USNCO Coaching Session
Local Exam Preparation
Tutorial Notes:
Oxidation and Reduction

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18 Feb 2022
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Electrons are transferred

Oxidation
Loss
Reduction
Gain

LEO SAYS GER
Agents

An agent causes something to happen.

Metals tend to be oxidizing agents - give away electrons

An oxidizing agent allows something to be oxidized (lose electrons):

\[ 2 \text{Mg} + \text{O}_2 \rightarrow 2 \text{MgO} \]

reducing agent

Nonmetals tend to be reducing agents - desire for electrons

A reducing agent allows something to be reduced (gain electrons):

\[ 2 \text{Mg} + \text{O}_2 \rightarrow 2 \text{MgO} \]

oxidizing agent
## Oxidation Numbers - Rules

<table>
<thead>
<tr>
<th>Rule</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. The oxidation number of any uncombined element is 0.</td>
<td>The oxidation number of Na(s) is 0.</td>
</tr>
<tr>
<td>2. The oxidation number of a monatomic ion equals the charge on the ion.</td>
<td>The oxidation number of Cl(^-) is –1.</td>
</tr>
<tr>
<td>3. The more-electronegative element in a binary compound is assigned the number equal to the charge it would have if it were an ion.</td>
<td>The oxidation number of O in NO is –2.</td>
</tr>
<tr>
<td>4. The oxidation number of fluorine in a compound is always –1.</td>
<td>The oxidation number of F in LiF is –1.</td>
</tr>
<tr>
<td>5. Oxygen has an oxidation number of –2 unless it is combined with F, in which it is +1 or +2, or it is in a peroxide, in which it is –1.</td>
<td>The oxidation number of O in NO(_2) is –2.</td>
</tr>
<tr>
<td>6. Hydrogen’s oxidation state in most of its compounds is +1 unless it is combined with a metal, in which case it is –1.</td>
<td>The oxidation number of H in LiH is –1.</td>
</tr>
<tr>
<td>7. In compounds, the elements of Groups 1 and 2 as well as aluminum have oxidation numbers of +1, +2, and +3, respectively.</td>
<td>The oxidation number of Ca in CaCO(_3) is +2.</td>
</tr>
<tr>
<td>8. The sum of the oxidation numbers of all atoms in a neutral compound is 0.</td>
<td>The oxidation number of C in CaCO(_3) is +4.</td>
</tr>
<tr>
<td>9. The sum of the oxidation numbers of all atoms in a polyatomic ion equals the charge of the ion.</td>
<td>The oxidation number of P in H(_3)PO(_4) is +5.</td>
</tr>
</tbody>
</table>
Example Problem

37. What is the average oxidation state of tin in the mineral abhurite, Sn_{21}Cl_{16}(OH)_{14}O_6?

(A) +1.71  (B) +2.00  (C) +2.76  (D) +3.43

\[
\begin{align*}
21x - 1(16) - 1(14) - 2(6) &= 0 \\
21x - 16 - 14 - 12 &= 0 \\
21x - 42 &= 0 \\
x &= 2
\end{align*}
\]
**Electrode:** A conductor used to establish contact with a nonmetallic part of a circuit, such as an electrolyte

**Half Cell:** A metal electrode in contact with a solution of its own ions

**Anode:** The electrode where oxidation takes place. **Negative electrode**

**Cathode:** The electrode where reduction takes place. **Positive electrode**

**Salt Bridge:** A salt that will not precipitate with either ion. Balances charge
Cells generate electricity from chemical reactions

1. **Galvanic (Voltaic) cells** are spontaneous
   a. Voltage is positive

2. **Electrolytic cells** require external electricity to operate
   - electrolysis of water
Example Problem

Electrolysis - electrolytic cell

Electrolytic cell - anode is positive, cathode is negative

Electrons flow from **negative** to **positive**

Water molecules attracted to ANODE (+).

Loses electrons, $O_2$ is formed

$H^+$ ions attracted to CATHODE (-).

Gains electrons.

Twice as much $H_2$ (left) than $O_2$ (right)

40. Electrolysis of water containing sulfuric acid as an electrolyte is carried out as shown and the gases produced at the electrodes collected in two identical tubes, both initially filled with the sulfuric acid solution. After electrolysis has been carried out for a certain time, which picture best represents the appearance of the tubes?
Galvanic Cell - Example

Zn loses electrons
Cu gains electrons
Shorthand notation:
\[ \text{Zn}|\text{Zn}^{2+}|\text{Cu}^{2+}||\text{Cu} \]
Half Reactions

**Anode:**

Oxidation: \( \text{Zn}_\text{s} \rightarrow \text{Zn}^{2+}_\text{aq} + 2e \)

**Cathode**

Reduction: \( \text{Cu}^{2+}_\text{aq} + 2e \rightarrow \text{Cu}_\text{s} \)
Balancing Redox Reactions

- Separate half reactions: oxidation and reduction
- Balance atoms - add in hydrogen or water as needed
- Balance charges - electrons
- Add the 2 halves together again
Example Problem

37. When the chemical equation is balanced, what is the ratio of the coefficient of Ag(s) to the coefficient of H₂O(l)?

\[ \underline{\text{__ Ag(s)}} + \underline{\text{__ NO}_3^-(aq)} + \underline{\text{__ H}^+(aq)} \rightarrow \]
\[ \underline{\text{__ Ag}^+(aq)} + \underline{\text{__ NO(g)}} + \underline{\text{__ H}_2\text{O(l)}} \]

(A) 1 : 1  (B) 2 : 1  (C) 3 : 1  (D) 3 : 2

\[ 3\text{Ag(s)} + 4\text{NO}_3^-(aq) + 4\text{H}^+(aq) \rightarrow 3\text{Ag}^+(aq) + 4\text{NO(g)} + 2\text{H}_2\text{O(l)} \]

- Balance oxygen
- Balance hydrogen
- Balance charge (+3 both sides)

Ratio of Ag : H₂O \( 3 : 2 \)
Standard Reduction Potential

Likelihood of something being reduced
Based on hydrogen - which is zero
Higher number = higher possibility of reduction
Activity series - more active metals replace less active ones
<table>
<thead>
<tr>
<th>Reduction Half-Reaction</th>
<th>Standard Reduction Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_2(\text{g}) + 2e^- \rightarrow 2\text{F}^-(\text{aq})$</td>
<td>+2.87</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2e^- \rightarrow 2\text{SO}_4^{2-}(\text{aq})$</td>
<td>+2.01</td>
</tr>
<tr>
<td>$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightarrow 2\text{H}_2\text{O}(l)$</td>
<td>+1.23</td>
</tr>
<tr>
<td>$\text{Br}_2(l) + 2e^- \rightarrow 2\text{Br}^-(\text{aq})$</td>
<td>+1.09</td>
</tr>
<tr>
<td>$\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag(s)}$</td>
<td>+0.80</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(\text{aq}) + e^- \rightarrow \text{Fe}^{2+}(\text{aq})$</td>
<td>+0.77</td>
</tr>
<tr>
<td>$\text{I}_2(l) + 2e^- \rightarrow 2\text{I}^-(\text{aq})$</td>
<td>+0.54</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)}$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$\text{Sn}^{4+}(\text{aq}) + 2e^- \rightarrow \text{Sn}^{2+}(\text{aq})$</td>
<td>+0.15</td>
</tr>
<tr>
<td>$\text{S(s)} + 2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2\text{S}(\text{g})$</td>
<td>+0.14</td>
</tr>
<tr>
<td>$2\text{H}^+(\text{aq}) + 2e^- \rightarrow \text{H}_2(\text{g})$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{Sn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Sn(g)}$</td>
<td>-0.14</td>
</tr>
<tr>
<td>$\text{V}^{3+}(\text{aq}) + e^- \rightarrow \text{V}^{2+}(\text{aq})$</td>
<td>-0.26</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Fe(s)}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$\text{Cr}^{3+}(\text{aq}) + 3e^- \rightarrow \text{Cr(s)}$</td>
<td>-0.74</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Zn(s)}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Mn(s)}$</td>
<td>-1.18</td>
</tr>
<tr>
<td>$\text{Na}^+(\text{aq}) + e^- \rightarrow \text{Na(s)}$</td>
<td>-2.71</td>
</tr>
<tr>
<td>$\text{Li}^+(\text{aq}) + e^- \rightarrow \text{Li(s)}$</td>
<td>-3.04</td>
</tr>
</tbody>
</table>
Calculating Standard Cell Potentials

Use half-cell reactions

Half-cell with higher SRP will be reduced

Half-cell with lower SRP will be oxidized

Positive = spontaneous
Example Problem

\[ \text{E}^0_{\text{cell}} = \text{E}^0_{\text{red}} - \text{E}^0_{\text{ox}} \]

Silver is reduced (gains electrons)
Nickel is oxidized (loses electrons)

\[ \text{E}^0_{\text{cell}} = +0.80 - (-0.23) = 1.03 \text{ V} \]

Half reactions would have to have equal amounts of electrons lost and gained. NOT voltages!!

40. What is the standard cell potential of the following electrochemical cell?

\[ \text{Ni(s)} \mid \text{Ni}^{2+}(aq), \; 1.0 \; \text{M} \; || \; \text{Ag}^+(aq), \; 1.0 \; \text{M} \; || \; \text{Ag(s)} \]

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^0 ), V</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni(s)} )</td>
<td>-0.23</td>
</tr>
<tr>
<td>( \text{Ag}^+(aq) + e^- \rightarrow \text{Ag(s)} )</td>
<td>+0.80</td>
</tr>
</tbody>
</table>

(A) -1.83 V  (B) 0.57 V  (C) 1.03 V  (D) 1.83 V
Inert Electrodes

Some materials are poor conductors

No solid conducting metal

A different material is used for the electrode - inert electrode

Platinum, gold are common choices.
Example Problem

38. If used in an electrochemical cell, which of the following half-reactions would require an inert electrode?

I. \(2 \text{Cl}^- (aq) \rightleftharpoons \text{Cl}_2(g) + 2 \text{e}^-\)
II. \(\text{Fe(CN)}_6^{3-} (aq) + \text{e}^- \rightleftharpoons \text{Fe(CN)}_6^{4-} (aq)\)

(A) I only  (B) II only
(C) Both I and II (D) Neither I nor II

Answer: C

Iron is in aqueous phase on both sides of the equation.

Chlorine is not solid on either side of the equation.
Relationship between $\Delta G$ and $E^0$

$\Delta G$ = amount of energy available to do work

In galvanic cells, $\Delta G$ is negative. $E^0_{\text{cell}} > 0$

Formula: $\Delta G = -nFE^0$

$n$ = moles of electrons

$F$ = Faraday constant (amount of charge carried by 1 mole of electrons)

$E^0$ = Cell potential
Example Problem

40. What is the standard reduction potential of Cr\(^{3+}(aq)\) to form metallic chromium?

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>(E^\circ, \text{ V})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}^{3+}(aq) + e^- \rightarrow \text{Cr}^{2+}(aq))</td>
<td>(-0.41)</td>
</tr>
<tr>
<td>(\text{Cr}^{2+}(aq) + 2e^- \rightarrow \text{Cr}(s))</td>
<td>(-0.91)</td>
</tr>
<tr>
<td>(\text{Cr}^{3+}(aq) + 3e^- \rightarrow \text{Cr}(s))</td>
<td>???</td>
</tr>
</tbody>
</table>

(A) \(-0.74 \text{ V}\) 
(B) \(-1.32 \text{ V}\) 
(C) \(-1.73 \text{ V}\) 
(D) \(-2.23 \text{ V}\)
Solution to Problem 40

• Calculate $\Delta G$ for both half-reactions
• Add together
• Convert back to $E^o$
• Total # of $e^-$ = amount of energy to do work.

$\text{Cr}^{3+} (aq) + e^- \rightarrow \text{Cr}^{2+} (aq)$

$\Delta G = -nFE^o$
$\quad = -1 \times 96500 \times -0.41$
$\quad = 39565 \text{ J}$

$\text{Cr}^{2+} (aq) + 2e^- \rightarrow \text{Cr} (s)$

$\Delta G = -nFE^o$
$\quad = 2 \times 96500 \times -0.91$
$\quad = 175630 \text{ J}$

For $\text{Cr}^{3+} (aq) + 3e^- \rightarrow \text{Cr} (s)$

$\Delta G = -nFE^o$
$\quad = 3 \times 96500 \times E^o$
$\quad = 215195$

$E^o = -0.743 \text{ V}$

\[ A \]
Example Problem

Flip the half reactions to get highest
(most positive) cell potential!

Units!

41. What is the change in standard free energy at 298 K for the conversion of ozone to molecular oxygen as shown in the equation below?

\[ 2 \text{O}_3(g) \rightarrow 3 \text{O}_2(g) \]

\[ \Delta G^\circ = ??? \]

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^\circ, \text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_3(g) + 2 \text{H}^+(aq) + 2e^- \rightarrow \text{O}_2(g) + \text{H}_2\text{O}(l) )</td>
<td>+2.08</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 4 \text{H}^+(aq) + 4e^- \rightarrow 2 \text{H}_2\text{O}(l) )</td>
<td>+1.23</td>
</tr>
</tbody>
</table>

\[ \Delta G = -nFE^\circ \]
\[ = -4 \times 96500 \times (2.08 - 1.23) \]
\[ = -328,100 \text{J mol}^{-1} \]
\[ \frac{1000}{1000} \]
\[ \Delta G = -328 \text{kJ mol}^{-1} \]

- (A) \(-164 \text{kJ mol}^{-1}\)
- (B) \(-328 \text{kJ mol}^{-1}\)
- (C) \(-401 \text{kJ mol}^{-1}\)
- (D) \(-492 \text{kJ mol}^{-1}\)
Amps, Time and Mass

Electrolysis problems = Stoichiometry + Current

amps & time $\leftrightarrow$ Coulombs $\leftrightarrow$ Faradays $\leftrightarrow$ moles of electrons

1 Faraday = 96,500 C = 1 mole of electrons

Current (amperes or Amps or A) x time = Coulombs (electrical charge)
Example Problem

39. Chromium is electroplated industrially by the electrolysis of solutions of K₂Cr₂O₇. How much time would be required to deposit 1.00 kg of Cr using a current of 200.0 A?

(A) 2.58 h  (B) 7.74 h  (C) 15.5 h  (D) 31.0 h

\[ \text{Mass} \rightarrow \text{moles} \quad 1000 \text{g} \times \frac{\text{1 mole Cr}}{52.00 \text{g}} = 19.23 \text{moles} \]

- Oxidation state of Cr?

\[ \text{K}_2\text{Cr}_2\text{O}_7 = 0 \\
2(\text{+3}) + 2x + 7(\text{-2}) = 0 \]
\[ 2 + 2x - 14 = 0 \]
\[ 2x = 14 - 2 \]
\[ 2x = 12 \]
\[ x = 6 \]

- Half reaction: \( \text{Cr}^{6+}(\text{aq}) + 6e^- \rightarrow \text{Cr}(\text{s}) \)

- Moles of \( e^- \): \( 19.23 \text{ moles Cr} \times \frac{6 \text{ moles } e^-}{1 \text{ mole of Cr}} = 115.38 \text{ moles of } e^- \)

- Convert moles of \( e^- \) to \( C \)

\[ \frac{115.38}{96500} \times \frac{96500 \text{ C}}{\text{mole of } e^-} = 11 \times 10^7 \text{ C} \]
Example Problem

39. Chromium is electroplated industrially by the electrolysis of solutions of $\text{K}_2\text{Cr}_2\text{O}_7$. How much time would be required to deposit 1.00 kg of Cr using a current of 200.0 A?

(A) 2.58 h  (B) 7.74 h  (C) 15.5 h  (D) 31.0 h

\[\text{Calculate time: } \text{Charge} = \text{current} \times \text{time} \ (s)\]

\[1.1 \times 10^7 = \frac{200.0 \text{C}}{200.0 \text{A}} \times t\]

\[\frac{200.0}{200.0} \times 55,671 \text{ s} / 3600 \text{ s} = t\]

\[t = 15.5 \text{ hours.}\]
Nernst Equation

Determine $E^0$ under nonstandard conditions

$E = \text{nonstandard } E_{\text{cell}}$

$E^0 = \text{cell potential standard conditions 298 Kelvin, 1M concentrations}$

$R = \text{Universal gas constant (8.314)}$

$T = \text{Temperature}$

$n = \text{number of moles}$

$F = \text{Faraday constant}$

$Q = \text{Reaction quotient - not at equilibrium}$

\[ E = E^0 - \frac{RT}{nF} \ln Q \]
Reaction Quotient

For the reaction:

\[ aA + bB \rightleftharpoons cC + dD \]

\[ Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

Must be for aqueous ONLY! Use coefficients as exponents.
### Using Nernst 1

<table>
<thead>
<tr>
<th>If…</th>
<th>Then…</th>
</tr>
</thead>
<tbody>
<tr>
<td>[REACTANTS] increases</td>
<td>equilibrium moves more to the right</td>
</tr>
<tr>
<td>[PRODUCTS] decreases</td>
<td>- more spontaneous E increases</td>
</tr>
<tr>
<td>[REACTANTS] decreases</td>
<td>equilibrium moves more to the left</td>
</tr>
<tr>
<td>[PRODUCTS] increases</td>
<td>- less spontaneous E = decreases</td>
</tr>
</tbody>
</table>
Using Nernst 2

Use “If…Then…” for help

Calculate Q

If reaction is at 298 K, use:

$$E = E^o - \frac{0.0592 \, V}{n} \log_{10} Q$$

Balance half reactions to get moles of electrons
Determining Equilibrium Constant with the Nernst

When reactants and products reach equilibrium, $\Delta G = 0$.

Also, reaction quotient and equilibrium constant ($K_c$) are equal.

Since $\Delta G = -nFE^0$, cell potential $= 0$.

Substitute values of $E$ and $Q$ into Nernst

$0 = E^0 - (RT/nF) \ln K_c$

$E^0 = 0.0591/n \log K_c$

$log K_c = nE^0/0.0591$