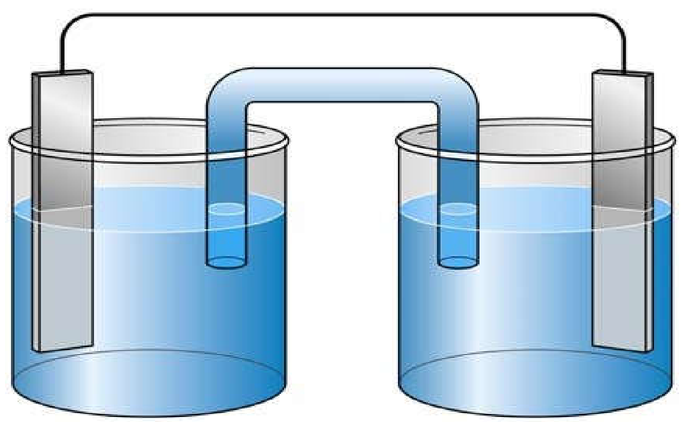
- Oxidation occurs at the **anode** (negative sign).
- Reduction occurs at the **cathode** (positive sign).

Electrochemical Cells



- Are any components essential for a functioning cell missing?
- Identify the anode and cathode and indicate the direction of the electron flow
- Write a balanced equation for the cell reaction.

Electrochemical Cells



- Design a galvanic cell that uses the redox reaction:

$Fe\ (s) + 2\ Fe^{3+}\ (aq) \rightarrow 3\ Fe^{2+}\ (aq)$

Electrochemical Cells – Shorthand Notation

- The shorthand notation for describing the cell:

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

$$\overbrace{Zn(s)\,|\,Zn^{2+}(aq)}^{\text{Anode half-cell}}\ \overset{\text{Salt bridge}}{||}\ \overbrace{Cu^{2+}(aq)\,|\,Cu(s)}^{\text{Cathode half-cell}}$$

Phase boundary $\qquad \xrightarrow{\text{Electrons flow this way}} \qquad$ Phase boundary

- Electrons flow from anode to cathode.
- Anode is placed on left by convention.

Electrochemical Cells

- Write the shorthand notation for a galvanic cell that uses the reaction:

$$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$$

- Write the balanced equation for the overall cell reaction and give a brief description of a galvanic cell represented by the following shorthand notation:

$$Pb(s)\,|\,Pb^{2+}(aq)\ ||\ Br_2(l)\,|\,Br^{-}(aq)\,|\,Pt(s)$$

Electromotive Force (EMF)

- The driving force to move the electrons from the anode towards the cathode is an electrical potential called the **electromotive force (EMF)**

  This is also known as the cell potential (E) or the cell voltage
- This force is the natural tendency of one substance to lose electrons and a second substance to gain electrons
- The greater this tendency, the higher the cell voltage
- The SI unit of EMF is the **volt (V)**
  - The relationship between the volt, the joule (energy) and the coulomb (electric charge) is:

$$\mathbf{1\ J = 1\ C \bullet 1\ V}$$

Standard Reduction Potentials

- The standard cell potential of any galvanic cell is the sum of the standard half-reaction potentials for the oxidation and reduction half-cells.

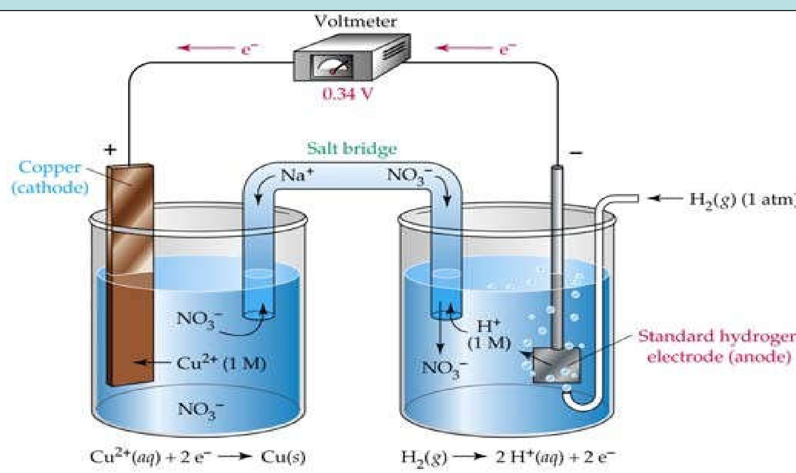
$$E^\circ_{\text{cell}} = E^\circ_{\text{oxidation}} + E^\circ_{\text{reduction}}$$

- Standard half-cell potentials are always quoted as a **reduction process** (See below table).
- If your half-reaction is an oxidation, the numerical value is the same as in the Table but the **sign must be changed**.

Standard Reduction Potentials

- It is not possible to measure the potential of a single half reaction (remember, you must always have both ½ rxns!)
- The **standard half-cell potentials (E°)** have been determined experimentally by measuring the **difference** between two electrodes, the target electrode and a standard or reference electrode.
- The reference electrode is called the **standard hydrogen electrode** (SHE) and consists of a platinum electrode in contact with H_2 gas (1 atm) and aqueous H^+ ions (1 M).
- The **standard hydrogen electrode** is assigned an arbitrary value of exactly <u>**0.00 V**</u>.

Standard Reduction Potentials



$$\mathbf{Pt(s)\,|\,H_2(1\ atm)\,|\,H^+(1\ M)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)}$$

$$\mathbf{E°_{cell} = E°_{H_2\rightarrow H^+} + E°_{Cu2+\rightarrow Cu}}$$

$$\mathbf{0.34\ V = 0\ V + E°_{Cu2+\rightarrow Cu}}$$

Standard Reduction Potentials

TABLE 18.1 Standard Reduction Potentials at 25°C

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

Spontaneity of a Reaction

The value of E°_{cell} is also related to the thermodynamic quantity of ΔG°.

$$\Delta G^\circ = -nFE^\circ_{cell}$$

n = # of moles of e^- transferred

F = the Faraday constant (96,485 C/mol e^-)

- For spontaneous reactions, **ΔG° is negative** and **E°_{cell} is positive**
- Calculate the free energy change at 25°C for the following reaction. The standard cell potential is 1.10V.

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

Standard Reduction Potentials

- Remember, a positive value for E° means that the reaction is spontaneous.
- When deciding which half cell is the cathode and which is the anode, the half-cell reaction with the **more negative value** will form the **oxidation half-cell (the anode)**.
- If the half reactions do not have the same number of electrons, you must balance to get the correct cell reaction; however, you **DO NOT** change the standard reduction potential!

- Consider the reaction between zinc and copper, then zinc and silver:

Cu^{2+} (*aq*) + 2e$^-$ → Cu(*s*) E° = 0.34 V

Ag^+ (*aq*) + 1 e$^-$ → Ag(*s*) E° = 0.80 V

Zn^{2+}(*aq*) + 2 e$^-$ → Zn(*s*) E° = – 0.76 V

Identify the oxidation and the reduction half-cells

What are the two half-cell standard potentials?

What is the standard potential of the cell?

Standard Reduction Potentials

- Using the standard reduction potentials, predict whether Pb^{2+}(aq) can oxidize Al(s) or Cu(s)

Pb^{2+}(aq) + 2 e$^-$ → Pb(s) E° = -0.13

Al^{3+}(aq) + 3 e$^-$ → Al(s) E° = -1.66

Cu^{2+}(aq) + 2 e$^-$ → Cu(s) E° = 0.34

Given the electrochemical retivitytion shown, if the standard reduction potential of $Cu^{2+} \rightarrow Cu$ is +0.34 V, **what is the standard reduction potential** of $Sn^{2+} \rightarrow Sn$ **?**

$$Sn \;/\; Sn^{2+}(aq) \;//\; Cu^{2+}(aq) \;/\; Cu \qquad E^0 = +0.48\ V$$

The oxidation of hydrogen by oxygen is one of the most-used reactions in fuel-cell technology. The overall reaction, which is given below, has a Δ*G*° value of –474 kJ/mol. What is the standard cell potential for this fuel cell?

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta G^\circ = -474\ kJ/mol$$

The Nernst Equation

- Cell potentials can be modified by **<u>temperature</u>** and **<u>composition</u>** changes according to the Nernst equation:

$$\Delta G = \Delta G° + RT \ln Q$$

$$-nFE = -nFE° + RT \ln Q$$

$$E = E° - \frac{2.303\,RT}{nF}\log Q \qquad E = E° - \frac{0.0592\text{ V}}{n}\log Q$$

At 25°C

The Nernst Equation

- Consider the reaction of metallic zinc with hydrochloric acid. Calculate the cell potential at 25°C when $[H^+]$ = 1.0 M, $[Zn^{2+}]$ = 0.0010 M, and P_{H_2} = 0.10 atm.

- Consider the reaction of metallic copper with iron (III) to give copper (II) and iron(II). What is the potential of a cell when $[Fe^{3+}]$ = 0.0001 M, $[Cu^{2+}]$ = 0.25 M, and $[Fe^{2+}]$ = 0.20 M?

The Nernst Equation and pH

- A particularly important use of the Nernst equation is in the electrochemical determination of pH
- Consider a cell with a hydrogen electrode as the anode and second electrode as the cathode

Pt | H_2 (1 atm) | H^+ (? M) || Reference Cathode

$E_{cell} = E_{H_2 \rightarrow H^+} + E_{ref}$

- The Nernst equation relates the concentration of any chemical species, including H^+ to the cell potential.
- This relationship is used in a pH meter which measures a cell potential and displays its value in terms of pH
- The Nernst equation can be applied to the half-reaction:

$$H_2\,(g) \rightarrow 2\,H^+(aq) + 2\,e^-$$

The Nernst Equation and pH

- The Nernst equation can be applied to the half-reaction :

$$H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-$$

$$E_{H_2 \rightarrow H^+} = E°_{H_2 \rightarrow H^+} - \frac{0.0592\ V}{n} \log\left(\frac{[H^+]^2}{P_{H_2}}\right)$$

- E° = 0 V for this reaction (standard hydrogen electrode), n = 2 and P_{H_2} is 1 atm.

$$E_{H_2 \rightarrow H^+} = 0 - \frac{0.0592\ V}{2} \log\left([H^+]^2\right)$$

$$E_{H_2 \rightarrow H^+} = -0.0592\ V \bullet \log\left([H^+]\right)$$

$$\boxed{E_{H_2 \rightarrow H^+} = 0.0592\ V \bullet pH}$$

The Nernst Equation and pH

- So, for the overall cell potential:

$$E_{cell} = E_{H_2 \rightarrow H^+} + E_{ref}$$

$$E_{Cell} = (0.0592\ V \bullet pH) + E_{ref}$$

$$\boxed{pH = \frac{E_{Cell} + E_{Ref}}{0.0592\ V}}$$

- A higher cell potential indicates a higher pH, therefore we can measure pH by measuring E_{cell}.
- A glass electrode (Ag/AgCl wire in dilute HCl) with a calomel reference is the most common arrangement.

Glass: $Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$ $E° = -0.22$ V

Calomel: $Hg_2Cl_2(s) + 2\ e^- \rightarrow 2\ Hg(l) + 2\ Cl^-(aq)$ $E° = 0.28$ V

The Nernst Equation and pH

- The following cell has a potential of 0.55 V at 25°C:

Pt(s) | H_2 (1 atm) | H^+ (? M) || Cl^- (1 M) | Hg_2Cl_2(s) | Hg(l)

What is the pH of the solution at the anode?

- The following cell has a potential of 0.28 V at 25°C:

Pt(s) | H_2 (1 atm) | H^+ (? M) || Pb^{2+} (1 M) | Pb(s)

What is the pH of the solution at the anode?

Cell Potentials and Equilibrium

- The value of K_{eq} is related to ΔG° by:

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

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$-nFE^\circ = -RT \ln K_{eq}$$

$$E^\circ_{Cell} = \frac{RT}{nF} \ln K_{eq} \qquad E^\circ_{Cell} = \frac{0.0592\ V}{n} \log K_{eq}$$

At 25°C

Cell Potentials and Equilibrium

- Calculate the standard free energy change (ΔG°) and the equilibrium constant (K) for the following reactions at 25°C:

$Sn(s) + 2\ Cu^{2+}(aq)$ □ $Sn^{2+}(aq) + 2\ Cu^{+}(aq)$

$Fe^{2+}(aq) + 2\ Ag(s)$ □ $Fe(s) + 2\ Ag^{+}(aq)$

$4\ Fe^{2+}(aq) + O_2(g) + 4\ H^{+}(aq)$ □ $4\ Fe^{3+}(aq) + 2\ H_2O(l)$

What is E° for the following balanced reaction, if $K = 4.38 \times 10^{10}$?

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s) \quad K = 4.38\ x\ 10^{10}$$