Skills to Develop

• Explain electromotive force.
• Construct the reference hydrogen electrode and explain why it is a reference.
• Distinguish reduction potentials from oxidation potentials.
• Calculate the standard potential from the reduction potentials.

Electromotive Force (EMF)

The electromotive force (EMF) is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (lose) electrons. For example, the maximum potential between \(\ce{Zn^{2+}}\) and \(\ce{Cu^{2+}}\) of a well known cell

\[
\ce{Zn_{(s)} | Zn^{2+} (1\: M) || Cu^{2+} (1\: M) | Cu_{(s)}}
\]

has been measured to be 1.100 V. A concentration of 1 M in an ideal solution is defined as the standard condition, and 1.100 V is thus the standard electromotive force, \(\Delta E^0\), or standard cell potential for the \(\ce{Zn-Cu}\) galvanic cell.

The standard cell potential, \(\Delta E^0\), of a galvanic cell can be evaluated from the standard reduction potentials of the two half cells \(E^0\). The reduction potentials are measured against the standard hydrogen electrode (SHE):

\[
\mathrm{Pt_{(s)}} \,|\, \ce{H_{2}(g, 1.0 \text{ atm})} \,|\, \ce{H^{+}(1.0 \text{ M})}
\]

Its reduction potential or oxidation potential is defined to be exactly zero.
The reduction potentials of all other half-cells measured in volts against the SHE are the difference in electrical potential energy per coulomb of charge.

Note that the unit for energy $J = \text{Coulomb volt}$, and the Gibbs free energy $G$ is the product of charge $q$ and potential difference $E$:

$$G \text{ in J} = q \times E \text{ in C V}$$

for electric energy calculations.

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**Evaluating Standard Cell Potential $\Delta E^\circ$ of Galvanic Cells**

A galvanic cell consists of two half-cells. The convention in writing such a cell is to put the (reduction) cathode on the right-hand side, and the (oxidation) anode on the left-hand side. For example, the cell

$$\text{\begin{array}{c}
\text{Pt} \\
\text{H}_2 \text{ gas} \\
1.0 \text{ atm} \\
\text{H}^+ \text{ 1.0 M}
\end{array}}$$

consists of the oxidation and reduction reactions:

- $\text{H}_2 \rightarrow 2 \text{e}^- + 2 \text{H}^+$ (anode (oxidation) reaction)
- $\text{Zn}^{2+} + 2 \text{e}^- \rightarrow \text{Zn}$ (cathode (reduction) reaction)

If the concentrations of $\text{H}_2$ and $\text{Zn}^{2+}$ ions are 1.0 M and the pressure of $\text{H}_2$ is 1.0 atm, the voltage difference between the two electrodes would be $-0.763 \text{ V}$ (the $\text{Zn}^{2+}$ electrode being the negative electrode). The conditions specified above are called the **standard conditions** and the EMF so obtained is the **standard reduction potential**.

Note that the above cell is in reverse order compared to that given in many textbooks, but *this arrangement gives the standard reduction potentials* directly, because the $\text{Zn}^{2+}$ half cell is a reduction half-cell. The negative voltage indicates that the reverse chemical reaction is spontaneous. This corresponds to the fact that $\text{Zn}$ metal reacts with an acid to produce $\text{H}_2$ gas.

As another example, the cell
\[
\text{Pt, \, H}_2, \, \text{H}^+, \, \text{Cu}^+, \, \text{Cu}
\]

consists of an oxidation and a reduction reaction:

- \[
\text{H}_2 \rightarrow 2 \text{e}^- + 2 \text{H}^+ \quad \text{(anode reaction)}
\]
- \[
\text{Cu}^2+ + 2 \text{e}^- \rightarrow \text{Cu} \quad \text{(cathode reaction)}
\]

and the standard cell potential is 0.337 V. The positive potential indicates a spontaneous reaction,

\[
\text{Cu}^2+ + \text{H}_2 \rightarrow \text{Cu} + 2 \text{H}^+
\]

but the potential is so small that the reaction is too slow to be observed.

**Example 1**

**What is the potential for the following cell?**

\[
\text{Zn, \, Zn}^{2+}:(1.0\, \text{M}), \, \text{||, \, Cu}^{2+}:(1.0\, \text{M}), \, \text{Cu}
\]

**SOLUTION**

From a table of standard reduction potentials we have the following values

\[
\text{Cu}^2+ + 2 \text{e}^- \rightarrow \text{Cu} \quad E^\circ = 0.337 \tag{1}
\]
\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \quad E^* = 0.763 \tag{2}
\]

Add (1) and (2) to yield

\[
\text{Zn + Cu}^2+ \rightarrow \text{Zn}^{2+} + \text{Cu} \quad \Delta E^\circ = E^\circ + E^* = 1.100 \text{ V}
\]

Note that \(E^*\) is the oxidation standard potential, and \(E^\circ\) is the reduction standard potential, \(E^* = -E^\circ\). The standard cell potential is represented by \(\Delta E^\circ\).

**DISCUSSION**

The positive potential confirms your observation that zinc metal reacts with cupric ions in solution to produce copper metal.

**Example 2**

**What is the potential for the following cell?**

\[
\text{Ag, \, Ag}^{+}:(1.0\, \text{M}), \, \text{||, \, Li}^{+}:(1.0\, \text{M}), \, \text{Li}
\]

**SOLUTION**

From the table of standard reduction potentials, you find
According to the convention of the cell, the reduction reaction is on the right. The cell on your left-hand side is an oxidation process. Thus, you add (4) and (3) to obtain

\[ \ce{Li+ + Ag \rightarrow Ag+ + Li} \hspace{15px} \text{d} E^\circ = -3.844 \text{ V} \]

**DISCUSSION**

The negative potential indicates that the reverse reaction should be spontaneous.

Some calculators use a lithium battery. The atomic weight of \(\ce{Li}\) is 6.94, much lighter than \(\ce{Zn}\) (65.4).

**Summary**

- The **electromotive force (EMF)** is the maximum potential difference between two electrodes of a galvanic or voltaic cell.
- The standard reduction potential of \(\ce{M^n+}, \ce{1 \ M} \ | \ce{M}\) couple is the standard cell potential of the galvanic cell:

  \[ \text{(Pt, } \ce{H_2}, \text{ 1 atm, } \ce{H^+}, \text{ 1 M, } \mathit M^{n+}, \text{ 1 M, } \mathit M) \]

- The standard oxidation potential of \(\ce{M}, \ce{M^n+}, \ce{1 M}\) couple is the standard cell potential of the galvanic cell:

  \[ \text{(mathrm{Pt, } \mathit M, \text{ |, } \mathit M^{n+}, \text{ 1 M, } ||, \text{ H^+}, \text{ 1 M, } \text{ |, H_2}, \text{ 1 atm, } \text{ |, Pt})} \]

- If the cell potential is negative, the reaction is reversed. In this case, the electrode of the galvanic cell should be written in a reversed order.

**Questions**

1. In which cell does reduction take place? The right-hand cell or the left-hand cell in the notation

   \[ \ce{[\text{left, left^+, left^+, right}^+, |, right, |]}? \]

2. Reduction potentials of half cells are measured against what?
   - A. **The zinc half cell** \(\ce{[\text{Zn, Zn^2+, 1 M}]}\).
   - B. **The hydrogen half cell** \(\ce{[\text{Pt, H_2, H^+, 1 M}]}\).
   - C. **The hydrogen half cell** \(\ce{[\text{H^+, 1 M, H_2, Pt}]}\).
   - D. **The copper half cell** \(\ce{[\text{Cu^{+2+, 1 M, Cu}}]}\).
   - E. **The hydrogen half cell** \(\ce{[\text{Pt, H_2, H^+, 10^{-7}}]}\).

3. Is the potential for the battery
\( \{ \text{Pt} \, | \, H_2 \, | \, H^+ \, || \, Cl_2 \, | \, Cl^- \, | \, \text{Pt} \} \)

positive or negative?

Solutions

1. Answer: Right
   Consider...
   Oxidation takes place in the left hand cell.
   Reduction takes place in the right hand cell or cathode.

2. Answer: B.
   Consider...
   \( \{ \text{Pt} \, | \, H_2 \, | \, H^+ \, || \, \text{right}^+ \, | \, \text{right} \} \)
   gives the reduction potential.

3. Answer: Positive
   Consider...
   \[
   \begin{align}
   Cl_2 + 2 e^- \rightarrow 2 Cl^- & \quad E^\circ = 1.36 \\
   H_2 \rightarrow 2 H^+ + 2 e^- & \quad E^\circ = 0.00 \\
   \overline{140px} & \overline{100px} \\
   Cl_2 + H_2 \rightarrow 2 HCl & \quad E^\circ = 1.36 \\
   \end{align}
   \]
   The reaction is spontaneous.

Contributors

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)