Redox Reactions and Electrochemistry

Problem Set
Chapter 5: 21-26, Chapter 21: 15-17, 32, 34, 43, 53, 72, 74

Oxidation/Reduction & Electrochemistry

Oxidation – a reaction in which a substance gains oxygen atoms
(e.g. the oxidation of a hydrocarbon)

Reduction - a reaction in which a substance loses oxygen atoms

(i.e. this is equivalent to the combustion of a hydrocarbon)

Oxidation/Reduction & Electrochemistry

• A different type of “redox” (i.e. reduction plus oxidation) reaction does not involve gain or loss of oxygen.
  • Tarnishing of silver is a redox reaction that produces Ag₂S.
    • This spontaneous reaction can be reversed with a coupled reaction (add 80 g of baking soda and 80 g of table salt per litre of near boiling water in an aluminum pan to a depth covering the silver object).

  \[ 3 \text{Ag}_2\text{S} + 2 \text{Al} + 6 \text{H}_2\text{O} \rightarrow 6 \text{Ag} + 2 \text{Al(OH)}_3 + 3 \text{H}_2\text{S} \]
Let’s look at a simple case of this type of redox reaction:

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

The reaction can be represented by two half-reactions in which electrons are either gained or lost and the "oxidation state" of elements changes:

\[
\begin{align*}
\text{Cu}^{2+}(aq) & \rightarrow \text{Cu}(s) & \text{oxidation state of Cu} & +2 \rightarrow 0 \\
\text{Zn}(s) & \rightarrow \text{Zn}^{2+}(aq) + 2e^- & \text{oxidation state of Zn} & 0 \rightarrow +2
\end{align*}
\]

**Reduction** — a process in which electrons are gained. (The oxidation state of an element decreases and electrons appear on the left side of the half-reaction.)

**Oxidation** — a process in which electrons are lost. (The oxidation state of an element increases and electrons appear on the right side of the half-reaction.)

**Oxidation States - Review**

1. Oxidation state of an atom in a free element is 0.
2. Total of the oxidation states of atoms in a molecule or ion is equal to the total charge on the molecule or ion.
3. Group 1A and Group 2A metals have oxidation state of +1 and +2 respectively.
4. F always has an oxidation state of –1. Cl also has oxidation state of –1 unless it is bonded to oxygen or fluorine.
5. H almost always has an oxidation state of +1.
6. O has oxidation state of –2 (unless bonded to itself or F).
7. When bound to metals, group 7A, 6A and 5A elements have oxidation states of -1, -2, -3 respectively.
Example
What is the formal oxidation state of P in:

\[ \text{H}_3\text{PO}_4 \]

\[ 3 \times (+1) + ? + 4 \times (-2) = 0 \text{ (charge on molecule)} \]
oxidation state of P = +5

\[ \text{H}_2\text{PO}_4^- \]

\[ 2 \times (+1) + (\text{O.S. of P}) + 4 \times (-2) = -1 \text{ (charge on ion)} \]
oxidation state of P = +5

\[ \text{HPO}_4^{2-} \]

oxidation state of P = +5

If the oxidation state of elements do not change in a reaction, it is NOT a redox reaction!

\[ \text{H}_3\text{PO}_4(\text{aq}) + 3 \text{ OH}^-(\text{aq}) \rightarrow 3\text{H}_2\text{O} + \text{PO}_4^{3-}(\text{aq}) \text{ acid/base reaction} \]

Balancing Redox Reactions
Half-reaction method (not the same as method in textbook).

1) Identify species in which the oxidation state of an element is changing. Write the skeleton half-reactions including balancing of the redox atoms if necessary.

2) Identify oxidation state on both sides of equation for elements that have a change in oxidation state.

3) Add appropriate number of electrons to either left or right to balance oxidation states of redox atom(s).

4) Balance changes on left and right side of equation by adding H\(^+\) (if in acidic solution) or OH\(^-\) (if in basic solution).

5) Add appropriate number of H\(_2\)O’s to left or right side of equation to balance atoms in the half-reaction.
Balancing Redox Reactions, cont’d

At this point, both half-reactions should be balanced. The next step is to combine the two half-reactions to form an overall equation.

6) Multiply through each half-reactions by appropriate coefficients to match electrons in each half-reaction. (i.e. number of electrons lost by the oxidized species must equal the number gained by the reduced one)

7) Add half-reactions and cancel electrons and other common species on left and right sides of the equation.

8) Check Reaction! It should be balanced in terms of oxidation states, charge and atoms.

IF NOT, YOU HAVE MADE A MISTAKE!

Examples

Determining sulfite in wastewater.

Sulfite is reacted with permanganate to produce sulfate and Mn(II) ion in acidic solution. Balance the redox reaction.

\[ \text{SO}_3^{2-} + \text{MnO}_4^- \rightarrow \text{SO}_4^{2-} + \text{Mn}^{2+} \]

skeleton reaction

1. Identify oxidation states:
   - \( \text{SO}_3^{2-} \): +4
   - \( \text{SO}_4^{2-} \): +6

2. Balance O.S. with electrons:
   - \( \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2e^- \)

3. Balance charges with \( \text{H}^+ \):
   - \( \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2e^- + 2\text{H}^+ \)

4. Balance atoms with \( \text{H}_2\text{O} \):
   - \( \text{H}_2\text{O} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2e^- + 2\text{H}^+ + \text{H}_2\text{O} \)

Cont’d, Mn half-reaction

1. Identify oxidation states:
   - \( \text{MnO}_4^- \): +7
   - \( \text{Mn}^{2+} \): 0

2. Balance O.S. with electrons:
   - \( \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 5e^- \)

3. Balance charges with \( \text{H}^+ \):
   - \( 8 \text{H}^+ + \text{MnO}_4^- + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \)

Balanced Half-Reactions

\[ \text{H}_2\text{O} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2e^- + 2\text{H}^+ \times 5 \]

\[ 8 \text{H}^+ + \text{MnO}_4^- + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \times 2 \]

to balance e’s
Balancing full equation

Balanced full reaction:

\[
\begin{align*}
5H_2O + 5SO_3^{2-} & \rightarrow 5SO_4^{2-} + 10e^- + 10H^+ \\
16 H^+ + 2MnO_4^- + 10e^- & \rightarrow 2Mn^{2+} + 8H_2O \\
5SO_3^{2-} + 2MnO_4^- + 6 H^+ & \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O
\end{align*}
\]

Check atom balance. OK

Try example 5.7 using this approach, use OH\(^-\) to balance charge in basic solution. Much easier.
This method forces you to know oxidation states.

Another Example

Write the half reaction for \(Cr_2O_7^{2-} \rightarrow Cr^{3+}\)

\[
\begin{align*}
Cr_2O_7^{2-}_{(aq)} & \rightarrow Cr^{3+}_{(aq)} \quad \text{skeleton (in acidic solution)} \\
Cr_2O_7^{2-}_{(aq)} & \rightarrow 2 Cr^{3+}_{(aq)} \quad \text{balance redox atoms} \\
Cr_2O_7^{2-}_{(aq)} & \rightarrow 2 Cr^{3+}_{(aq)} \quad \text{determine O.S. of redox atoms} \\
Cr_2O_7^{2-}_{(aq)} + 2(3e^-) & \rightarrow 2 Cr^{3+}_{(aq)} \quad \text{balance O.S. with e^-s} \\
Cr_2O_7^{2-}_{(aq)} + 6e^- & \rightarrow 2 Cr^{3+}_{(aq)} \quad \text{determine O.S. of redox atoms} \\
14 H^+ + Cr_2O_7^{2-}_{(aq)} + 6e^- & \rightarrow 2 Cr^{3+}_{(aq)} + 7H_2O \quad \text{balance charges with H^+} \\
14 H^+ + Cr_2O_7^{2-}_{(aq)} + 6e^- & \rightarrow 2 Cr^{3+}_{(aq)} + 7H_2O \quad \text{balance atoms with H_2O}
\end{align*}
\]

Extra Practise Balancing Redox Reactions (solutions on web site)

#1) \(Cl_2 \rightarrow ClO^- + Cl^-\) in basic solution

#2) \(I^- + IO_3^- \rightarrow I_3\) in acidic solution

#3) \(H_2O_2(aq) \rightarrow O_2(g)\)
(in either acidic or basic solution)
Disproportionation Reactions

A disproportionation reaction occurs when an element in a substance is both oxidized and reduced.

Example:

\[ 2 \text{H}_2\text{O}_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\ell) + \text{O}_2(\text{aq}) \]

Hydrogen peroxide: antiseptic agent, \( \text{O}_2 \) acts as germicide

Ox/Red Agents, cont’d

**Oxidizing Agent** – a chemical substance that oxidizes (removes electrons from) other substances in a chemical reaction. In the process of oxidizing something, the oxidant becomes reduced; its oxidation state decreases.

**Reducing Agent** – a chemical substance that reduces (loses electrons to) other substances. In the process of reducing, the reductant becomes oxidized; its oxidation state increases.

Oxidizing and Reducing Agents
**Oxidizing Agents**

O₂ – Probably the most common and most important oxidant known to us. Ubiquitous.

**Organic Oxidation Schemes (Example: methane)**

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{H}_2\text{C}-\text{OH} & \text{formaldehyde} \\
\text{methanol} (\text{alcohol}) & & (\text{aldehyde}) \\
\text{H}_2\text{C}=\text{O} & \rightarrow \text{CH}_3\text{OH} & \text{formic acid} \\
& & (\text{carboxylic acid}) \\
\text{OC} & \rightarrow \text{O} & \text{carbon dioxide} \\
& & (\text{inorganic carbon})
\end{align*}
\]

**Other oxidizing agents**

Oxides in their highest oxidation state are frequently strong oxidizing agents.

\[
\begin{align*}
\text{NO}_3^- & \rightarrow \text{HNO}_3 & \text{NO}_2 & \rightarrow \text{NO} \\
\text{NO}_2 & \rightarrow \text{NO}_2 & \text{N}_2 & \rightarrow \\
\text{HClO}_4 & \rightarrow \text{HClO}_2 & \text{HClO} & \\
\text{HNO}_3 \text{ and } \text{HClO}_4 \text{ are oxidizing acids.}
\end{align*}
\]

Non-oxidizing acids – HCl, HBr, HI, acids for which the only possible reduction half-reaction is:

\[
2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})
\]

**Oxidizing Agents, cont’d**

HNO₃ is a much stronger oxidizing agent than H⁺.

<table>
<thead>
<tr>
<th>Metals that dissolve in dilute H⁺ to produce H₂</th>
<th>Metals that will not dissolve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li, Na, K (1A metals)</td>
<td>Cu, Ag, Au, Hg</td>
</tr>
<tr>
<td>Mg, Ca (2A metals)</td>
<td></td>
</tr>
<tr>
<td>Al, Zn</td>
<td></td>
</tr>
<tr>
<td>Fe, Sn, Pb</td>
<td></td>
</tr>
</tbody>
</table>

**Practice problem** – Cu will dissolve in HNO₃ producing Cu²⁺ in solution and the brown gas NO₂. Write a balanced equation for this process.
Electrochemistry

(a) Cu(s) / Ag⁺(aq)
Cu²⁺(aq)/ Ag(s)
Spontaneous! (∆G < 0)
Ag⁺(aq) + e⁻ → Ag(s)  reduction
Cu(s) → Cu²⁺(aq) + 2 e⁻  oxidation

(b) Cu(s) / Zn²⁺(aq)
No reaction!
Not spontaneous! (∆G > 0)

We can connect half-reactions in separate containers through an electrical circuit. This will produce a current (electron flow) and voltage according to the spontaneity of the reactions.

Electrochemical Cells
Flow of electrons (current) can do work.

We can connect half-reactions in separate containers through an electrical circuit. This will produce a current (electron flow) and voltage according to the spontaneity of the reactions.

Atomic view of a Voltaic (galvanic) cell

Anode – oxidation  Cathode - reduction

Salt bridge (e.g. KNO₃) maintains neutrality
Cell Diagrams

- anode (oxidation) is placed at left side of diagram
- cathode (reduction) is placed on right side of diagram
- boundary line, |, indicates a boundary between different phase (i.e. solution|solid)
- a double boundary line || indicates a boundary (i.e. salt bridge) between the two half-cell compartments

\[
\text{Zn(s)} \mid \text{Zn}^{2+}(aq) \ || \ \text{Cu}^{2+}(aq) \mid \text{Cu(s)}
\]

anode (oxidation)  cathode (reduction)

Voltages and Current

Electromotive Force (EMF) - The voltage difference between two solutions provides a measure of the driving force of the electron transfer reaction.

Standard Electrode Potentials

In electronics and electricity theory, a voltage is a measurement of the potential to do electrical work measured between two points in a circuit. Absolute measurements of potential (voltage) at a single point are meaningless, UNLESS, they are measured against some known reference.

In electricity, that reference is known as “ground”.

In electrochemistry, that reference is the standard hydrogen electrode (SHE).

A Standard Electrode potential, $E^\circ$, measures the tendency for the reduction process to occur at an electrode, when all species have unit activity (substances in solution are ~ 1.0 M or, if gases, are at 1 bar (~1 atm) pressure).
Standard Hydrogen Electrode (SHE)

\[ a_{H_2} = 1.0 \sim P_{H_2} = 1.0 \text{ bar} \sim 1.0 \text{ atm} \]

\[ a_{H_3O^+} = a_{H^+} = 1.0 \sim [H^+] = 1M \]

\[ \text{H}^+_\text{(aq)} (1M) \mid \text{H}_2\text{(g)} (1 \text{ atm}) \mid \text{Pt} \]

\[ 2\text{H}^+_\text{(aq)} + 2e^- \rightarrow \text{H}_2\text{(g)} \quad E^o = 0.00 \text{ V} \]

frequently written as: \( E^o_{\text{H}^+_\text{(aq)}/\text{H}_2\text{(g)}} \)

Easy to reduce, hard to oxidize (good oxidizing agents)

Hard to reduce, easy to oxidize (good reducing agents)

Table 1.17 - Some Selected Standard Oxidation Potentials

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>( E^o )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}^{2+} + 2e^- \rightarrow \text{Mg} )</td>
<td>-2.37</td>
</tr>
<tr>
<td>( \text{Ag}^+ + e^- \rightarrow \text{Ag} )</td>
<td>0.80</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} )</td>
<td>0.77</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} )</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{H}^+ + e^- \rightarrow \text{H}_2\text{(g)} )</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Standard Electrode (reduction) Potentials

The potential of an electrochemical cell under standard conditions may be calculated by

\[ E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}} \]

where the \( E^o \)'s are standard reduction potentials taken from a table.

The cathode is the electrode at which reduction occurs (electrons on left side of equation, oxidation state decreasing).

The anode is the electrode at which oxidation occurs (electrons on right side of equation, oxidation state increasing).

Also for a spontaneous reaction, \( E^o_{\text{cell}} > 0 \), as we will see shortly.
Example 21-2
A new battery system currently under study for possible use in electric vehicles is the ZnCl₂ battery.

Reaction: \( \text{Zn}(s) + \text{Cl}_2(g) \rightarrow \text{ZnCl}_2(aq) \)

What is the standard potential of the cell, \( E^\circ \)?

- \( \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s) \) \( E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763 \text{V} \)
- \( \text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq) \) \( E^\circ_{\text{Cl}_2/\text{Cl}^-} = +1.358 \text{V} \)

\( E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = +1.358 - (-0.763) \text{V} = 2.121 \text{V} \)

OR

\( E^\circ_{\text{cell}} = \sum E^\circ_{\text{reaction}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} + E^\circ_{\text{Cl}_2/\text{Cl}^-} = -0.763 + 1.358 = +0.595 \text{V} \)

Spontaneous change in a Cell
Previously, it was said \( E^\circ_{\text{cell}} > 0 \) for a spontaneous reaction. Where did this come from?

Electrical work:
\[ \text{W}_{\text{electrical}} = Q \times V \]
- \( Q = \text{charge}, V = \text{voltage} \)
- If \( Q \) in coulombs, \( V \) in volts, \( W \) in joules

Related: 
- \( P = IV \) \( P = \text{power}, I = \text{current (charge/time), V = voltage} \)
- If \( i \) - coulombs/sec (Amp), \( V \) - volts, \( P \) - joules/sec = watts

In an electrochemical cell,
\[ Q = n \times F \]
- \( n = \text{moles of electrons} \)
- \( F = \text{charge/mole of electrons} = \text{Faraday} \)
- \( F = 96485 \text{C/mole of electrons} \)

\[ V = E^\circ_{\text{cell}} \]

Spontaneous change, cont’d
\[ \text{W}_{\text{electrical}} = Q \times V = nFE^\circ_{\text{cell}} \]
- This applies to a reversible process (implying that the reaction is carried out slowly enough that the system maintains equilibrium). Previously it was argued that the amount of work we can extract from a chemical process is equal \( -\Delta G \) (pg 796, Petrucci “Are You Wondering” box).

\[ \Delta G = -W_{\text{electrical}} \]

\[ \Delta G = -nFE^\circ_{\text{cell}} \]

If \( E^\circ_{\text{cell}} > 0 \), \( \Delta G^\circ < 0 \) and the reaction is spontaneous
If \( E^\circ_{\text{cell}} < 0 \), \( \Delta G^\circ > 0 \) and reaction is nonspontaneous
Behavior of Metals

Previously we said that experimental evidence shows the following:

<table>
<thead>
<tr>
<th>Metals that dissolve in H+ to produce H2</th>
<th>Metals that will not dissolve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li, Na, K (1A metals)</td>
<td>Cu, Ag, Au, Hg</td>
</tr>
<tr>
<td>Mg, Ca (2A metals)</td>
<td>Fe, Sn, Pb</td>
</tr>
</tbody>
</table>

Now we can better understand this:

\[ M(s) \rightarrow M^{n+}(aq) + n\, e^- \text{ oxidation} \]
\[ 2\, H^+(aq) + 2\, e^- \rightarrow H_2(g) \text{ reduction} \]
\[ E^0 = 0.00\, V \]

\[ E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0 - E^\circ_{\text{M}^{n+}/M} \]

If \( E^\circ_{\text{M}^{n+}/M} < 0 \), \( E^\circ_{\text{cell}} > 0 \), the process is spontaneous.

If \( E^\circ_{\text{M}^{n+}/M} > 0 \), a stronger oxidizing agent than H+ is required (i.e. HNO3, HClO4).

Nernst Equation

Previously, we talked about standard electrode potentials in which everything was in its standard state.

Very rarely are things in standard state!

\[ \Delta G = \Delta G^0 + RT\ln Q \]
\[ R = \text{gas constant} \]
\[ T = \text{temperature (K)} \]
\[ Q = \text{reaction quotient} \]

\[ -nFE_{\text{cell}} = -nFE^0_{\text{cell}} + RT\ln Q \]

\[ E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln Q = E^0_{\text{cell}} - \frac{RT}{(2.303\, nF)} \log Q \]

\[ E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0592}{n} \log Q, \text{ for } T = 25^\circ C \text{ Nernst Equation} \]

Applications of the Nernst Equation

1) Draw the condensed cell diagram for the voltaic cell pictured at right.

2) Calculate the value of \( E_{\text{cell}} \).

1) Pt(Fe^{3+}(0.1M), Fe^{2+}(0.2M) || Ag^+(1.0M)|Ag(s)

2) The cell is in nonstandard conditions so we need to apply the Nernst equation - we will need to find \( E^0_{\text{cell}} \), \( n \), and \( Q \).
From table of Standard Reduction Potentials:

- \( \text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.771 \, \text{V} \)
- \( \text{Ag}^+ + e^- \rightarrow \text{Ag} \quad E^{\circ}_{\text{Ag}^+/\text{Ag}} = 0.800 \, \text{V} \)

**Overall reaction:**

Cathode: \( \text{Ag}^+ + e^- \rightarrow \text{Ag(s)} \)

Anode: \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad \text{Ag}^+ + \text{Fe}^{2+}_{(aq)} \rightarrow \text{Fe}^{3+}_{(aq)} + \text{Ag(s)} \)

What is \( Q \)?

\[ Q = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]} \]

\[ E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} \]

\[ = 0.800 \, \text{V} - 0.771 \, \text{V} = 0.029 \, \text{V} \]

**Example A:** Calculate \( E^{\circ}_{\text{cell}} \) for the following cell

\( \text{Al(0.36M)} || \text{Sn}^{4+} (0.086 \, \text{M}), \text{Sn}^{2+} (0.54 \, \text{M}) | \text{Pt} \)

Al\(^{3+} \rightarrow 3e^- \rightarrow \text{Al} \quad E^{\circ}_{\text{Al}^{3+}/\text{Al}} = -1.676 \, \text{V} \)

Sn\(^{4+} \rightarrow 2e^- \rightarrow \text{Sn}^{2+} \quad E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.154 \, \text{V} \)

Cathode: \( \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \times 3 \)

Anode: \( \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \times 2 \)

What is \( E^{\circ}_{\text{cell}} \)?

\[ E^{\circ}_{\text{cell}} = \frac{E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}}{n} = E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} - E^{\circ}_{\text{Al}^{3+}/\text{Al}} \]

\[ = 0.154 - (-1.676) \, \text{V} = 1.830 \, \text{V} \]

**Example A:** Calculate \( E^{\circ}_{\text{cell}} \) for the following cell

\( \text{Al(0.36M)} || \text{Sn}^{4+} (0.086 \, \text{M}), \text{Sn}^{2+} (0.54 \, \text{M}) | \text{Pt} \)

Al\(^{3+} \rightarrow 3e^- \rightarrow \text{Al} \quad E^{\circ}_{\text{Al}^{3+}/\text{Al}} = -1.676 \, \text{V} \)

Sn\(^{4+} \rightarrow 2e^- \rightarrow \text{Sn}^{2+} \quad E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.154 \, \text{V} \)

Cathode: \( \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \times 3 \)

Anode: \( \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \times 2 \)

What is \( E^{\circ}_{\text{cell}} \)?

\[ E^{\circ}_{\text{cell}} = \frac{E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}}{n} = E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} - E^{\circ}_{\text{Al}^{3+}/\text{Al}} \]

\[ = 0.154 - (-1.676) \, \text{V} = 1.830 \, \text{V} \]

**Example A:** Calculate \( E^{\circ}_{\text{cell}} \) for the following cell

\( \text{Al(0.36M)} || \text{Sn}^{4+} (0.086 \, \text{M}), \text{Sn}^{2+} (0.54 \, \text{M}) | \text{Pt} \)

Al\(^{3+} \rightarrow 3e^- \rightarrow \text{Al} \quad E^{\circ}_{\text{Al}^{3+}/\text{Al}} = -1.676 \, \text{V} \)

Sn\(^{4+} \rightarrow 2e^- \rightarrow \text{Sn}^{2+} \quad E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.154 \, \text{V} \)

Cathode: \( \text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \times 3 \)

Anode: \( \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \times 2 \)
Change in $E_{\text{cell}}$ with Conditions

$\text{Zn(s)} + \text{Cu}^{2+} (\text{aq}) \rightarrow \text{Zn}^{2+} (\text{aq}) + \text{Cu (s)}$

$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q = 1.103 \text{V} - \frac{0.0592}{2} \log \left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right]$

If we let cell reaction proceed, reaction shifts to right, $[\text{Zn}^{2+}]$ increases, $[\text{Cu}^{2+}]$ decreases and $E_{\text{cell}}$ decreases. When does it stop?

It stops at equilibrium, $E_{\text{cell}} = 0.00 \text{V}$

$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q_{\text{eq}}$

$K_{\text{eq}} = 10^{0.0592}$

We can calculate $K_{\text{eq}}$ from $E^\circ$ values! For above reaction, $K_{\text{eq}} = 1.5 \times 10^{37}$

Concentration Cells

Both half-cells are the same chemical system, just different concentrations. The driving force (i.e. the EMF) is provided by the difference in concentrations.

$\text{Pt} | \text{H}_2 (g, 1.0 \text{ atm}) | \text{H}^+ (\text{x M}) || \text{H}^+ (1 \text{ M}) | \text{H}_2 (g, 1.0 \text{ atm}) | \text{Pt(s)}$

$E_{\text{cell}} = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.00 - 0.00 = 0.00 \text{V}$

$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592}{n} \log Q = 0.00 \text{V} \Rightarrow \frac{0.0592}{2} \log \frac{[\text{H}_2\text{O}]}{[\text{H}^+]}$

$E_{\text{cell}} = -\frac{0.0592}{2} \log X = -\frac{0.0592}{2} \log [\text{H}]$

$E_{\text{cell}} = 0.0592 \log X$

Since $\text{pH} = -\log X$, $E_{\text{cell}} = 0.0592 \text{ pH}$

This concentration cell behaves as a pH meter! Other concentration cells can be used to measure unknown concentrations of other species (i.e. potentiometry).
Determination of $K_{sp}$ (see Example 21-10)

From measured $E_{\text{cell}}$, determine $K_{sp}$.

**Solution:**

Set up Nernst equation with $Ag^+$ ($x$M) at anode, 0.1M at cathode.

Solve Nernst equation to get $x$.

$$x = [Ag^+] = S_1, \quad I = S_2$$

$$K_{sp} = S_1^2$$

---

**Electrolysis**

The use of an externally applied voltage to force an electrochemical reaction, even if it is naturally nonspontaneous.

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$  \[ E^{\circ}_{\text{cell}} = +1.10 \text{ V} \]

*Spontaneous!*

What about the reverse process?

$Zn^{2+}(aq) + Cu(s) \rightarrow Zn(s) + Cu^{2+}(aq)$  \[ E^{\circ}_{\text{cell}} = -1.10 \text{ V} \]

*Nonspontaneous!*

But if we apply a potential > 1.10 V across the cell, we overcome the natural negative voltage, thus providing the driving force to make the reaction proceed.

Current is in opposite direction of voltaic, or galvanic, cell.

---

**Galvanic and Electrolytic Cells**

Galvanic Cell  Electrolytic Cell

Regardless of the cell type, anode and cathode always defined by the process: oxidation at the anode, reduction at the cathode.
Zn/Cu²⁺ electrolysis example continued...

The amount of current that flows in the electrolytic cell tells us how much Zn has been produced or how much Cu²⁺ has dissolved.

Faraday’s Law of Electrolysis:
The number of moles of product formed in an electrolysis cell by an electric current is chemically equivalent to the number of moles of electrons supplied.

\[ Q = nF = it \]

charge (coulombs) \hspace{1cm} \frac{\text{moles of electrons}}{\text{current (amperes)}} \hspace{1cm} \frac{\text{time (seconds)}}{\text{Faraday's constant} = 96485 \text{ C/mole of e}^-}

Note: 1 A = 1 C/s

Example 21-12
Electrodeposition of Cu can be used to determine Cu²⁺ content of a sample.

Cathode: Cu²⁺ + 2 e⁻ → Cu(s)

Anode: 2H₂O → O₂(g) + 4H⁺(aq) + 4e⁻

What mass of Cu is deposited in 1 hr if current = 1.62 A?

Solution: Find moles of electrons, then find moles of Cu, then find mass of Cu.

Mole of e⁻ = 1.62 A (C/s) x 3600 sec x 1/(96485 C/mole e⁻)

Mole of Cu = mole e⁻ x 1 mole Cu / 2 mole e⁻

Mass Cu = moles Cu x 63.456 g Cu/mole Cu

Answer = 1.92 g of Cu deposited in 1 hour

Cont'd

Example B: How long will it take to produce 2.62 L of O₂(g) at 26.2°C and 738 mmHg at a Pt anode with a constant current of 2.13 A?

Solution: Find moles of O₂, then find moles of electrons, then find charge, then find time.

Mole of O₂: \[ n = \frac{PV}{RT} = \frac{738 \text{ atm} \times 2.62 \text{ L}}{0.08206 \text{ Latm mol}^{-1} \text{ K}^{-1} \times 299.35 \text{ K}} \]

(recall anode reaction: 2H₂O → O₂(g) + 4H⁺(aq) + 4e⁻)

Mole of electrons = moles of O₂ x 4 mole electrons/mole O₂

Charge = moles of electrons x F (C/mole of electrons)

Time = Charge (C)/Current (C/s)

Answer = 18829 sec = 5.23 hr = 5 hr & 14 min
Chlor-Alkali Process
Electrolysis of NaCl solutions

\[ 2 \text{Cl}^-_{\text{aq}} (\text{anode}) \rightarrow \text{Cl}_2(g) + 2 \text{e}^- \quad E^\circ_{\text{Cl}_2/\text{Cl}^-} = -1.358 \text{ V} \]

\[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-_{\text{aq}} \quad E^\circ_{\text{H}_2/\text{H}_2} = -0.828 \text{ V} \]

\[ 2 \text{H}_2\text{O} + 2 \text{Cl}^-_{\text{aq}} (\text{cathode}) \rightarrow \text{Cl}_2(g) + \text{H}_2(g) + 2\text{OH}^-_{\text{aq}} \quad E^\circ_{\text{cell}} = -2.19 \text{ V} \]

- \( \text{Cl}_2 \) produced at anode
- \( \text{H}_2 \) and NaOH\(_{\text{aq}} \) produced at cathode
- membrane allows Na\(^+ \) movement
- 11% NaOH and 15% NaCl is concentrated, NaCl crystallized and removed
- final product, 50% NaOH (1% NaCl impurity), Cl\(_2\), H\(_2\)

---

**NEW Chemistry Degree programs with Special Focus**

Three-year and Four-year Degrees with Special Focus on

- **Analytical Chemistry**
- **Biological Chemistry**
- **Materials Chemistry**

---

Specialized Honours Chemistry, Stream in

- **Atmospheric Chemistry**

---

**Other programmes involving Chemistry**

- **Honours Major/Minor Degrees**
  - Major or Minor in Chemistry, combine with Major or Minor in Biology, Physics, EATS or any other science
  - Major or Minor in Chemistry, combine with Major or Minor in Arts, Fine Arts, Environmental Studies

- **Honours Double Major Degrees**
  - Major in Chemistry, combine with another Major in Science