Many chemical reactions involve the transfer of electrons between atoms or ions.

- All single displacement and combustion reactions
- Some synthesis and decomposition reactions
- The flow of electrons is associated with electricity.

Basic research into the nature of this relationship may, in the near future, lead to cheaper, more efficient ways of generating electricity.

- Fuel cell

19.1 Balancing Redox Reactions by the Half-Reaction Method

- was covered in CHM 1210. It is the student's responsibility to review if they've forgotten the materials.

Oxidation is the process that occurs when

- the oxidation number of an element increases,
- an element loses electrons,
- a compound loses hydrogen, or
a half-reaction has electrons as products.

Reduction is the process that occurs when

- the oxidation number of an element decreases,
- an element gains electrons,
- a compound gains hydrogen, or
a half-reaction has electrons as reactants.

Redox reactions are reactions in which one species is reduced and another is oxidized. Therefore, the oxidation state of the species involved must change

Oxidation Number (State): A value which indicates whether an atom is neutral, electron-rich, or electron-poor.

Writing half reactions

- We generally split the redox reaction into two separate **half-reactions**—a reaction just involving oxidation or reduction.

$$2Na(s) \quad + \quad Cl_2(g) \quad \rightarrow \quad 2NaCl(s)$$
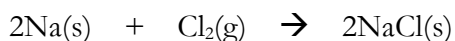
     – The oxidation half-reaction has electrons as products.

     – The reduction half-reaction has electrons as reactants.

     – Oxidizing agent:

     – Reducing agent:

19.2 Voltaic (or Galvanic) Cells:

Electrochemistry: The area of chemistry concerned with the interconversion of chemical and electrical energy.

Electrochemical cells have two types: Galvanic (or Voltaic) cells and electrolytic cells.
Electrolytic cells - Nonspontaneous redox reactions can be made by the addition of electrical energy.

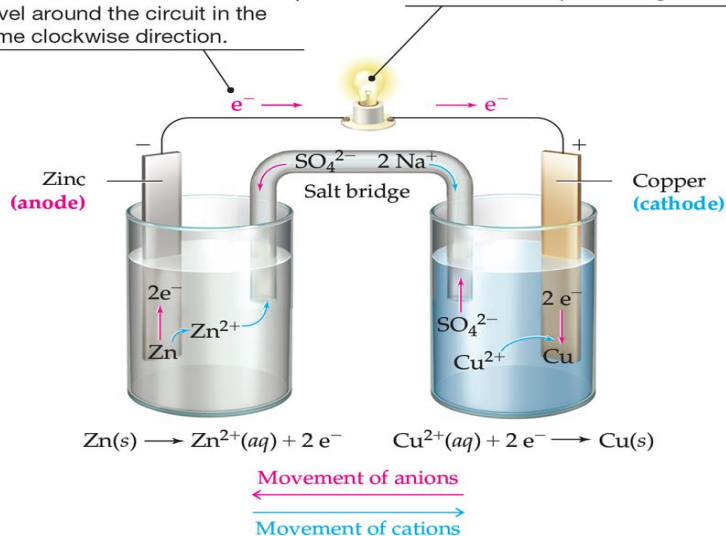## Galvanic Cells - Electrochemical Cell Components

- Generating Electricity from Spontaneous Chemical reaction

- Electrons flow through a conductor in response to an electrical potential difference similar to water flowing downhill in response to a difference in gravitational potential energy.

- Electric current – the amount of electric charge that passes a point in a given period of time
    - Whether as electrons flowing through a wire, or ions flowing through a solution

- Oxidation and reduction half-reactions are kept separate in half-cells.

- Electron flow through a wire along with ion flow through a solution constitutes an electric circuit.

- It requires a conductive solid electrode to allow the transfer of electrons.

    ✓ Through external circuit

    ✓ Metal or graphite

- Requires ion exchange between the two half-cells of the system.

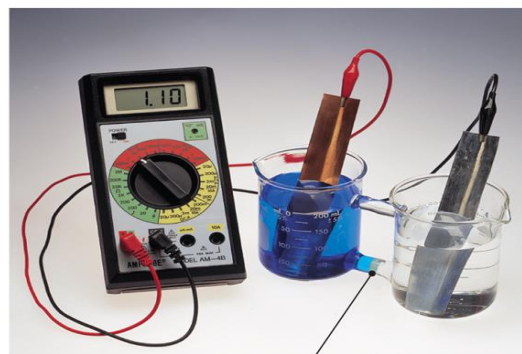Consider the reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

(a) A galvanic cell

The negative particles (electrons in the wire and anions in solution) travel around the circuit in the same clockwise direction.

The resulting electric current can be used to power a light bulb.

e^- ⟶   ⟶ e^-

Zinc
(anode)

SO_4^{2-} 2 Na$^+$
Salt bridge

Copper
(cathode)

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

$2\,e^-$
SO_4^{2-}
Cu^{2+} Cu

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

Movement of anions
Movement of cations

(b) An operating Daniell cell

1.10

The salt bridge in part (**a**) is replaced by a porous glass disk that allows ions to flow between the anode and cathode compartments but prevents bulk mixing. If Cu^{2+} crossed the membrane and came into direct contact with zinc, then electrons would be transferred directly and would not flow through the wire.

Two conductors (anode and cathode)

Electrolytes solution: solution that each electrode is immersed in it

External circuit: provide a pathway for electron to move from one electrode to another
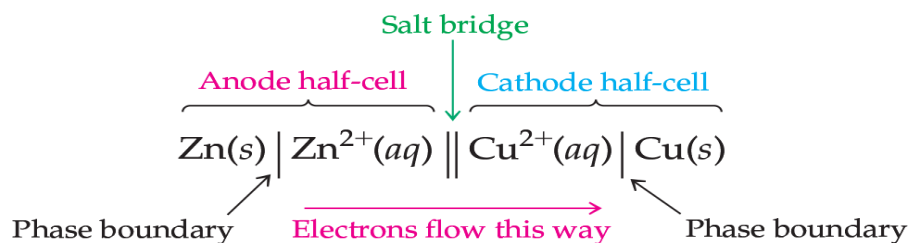
Salt Bridge: is necessary to complete the electrical circuit by providing neutrality

Anode:	**Cathode**:
• The electrode where oxidation occurs.	• The electrode where reduction occurs.
• The electrode where electrons are produced.	• The electrode where electrons are consumed.
• Is what anions migrate toward.	• Is what cations migrate toward.
Has a negative sign	• Has a positive sign.

19.3 Shorthand Notation for Galvanic Cells or Voltaic Cell: shorthand description of a voltaic cell

<p align="center">Electrode | electrolyte || electrolyte | electrode</p>

- Oxidation half-cell on the left; reduction half-cell on the right

- Single | = phase barrier

  If multiple electrolytes in same phase, a comma is used rather than |

- Double line || = salt bridge

<p align="center">Salt bridge</p>

<p align="center">Anode half-cell   Cathode half-cell</p>

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

<p align="center">Phase boundary   Electrons flow this way   Phase boundary</p>

Cell involving gas or no metal electrode present

    ° **Inert electrode:** serve as a contact between the solution and the external circuit.

    ° Additional vertical line due to presence of addition phase

    ° List the gas immediately adjacent to the appropriate electrode

    ° Detailed notation includes ion concentrations and gas pressure
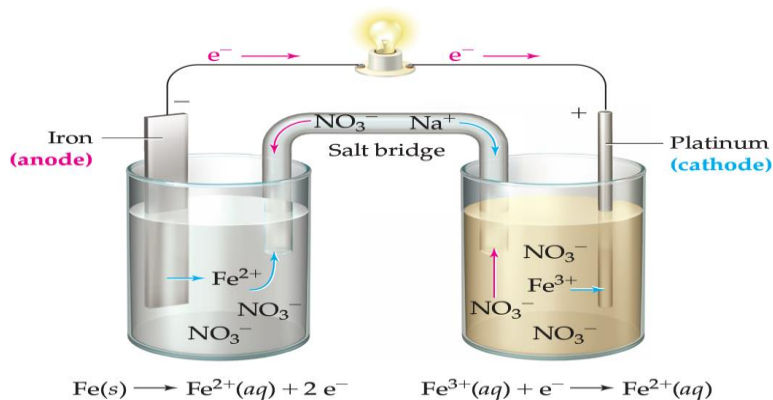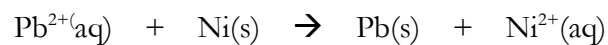
For instance, a cell that uses the reaction

$$Fe_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow 3Fe^{2+}_{(aq)}$$
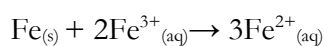
Oxidation half:

Reduction half:

Net equation:

Fe(s) ⟶ Fe²⁺(aq) + 2 e⁻   Fe³⁺(aq) + e⁻ ⟶ Fe²⁺(aq)

Short-hand notation:

Example: Give short hand notation and draw a galvanic cell that employs the overall reaction

$$Pb^{2+}(aq) \quad + \quad Ni(s) \quad \rightarrow \quad Pb(s) \quad + \quad Ni^{2+}(aq)$$

Use the diagram of the galvanic cell to identify the anode and cathode half-reactions and write an overall balanced reaction. Label the anode and the cathode, and identify the sign of each electrode.
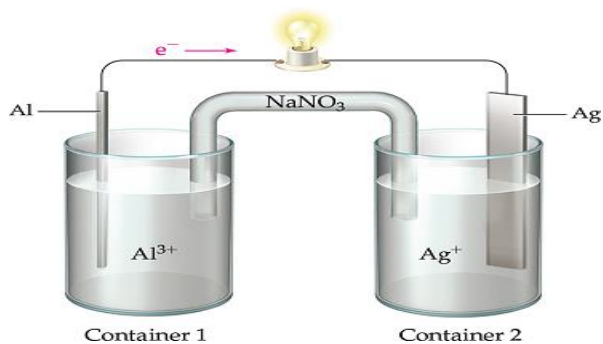
19.4   Cell Potentials and Free-Energy Changes for Cell Reactions

We've now seen two quantitative measures of the tendency for a chemical reaction to occur: the cell potential, E, and electrochemical quantity, and the free-energy change, G, a thermochemical quantity.   The values of G and E are directly proportional and are related by the equation

$$\Delta G = -nFE \qquad or \qquad \Delta G° = -nFE°$$

Where F = **Faraday constant** =   **96,500 C/mol e⁻** (3sf)   **J = C x V**

Two features of the equation $\Delta G° = -nFE°$ are worth noting: the units and the minus sign. When we multiply the charge transferred (nF) in coulombs by the cell potential (E) in volts, we obtain an energy ΔG in joules, in accord with the relationship. The minus sign is required because E and ΔG have opposite signs: The spontaneous reaction in a galvanic cell has a positive cell potential but a negative free-energy change. So, do you we obtain E°cell?

19.5 -19.6 Standard Reduction Potentials

Electromotive Force (emf): The force or electrical potential that pushes the negatively charged electrons away from the anode (− electrode) and pulls them toward the cathode (+ electrode).

- It is also called the **cell potential (E)** or the **cell voltage**

- The cell potential is a measure of the overall tendency of the redox reaction to occur spontaneously.

  - Unit = **volt (V)**

- A volt is the amount of energy it takes to transfer one coulomb of charge.

  – The voltage needed to drive electrons through the external circuit

J = C x V

1 coulomb is the amount of charge transferred when a current of 1 ampere (A) flows for 1 second.

C = A x s

- **E°cell** is the standard cell potential when both products and reactants are at their standard states:

  ○ Solutes at 1.0 M   Gases at 1.0 atm

  o   Solids and liquids in pure form   Temp = 25.0°C

The standard potential, **E°cell**, of any galvanic cell is the sum of the standard half-cell potentials for oxidation at the anode and the reduction at the cathode:

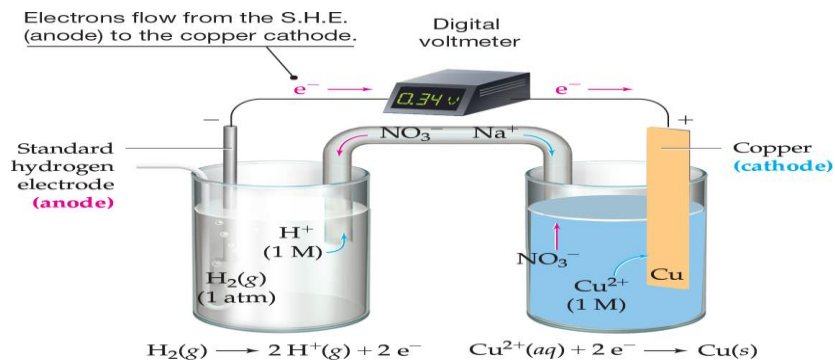$$\textbf{E°}_{cell} = \textbf{E°}_{ox} \quad + \quad \textbf{E°}_{red}$$

Standard Reduction Potentials

- The **standard reduction potential** is the tendency for a chemical species to be **reduced**, and is measured in volts at **standard** conditions. The more positive the **potential** is the more likely it will be **reduced**

- **Standard Hydrogen Electrode (SHE)** is an electrode that scientists use for reference on all half-cell potential reactions. The value of the standard electrode potential is zero, which forms the basis one needs to calculate cell potentials using different electrodes or different concentrations

  - Hydrogen gas at 1 atm is bubbled through 1M HCl solution, which is inert to the action of the 1M HCl, is used as an electrode.   Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.
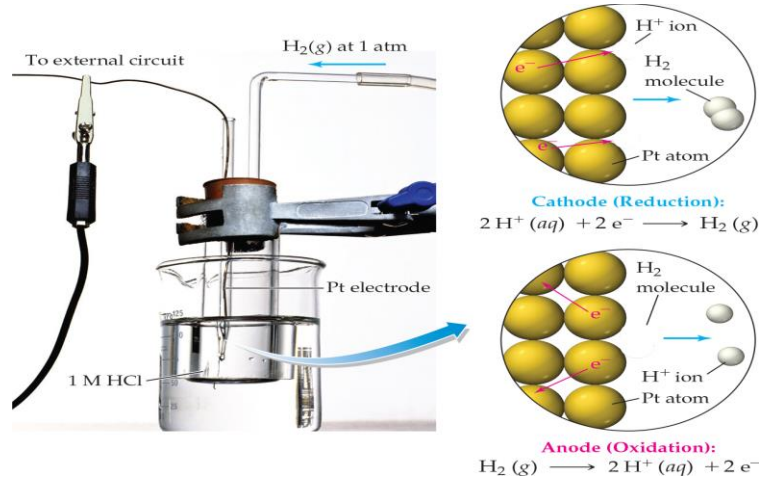
- Oxidation-Half: $\qquad$ $H_2(\ell, 1 \text{ atm}) \rightarrow 2H^+_{(aq}, 1 \text{ M}) + 2e^-$ $\qquad$ $E°_{ox} = 0.00 \text{ V}$

- Reduction-Half: $\qquad$ $Cu^{+2}_{(aq)}, 1M) + 2e^- \rightarrow Cu_{(s)}$ $\qquad$ $E°_{red} = 0.34 \text{ V}$

- Net-reaction: $\qquad$ $H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)}$ $\qquad$ $E°_{cell} = 0.34V$

$$E°_{cell} = E°_{ox} + E°_{red} = E°_{H_2 \rightarrow 2H^+} + E°_{Cu^{2+} \rightarrow Cu} = 0.34 \text{ V}$$

The following conventions are observed when constructing a table of half-cell potentials:

The half-reactions are written as reductions rather than as oxidations. This means that oxidizing agents and electrons are on the left side of each half-reaction and reducing agents are on the right side.

The listed half-cell potentials are standard reduction potentials, also known as standard electrode potentials.

The half-reactions are listed in order of decreasing standard reduction potential, meaning a decreasing tendency to occur in the forward direction and an increasing tendency to occur in the reverse direction.

TABLE 19.1 Standard Reduction Potentials at 25 °C

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

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To calculate the standard cell potential for a reaction

- Write the oxidation and reduction half-reactions for the cell.

- Look up the reduction potential, $E°_{reduction}$, for the reduction half-reaction in a table of reduction potentials

- Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction, **$E°_{oxidation} = -\,E°_{reduction}$**.

- Add the potentials of the half-cells to get the overall standard cell potential.

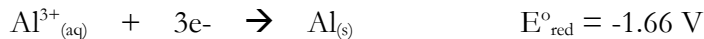   **Spontaniety** of the reaction can be determined by the **positive $E°_{cell}$ ($E° > 0$)** values

Note: $E°_{cell}$ is an intensive property; the value is independent of how much substance is used in the reaction

$Ag^+_{(aq)}$ +   e- → $Ag_{(s)}$ $E°_{red} = 0.80$ V

$2\,Ag^+_{(aq)}$ + 2e- → $2\,Ag_{(s)}$ $E°_{red} = 0.80$V
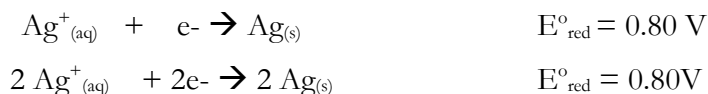
The reason why E° values are independent of the amount of reactant can be understood by looking at the equation $\Delta G° = -nFE°$. Free energy is an extensive property (Section 2.3) because it depends on the amount of substance. If twice as much Ag^+ is reduced, the free-energy change, $\Delta G°$, doubles. The number of electrons transferred, n, also doubles, however, so the ratio $E° = \Delta G°/nF$ is constant

Example: Of the two standard reduction half reactions below, write the net equation and determine which would be the anode and which would be the cathode of a galvanic cell.   Calculate $E°_{cell}$

$$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)} \qquad\qquad E°_{red} = -0.44 \text{ V}$$

$$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)} \qquad\qquad E°_{red} = -1.66 \text{ V}$$

Example: Use tabulated standard electrode potentials to calculate the standard cell potential for the following reaction occurring in an electrochemical cell at 25 °C. (The equation is balanced.) Determine if the reaction is spontaneous as written? If not, re-write the reaction.

$$O_{2(g)} + 2H_2O_{(l)} + 4Ag_{(s)} \rightarrow 4 {}^-OH_{(aq)} + 4 Ag^+_{(aq)}$$
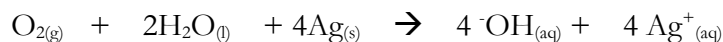
Example: Use tabulated electrode potentials to calculate $\Delta°G$ (in kJ) for the reaction.   Is the reaction spontaneous?

$$I_{2(s)} + 2 Br^-_{(aq)} \rightarrow 2 I^-_{(aq)} + Br_{2(l)}$$