Standard Electrode (Reduction) Potentials

The ***cell voltage*** of an electrochemical cell can be attributed to the difference in the tendencies of the two half-cells to undergo reduction= *reduction potential* (gain electrons)

- i.e. the difference between the potential energies at the anode and cathode
- voltage is also called the *electrical potential difference* or *electro-motive force (emf)* and is measured in *volts,V*

Cell Potential, E_{cell}

- the maximum voltage of the cell.
- depends upon the composition of the electrodes and the [ions] in each half-cell.

Standard Cell Potential, E^o_{cell}

- the potential of the cell at standard conditions:
  when all of the ions concentrations are 1.00 M,
  the temperature is 25°C,
  any gases involved in the cell reaction are at a pressure of 1 atm.

Reduction Potentials

A galvanic cell contains two half-cells and the overall potential can be imagined as a competition between the two cells. When the two half-cells are connected, the one with the larger reduction potential-the one with the greater tendency to undergo reaction- acquires electrons from the half-cell with the lower reduction potential, which is therefore forced to undergo oxidation. The measured cell potential actually represents the magnitude of the difference between the reduction potentials of the two half-cells.

Assigning E°

- No way to measure E° for the half-cell (a single half reaction cannot occur alone)
- To assign values of E°, a reference electrode is arbitrarily chosen and its E° value is chosen to be 0.00 V
  - The reference electrode is the Standard Hydrogen Electrode (SHE) which is taken to be at standard conditions (1 atm, 25 °C, 1.00M).

$2H^+_{(aq)} + 2e^- \_ H_{2(g)}$ $\qquad E^o_{H^+} = 0.00V$

Table of E° Half-Reactions (Half-cell Voltages)

- Arranged in decreasing order of reduction potential

- At the top they have a greater tendency to occur as reduction
  - eg. $F_{2(g)}$ has the greatest potential to undergo reduction (gain electrons)
  - ie. It is the strongest oxidizing agent and thus will have the strongest tendency to gain electrons from a reducing agent
  - Oxidizing agents occur on the left of the arrow

- At the bottom they have a greater tendency to occur as oxidation
  - eg. $Li_{(s)}$ has the least potential to undergo reduction but the strongest to undergo oxidation (lose electrons)
  - ie. It is the strongest reducing agent and thus will have the strongest tendency to lose electrons to an oxidizing agent
  - Reducing agents are located to the right of the arrow

- The substance with the greater E° value (higher on the table) will always undergo reduction while the other is forced to undergo oxidation

<u>To calculate the standard cell potential of a galvanic cell:</u>

- When calculating E^o for a reaction ***never*** multiply the half-cell voltage (E^o value) by the coefficients in the equation
- When reversing an equation from the table change the sign on the E^o value

eg. $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $E^o_{Cu2+} = +0.34$

$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ $E^o_{Cu} = -0.34$

Steps:
1. Obtain the E^o values from the Standard Reduction Potential Table
2. Identify the 2 half-reactions from the equation
3. Change the sign of the E^o value for any half reaction that is reversed
4. Add the two half reactions to get the overall equation and add the two E^o values to find the standard cell potential (cell voltage) for the electrochemical cell

<u>Example 1:</u>
Calculate the standard cell potential, E^o_{cell} for a silver-copper galvanic cell given the following reaction:

$$2Ag^+_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

Step 1:
$2e^- + 2Ag^+_{(aq)} \rightarrow 2Ag_{(s)}$ $E^o = +0.80$
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $E^o = +0.34$

Steps 2&3:
$2e^- + 2Ag^+_{(aq)} \rightarrow 2Ag_{(s)}$ $E^o = +0.80$ *Reduction (cathode)*
$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ $E^o = -0.34$ *Oxidation (anode)*

Step 4:
$2Ag^+_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$ $E^o_{cell} = +0.46$

SHORTCUTS!!!!!

Steps:
1. Write the two half reactions from the equation reversing the oxidation half-reaction
2. Use one of the methods below to find the standard cell potential

<u>Method 1</u>:

E^o_{cell} = (standard reduction potential of substance reduced) + (Standard reduction potential of substance oxidized)

$E^o_{cell} = E^o_{red} + E^0_{ox}$ or $E^o_{cell} = E^o_{cathode} + E^0_{anode}$

Note: reverse the sign of the E^0 value (E^0_{ox}) for the substance being oxidized

<u>Method 2:</u>

E^o_{cell} = (standard reduction potential of substance reduced) - (Standard reduction potential of substance oxidized)

$E^o_{cell} = E^o_{red} - E^0_{ox}$ or $E^o_{cell} = E^o_{cathode} - E^0_{anode}$

Note: do not reverse the sign of the E^0 value (E^0_{ox}) for the substance being oxidized

For the example above:

$$2Ag^+_{(aq)} + Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$$

$2e^- + 2Ag^+_{(aq)} \rightarrow 2Ag_{(s)}$ *Reduction (Cathode)*
$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ *Oxidation (Anode)*

Ag^+ must have a greater tendency to react than Cu^{2+} , because Ag^+ is reduced. This means that the reduction potential for Ag^+, $E^o_{Ag^+}$, must be larger than the standard reduction potential for Cu^{2+}, $E^o_{Cu^{2+}}$.

Therefore: $E^o_{cell} = E^o_{Ag^+} + E^o_{Cu}$ or $E^o_{cell} = E^o_{Ag^+} - E^o_{cu}$

Reduced Oxidized Cathode Anode

Method 1:
$E^o_{cell} = E^o_{Ag^+} + E^o_{Cu}$
$E^o_{cell} = 0.80V + -0.34V$ *(sign reversed)*
$E^o_{cell} = 0.46V$

Method 2:
$E^o_{cell} = E^o_{Ag^+} - E^o_{cu}$
$E^o_{cell} = 0.80\ V - 0.34V$ *(sign not reversed)*
$E^o_{cell} = 0.46V$

Example 2:
Calculate the standard reduction potential for copper in the following reaction.

$Cu^{2+}{}_{(aq)} + H_{2(g)} \rightarrow Cu_{(s)} + 2H^+{}_{(aq)}$ $E^o_{cell} = 0.34\ V$

Example 3:
What is the E^o_{Zn} in the following reaction?

$Zn_{(s)} + 2H^+{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + H_{2(g)}$ $E^o_{cell} = 0.76V$

Example 4:
Calculate the standard cell potential, E^o_{cell} , for the reaction of gold nitrate with zinc.

$2Au(NO_3)_{3\ (aq)} + 3Zn_{(s)} \rightarrow 3Zn(NO_3)_{3\ (aq)} + 2Au_{(s)}$

Example 5:
What is the cell reaction and the standard cell potential for a voltaic cell composed of the following half-cells?

$Fe^{3+} + e- \rightarrow Fe^{2+}$ $E^o_{Fe3+} = +0.77V$
$Ni^{2+} + 2e- \rightarrow Ni$ $E^o_{Ni^{2+}} = -0.25V$

Example 6:
What is E^o_{cell} for the reaction in which $Cl_{2\ (g)}$ oxidizes $Fe^{2+}{}_{(aq)}$ to $Fe^{3+}{}_{(aq)}$?

Example 7:
Consider the following galvanic cell:

$Cd_{(s)} / Cd^{2+}{}_{(aq)}$ (1M) // $Cu^{2+}{}_{(aq)} /Cu_{(s)}$ $E^o_{cell} = 0.743$ v

What is the standard reduction potential for the Cd^{2+}/Cd electrode?

Predicting Spontaneity

1. A spontaneous reaction only occurs when the oxidizing agent is above the reducing agent in the *Table of Reduction Potentials*.

2. For any functioning galvanic cell, the measured cell potential has a positive value.
$E^o_{cell} =$ positive, the reaction will occur and is spontaneous
$E^o_{cell} =$ negative, the reaction will not occur and is not spontaneous

Examples:

1. Is the following reaction spontaneous as written?
$Cu_{(s)} + 2H^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + H_{2(g)}$

$2H^{+}_{(aq)} + 2e^- \rightarrow H_{2(g)}$	*Reduction (Cathode)*	$E^o = 0$
$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$	*Oxidation (Anode)*	$E^o = -0.34$

$E^o_{cell} = E^o_{H^+} + E^o_{Cu^{2+}}$
$E^o_{cell} = 0 + (-0.34V)$

$E^o_{cell} = - 0.34V$, the value is negative, therefore it is non-spontaneous.

2. Is the following a spontaneous reaction?
$Zn_{(s)} + Cr^{3+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cr^{2+}_{(aq)}$

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ELECTROCHEMISTRY WORKSHEET #5

1. Calculate the standard cell potential, E^o_{cell} , for the following reactions and indicate if the reaction is spontaneous or nonspontaneous:

    a.) $Sn^{2+} + 2Ag \rightarrow Sn + 2Ag^+$

    b.) $H_2 + I_2 \rightarrow 2H^+ + 2I^-$

    c.) $Sn / Sn^{2+} / / Br_2 / Br^-$

    d.) $Cr^{2+} / Cr^{3+} // Zn^{2+} / Zn$

2. Is 1.0M H^+ solution under hydrogen gas capable of oxidizing silver metal in the presence of 1.0 M silver ion?

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