Basic Concepts: Overview of Electrochemical Process at Constant $T$, $P$; 14-1

$$\Delta G = \Delta G^o + RT \ln Q$$

$$\Delta G^o = w_{\text{elec}} \text{(maximum)}$$

$$= - qE = - IT (\text{exp})$$

$(E$ intensive parameter, $q$ extensive)

$$= - nFE \quad \text{(theory)}$$

or rearranging to the **Nernst equation** (14.4)

$$E = E^o - \frac{RT}{nF} \ln Q \quad \text{where} \quad E^o = - \frac{\Delta G^o}{nF}. \quad \text{Then at } 25^oC$$

$$= E^o - 0.05916/n \log Q \quad \text{at } 25^oC = E^o - (0.05916/n) \log Q \quad \text{Eq (14-23)}$$

1. $n$ determined by balancing redox equation
2. $E^o$ determined by $E^o$ of species being oxidized and $E^o$ of species being reduced (**standard reduction potentials**)
3. therefore only $Q$ (**reaction quotient**) can change the voltage

**Oxidation - Reduction Reactions** (Appendix D)

- **Cu oxidized**, oxidation number increases; **Cu** is the reducing agent.
- **Cu(s) + 2 Ag^+ (aq) → Cu^{2+} (aq) + 2 Ag(s)**
- **Ag^+ reduced**, oxidation number decreases; **Ag^+** is the oxidizing agent.

oxidation

reduction
Balancing Redox Equations (half-reaction method, Appendix D)

oxidation numbers, ON (in order of priority)

1. Sum of the oxidation numbers of atoms in a neutral species is zero; in an ion the sum equals the ion charge.
2. Alkali metals (Group I) ON = 1, alkaline earth metals (Group II) ON = 2, Group III usually have ON = 3.
3. Fluorine ON = -1 always. Other halogens usually have ON = -1 except in compounds with oxygen or other halogens when the oxidation number can be positive (follows the trend in electronegativity).
4. Hydrogen has ON = 1 except in metal hydrides when the oxidation number is negative.
5. Oxygen usually has ON = -2 except in compounds with fluorine when the oxidation number can be positive and in compounds containing the O-O bond. For peroxides ON = -1 and for superoxides (e.g., NaO) ON = -1/2.

Steps in Balancing Oxidation-Reduction Equations by Half-Reaction Method (Appendix D)

Basically two ways to balance:
1. start with electrons in half-reactions determined from oxidation numbers
   OR
2. use electrons to balance charge after all elements are balanced
EX 1. Balance in acidic solution

\[ \text{SO}_2(aq) + \text{Cr}_2\text{O}_7^{2-}(aq) \rightarrow \text{Cr}^{3+}(aq) + \text{SO}_4^{2-}(aq) \]

EX 2. Balance in basic solution

\[ \text{Ag}(s) + \text{CN}^{-}(aq) + \text{O}_2(g) \rightarrow \text{Ag(CN)}_2^{-}(aq) \]

Galvanic Cells, 14-2

- half-cells
- electrodes
- anode
- cathode
- electrolyte
- salt bridge
types of electrochemical cells

\[ \Delta G = w_{\text{elec(max)}} = -nFE \]

1. spontaneous: \( \Delta G < 0, \ E > 0 \)
2. nonspontaneous: \( \Delta G > 0, \ E < 0 \)

FIG II - Electrochemical Cells

a) spontaneous: galvanic (voltaic)

\[ \text{OXIDATION half-reaction: } Sn(s) \rightarrow Sn^{2+}(aq) + 2e^- \]
\[ \text{REDUCTION half-reaction: } Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \]
\[ \text{OVERALL: } Cu^2+(aq) + Sn(s) \rightarrow Cu(s) + Sn^{2+}(aq) \]

b) nonspontaneous: electrolytic

\[ \text{OXIDATION half-reaction: } Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \]
\[ \text{REDUCTION half-reaction: } Sn^{2+}(aq) + 2e^- \rightarrow Sn(s) \]
\[ \text{OVERALL: } Sn^{2+}(aq) + Cu(s) \rightarrow Sn(s) + Cu^{2+}(aq) \]

electrochemical cell notation (line notation or cell diagram on p. 314)

Cell Diagram or Line Notation for Galvanic Cells

half-cell notation
different phases separated by vertical lines
species in same phase separated by commas
types of electrodes
- active electrode – involved in electrode half-reaction (most metal electrodes)
  \[ \text{ex: } Zn^{2+}/Zn \text{ metal electrode} \]
  \[ Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \text{ (oxidation)} \]
  notation: \( Zn \| Zn^{2+} \)
- inert electrode – not involved in electrode half-reaction (inert solid conductors which
  serve to contact solution with external electrical circuit)
  \[ \text{ex: } Pt \text{ electrode in } Fe^{3+}/Fe^{2+} \text{ solution} \]
  \[ Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \text{ (reduction)} \]
  notation: \( Fe^{3+}, Fe^{2+} | Pt \)
  - electrodes involving metals and their slightly soluble salts
  \[ \text{ex: } Ag/AgCl \text{ electrode} \]
  \[ AgCl(s) + e^- \rightarrow Ag(s) + Cl^{-}(aq) \text{ (reduction)} \]
  notation: \( Cl^{-}, AgCl | Ag \)

- electrodes involving gases – a gas is bubbled over an inert electrode
  \[ \text{ex: } H_2 \text{ gas over } Pt \text{ electrode} \]
  \[ H_2(g) \rightarrow 2H^+(aq) + 2e^- \text{ (oxidation)} \]
  notation: \( Pt \| H_2, H^+ \)

cell notation
anode half-cell written to left of cathode half-cell (ordered way spontaneous reaction goes)
electrodes appear on the far left (anode) and far right (cathode) in notation
salt bridges represented by double vertical lines

\[ Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \text{ (anode, oxidation)} \]
\[ Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \times 2 \text{ (cathode, reduction)} \]
\[ Zn + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+} \]
notation: \( Zn \| Zn^{2+}, Fe^{3+}, Fe^{2+} | Pt \)
coulombs, current, and quantity of reaction, 14-1 (their relationships)  **OMIT**

EX 3. A galvanic (voltaic) electrochemical cell whose overall reaction is

\[ \text{Cu}(s) + 2 \text{Ag}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + 2 \text{Ag}(s) \]

oxidizes metallic copper at the anode dissolving the metal

\[ \text{Cu}(s) \rightarrow \text{Cu}^{2+}(aq) + 2 e^- \]

and reduces silver ions in solution by plating them out as metallic silver at the cathode.

\[ \text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \]

a) The cell delivers 0.1 A. How long does it take to dissolve 5.00 g of copper at the anode? \( (M_{\text{Cu}} = 63.546) \)

\[ 2 \text{H}^+(aq, 1 \text{ M}) + 2 e^- \rightarrow \text{H}_2(g, P = 1 \text{ atm}) \]

**RED:** \[ 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) \Rightarrow \text{H}^+(aq, 1 \text{ M})|\text{H}_2(g, 1 \text{ atm})|\text{Pt} \]

**OX:** \[ \text{H}_2(g) \rightarrow 2\text{H}^+(aq) + 2e^- \Rightarrow \text{Pt}||\text{H}_2(g, 1 \text{ atm})|\text{H}^+(aq, 1 \text{ M}) \]

b) An external power source is connected to the cell and the cell is run electrolytically. If the cell produces 0.500 A for 101 minutes, how much copper is deposited and how much silver dissolves? \( (M_{\text{Ag}} = 107.87 \text{ g/mol}) \)

**Standard Potentials, 14-3**

**standard states** – stable form (allotrope) at \( P = 1 \text{ atm} \) and specified \( T \) (usually 25°C)

- pure solid
- pure liquid
- gas – ideal gas behavior
- 1 molar (1 M) solution – ideal solution behavior

**standard cell potential, \( E^0 \)** – there is no way to separately measure the potential of an oxidation or reduction half-reaction so conveniently define a zero for the scale

**standard reduction potential, \( E^0 \)** – by international convention, \( E^0 \) for the reduction of \( \text{H}^+(aq) \) to give \( \text{H}_2(g) \) is taken to be zero at all temperatures:

\[ 2 \text{H}^+(aq, 1 \text{ M}) + 2 e^- \rightarrow \text{H}_2(g, P = 1 \text{ atm}) \]

**RED:** \[ 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) \Rightarrow \text{H}^+(aq, 1 \text{ M})|\text{H}_2(g, 1 \text{ atm})|\text{Pt} \]

**OX:** \[ \text{H}_2(g) \rightarrow 2\text{H}^+(aq) + 2e^- \Rightarrow \text{Pt}||\text{H}_2(g, 1 \text{ atm})|\text{H}^+(aq, 1 \text{ M}) \]
EX 4. Will Ag\(^+\) oxidize Zn metal or will Zn\(^{2+}\) oxidize metallic silver?

Note use of activities \(\mathcal{A}\) rather than pressures or molarities.
Nernst Equation, 14-4 (Dependence of the Cell Potential on Concentration)

The Nernst Equation

\[
E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln(Q) \quad \text{(where } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}) = E^+ - E^-
\]

\[
= E^{\circ}_{\text{cell}} - \left(\frac{0.05916}{n}\right) \log_{10} Q \quad \text{at 25°C}
\]

Half-Cells

EX 5. Determine \(E\) for the hydrogen electrode: \(2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\)

a) \([\text{H}^+]=0.00100 \text{ M}, P_{\text{H}_2} = 0.500 \text{ atm}\)

b) \(\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2; [\text{H}^+] = 0.00100 \text{ M}, P_{\text{H}_2} = 0.500 \text{ atm}\)

c) \([\text{H}^+] = 1.00 \times 10^{-14} \text{ M}, P_{\text{H}_2} = 1.00 \text{ atm}\)

d) rewrite hydrogen electrode equation in base, \([\text{OH}^-] = 1.00 \text{ M}, P_{\text{H}_2} = 1.00 \text{ atm}\)
EX 6. If \([\text{Cu}^{2+}] = 0.10\ M\) and \([\text{Ag}^+] = 0.20\ M\), what is the voltage of an electrochemical cell based upon the couple: \(E^\circ(\text{Cu}^{2+}|\text{Cu}) = 0.340\ V\) and \(E^\circ(\text{Ag}^+|\text{Ag}) = 0.800\ V\)?

EX 7. An electrochemical cell is based upon the couple: \(E^\circ(\text{Cu}^{2+}|\text{Cu}) = 0.340\ V\) and \(E^\circ(\text{Ag}^+|\text{Ag}) = 0.800\ V\). If the voltage of the cell were 0.448 V when \([\text{Cu}^{2+}] = 0.10\ M\), what is the silver ion concentration?

EX 8. If the cell voltage is 0.473 V what is the pH of the cathode compartment for the following cell where \(E^\circ(\text{Zn}^{2+}|\text{Zn}) = -0.7618\ V\)?

\[
\text{Zn}(s)|\text{Zn}^{2+}(aq, 1.00\ M)|\text{H}^+(aq, ?\ M)|\text{H}_2(g, 1\ atm)|\text{Pt}(s)
\]

\(E^\circ\) and the Equilibrium Constant, 14-5

<table>
<thead>
<tr>
<th>Reaction Parameters at Standard State</th>
<th>(K)</th>
<th>(E^\circ) cell</th>
<th>Reaction at standard-state conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0</td>
<td>&gt; 1</td>
<td>&gt; 0</td>
<td>spontaneous</td>
</tr>
<tr>
<td>= 0</td>
<td>= 1</td>
<td>= 0</td>
<td>at equilibrium</td>
</tr>
<tr>
<td>&gt; 0</td>
<td>&lt; 1</td>
<td>&lt; 0</td>
<td>nonspontaneous</td>
</tr>
</tbody>
</table>

\[
E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K
\]
EX 9. If \( E^0(\text{Cr}^{3+}|\text{Cr}) = -0.74 \text{ V} \) and \( E^0(\text{Zn}^{2+}|\text{Zn}) = -0.7628 \text{ V} \) what is the equilibrium constant for

\[
2 \text{Cr}^{3+}(aq) + 3 \text{Zn}(s) \rightarrow 2 \text{Cr}(s) + 3 \text{Zn}^{2+}(aq)
\]

Finding K for Reactions That Are Not Redox Reactions

EX 11. Determine the value of \( K_{sp}(\text{AgSCN}) \) given that

\[
\begin{align*}
\text{AgSCN}(s) + e^- &\rightarrow \text{Ag}(s) + \text{SCN}^-(aq) & E^0 &= 0.0898 \text{ V} \\
\text{Ag}^+(aq) + e^- &\rightarrow \text{Ag}(s) & E^0 &= 0.7996 \text{ V}
\end{align*}
\]
Nerve Transmission, 14-6

A nerve cell (neuron) can be likened to a receiver, transmitter, and transmission line between the two. Dendrites receive impulse signals from a neighboring neuron. Transmission of electrical signals within the receiving neuron proceeds from dendrites to synapse along the length of the axon. The signal is due to opening and closing of sodium channels in the axon’s membrane, allowing Na⁺ to enter or not enter the cell. Entering Na⁺ causes an increase in charge inside the cell.

At rest, the inside of a neuron is slightly negative (~ -70 mV) due to a higher concentration of K⁺ ions inside (concentration gradient balanced by a potential difference across the membrane, $E_{\text{inside}} - E_{\text{outside}}$ which can be calculated by modifying the Nernst equation).

\[
E = \text{constant} + \frac{0.05916}{n} \log \frac{x}{10^y}
\]

where $n$ is the charge of the ion. An impulse opens Na⁺ channels. When stimulated past a threshold Na⁺ rushes into the axon, causing a region of positive charge (depolarization) within the axon and a potential of ~30 mV across the membrane. The channels open in one direction along the axon as an opened channel needs a rest period before it can reopen. The region of positive charge causes nearby Na⁺ channels to close. Just after the Na⁺ channels close, K⁺ channels open and K⁺ exits the axon (repolarization). The membrane is brought back to its negative resting potential by Na⁺/K⁺ pumps in the cell membrane. This process continues as a chain-reaction along the axon. The influx of sodium ions depolarises the axon, and the outflow of potassium ions repolarises it.