Electrochemical Cells and Cell Potential (E^o)

Electrochemistry: a study of the interchange of electrical and chemical energy

- There are two types of electrochemical cells: galvanic (voltaic) and electrolytic.
  - Voltaic or Galvanic Cell (Battery): a thermodynamically favorable (i.e. spontaneous) redox reaction which generates useful electrical energy in the form of an electric current
  - Electrolytic Cell: requires electrical energy (direct current or DC power source) to drive a thermodynamically unfavorable (i.e. non-spontaneous) redox reaction.
- In short: galvanic (voltaic) cells produce current, while electrolytic cells use current!

QUICK REMINDERS

1) Oxidation is LOSS of electrons	2) Reduction is GAIN of electrons
OIL (LEO)	RIG (GER)
Ex: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	Ex: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Cell Potential (Ecell): a measure of the potential difference (how much Voltage exists) between two half cells an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half-cell to the other.

→ The cell potential is a quantitative description of the driving force behind an electrochemical reaction that pushes electrons through the wire (or external circuit).

Standard Cell Potential (E^o_{cell}): cell potential measured at standard conditions: **1 atm, 1 M solution, and 25°C.** A 'naught' sign (°) is used to show standard conditions. Usually measured in Volts (1 V = 1 Joule/Coulomb = 1 J/C)

The cell potential can be easily calculated by adding the oxidation and reduction potentials.

$$E^o_{cell} = E^o_{ox} + E^o_{red}$$

- E^o_{cell} is the standard cell potential.
- E^o_{ox} is the standard oxidation cell potential for the oxidation half-reaction.
- E^o_{red} is the standard reduction cell potential for the reduction half-reaction.

→ The more positive the value of E°_{cell}, the greater the driving force of electrons through the system (under standard conditions), thus the more likely the reaction will proceed → more spontaneous/more thermodynamically favorable.

When you balance a redox reaction, don't change the cell potential!
Cell potential is an intensive property and thus does not depend on how many times a reaction occurs.

To find a table of Standard Electrode Potentials: Tro (p. 873, Section 18.4) or Zumdahl, 5th ed. (p. 843, Section 17.2)

1. Because the values come from a chart of standard <u>reduction</u> potentials, you ***MUST REVERSE*** the sign of the E° of the ***oxidized*** species before adding to the E° of the reduced species.
2. For a spontaneous redox reaction to occur, the overall cell potential must be positive.] galvanic/voltaic cell
   a) The metal with the **greater** (more positive) reduction potential will be **reduced**!
3. For a non-spontaneous redox reaction to occur, the overall cell potential must be negative.] electrolytic cell
   a) The metal with the **greater** (more positive) reduction potential will be **oxidized**!
4. A reduction potential table can be used as an activity series: metals with a lower reduction potential are more active and will replace metals with more positive potentials. (in spontaneous rxns!)

Example: Consider the half reactions shown below and the standard electrode reduction potentials that follow.

reverse: $Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-$

$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ $E° = -1.66$ V $\Rightarrow E°_{ox} = +1.66$ V

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

1. Write the balanced redox reaction for copper and aluminum that is thermodynamically favorable (i.e. spontaneous). Calculate the standard cell potential of this reaction.

$$2Al_{(s)} + 3Zn^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Zn_{(s)}$$

$$E°_{cell} = E°_{ox} + E°_{red} = 1.66 - 0.76 = \boxed{0.90V}$$

2. Write the balanced redox reaction for copper and aluminum that is *not* thermodynamically favorable (i.e. non-spontaneous). Calculate the standard cell potential of this reaction.

flip rxn #1! $2Al^{3+}_{(aq)} + 3Zn_{(s)} \rightarrow 2Al_{(s)} + 3Zn^{2+}_{(aq)}$

$$E°_{cell} = E°_{ox} + E°_{red} = 0.76 - 1.66 = \boxed{-0.90V}$$

Now you try!

3. Identify the standard reduction potential, $E°_{red}$, for each half reaction (use reduction potential chart!). Determine which species will be oxidized and which will be reduced for a redox reaction that is thermodynamically favorable (spontaneous). Next, calculate the value of $E°_{cell}$ for the thermodynamically favorable cell. Justify why your calculated $E°_{cell}$ represents a thermodynamically favorable reaction.

$Ag^+(aq) + 1e^- \rightarrow Ag(s)$ E° = 0.80 V $= E°_{red}$

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

$E°_{cell} = 0.80 - 0.34 = \boxed{0.46V}$ $E°_{cell}$ is positive ⇒ this is a therm. favorable rxn!

4. For the net ionic equation below, determine the standard cell potential, E°, for the reaction. Next, use the calculated value of E° to determine if the reaction is thermodynamically favorable (spontaneous) as written. (Hint: the reduction potential chart is all REDUCTION values. Flipping the rxn changes the sign of E).

$$3\,Cu(s) + 2\,Al^{3+}(aq) \rightarrow 2\,Al(s) + 3\,Cu^{2+}(aq)$$

oxidized reduced

$E°_{ox} = -0.34$V $E°_{red} = -1.66$V

$E°_{cell} = -0.34 - 1.66 = \boxed{-2.00V}$ ⇒ $E°_{cell}$ is negative ⇒ this rxn is NOT therm. favorable!

For the two examples below, use the provided information to find the reduction potential of the missing half-reaction (**without** using the reduction potential chart ☺). Next, use the value of $E°_{cell}$ for the overall reaction to determine whether or not the reaction is thermodynamically favorable (spontaneous) as written.

1. $Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$ $\quad E^\circ_{red} = -1.66\text{ V}$

$Pb^{2+}(aq) + 2\,e^- \rightarrow Pb(s)$ $\quad E^\circ_{red} = ???$

$2\,Al^{3+}(aq) + 3\,Pb(s) \rightarrow 2\,Al(s) + 3\,Pb^{2+}(aq)$ $\quad E^\circ_{cell} = -1.79\text{ V}$] NOT therm. fav!

reduced oxidized

$$E^\circ_{cell} = E^\circ_{red} + E^\circ_{ox} = -1.66 + E^\circ_{ox} = -1.79$$

$$\Rightarrow E^\circ_{ox} = -1.79 + 1.66 = -0.13\text{ V}$$

$$\Rightarrow E^\circ_{red}(Pb^{2+}) = \boxed{+0.13\text{ V}}$$

2. $Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$ $\quad E^\circ_{red} = +1.36\text{ V}$

$Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$ $\quad E^\circ_{red} = ???$

$Ni(s) + Cl_2(g) \rightarrow 2\,Cl^-(aq) + 3\,Ni^{2+}(aq)$ $\quad E^\circ_{cell} = +1.59\text{ V}$] therm. fav!

reduced oxidized

$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red} = E^\circ_{ox} + 1.36 = 1.59$$

$$\Rightarrow E^\circ_{ox} = 1.59 - 1.36 = 0.23\text{ V}$$

$$\Rightarrow E^\circ_{red}(Ni^{2+}) = \boxed{-0.23\text{ V}}$$