Highlights of last lecture

Voltaic cells...

CONCEPTS
- Half-reaction
- Table of standard reduction potential
- Effect of concentration
- Link between $E$, $Q$ and $K$

CALCULATIONS
- Work out cell potential from reduction potentials;
- Work out cell potential for any concentration (Nernst equation)
Relationship between $\Delta G^\circ$ and $K$

At 298 K

$$K = e^{-\Delta G^0/RT}$$

<table>
<thead>
<tr>
<th>$\Delta G^\circ$ (kJ)</th>
<th>$K$</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>$9 \times 10^{-36}$</td>
<td>Essentially no forward reaction; reverse reaction goes to completion</td>
</tr>
<tr>
<td>100</td>
<td>$3 \times 10^{-18}$</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>$2 \times 10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$2 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>$7 \times 10^{-1}$</td>
<td>Forward and reverse reactions proceed to same extent</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>-10</td>
<td>$5 \times 10^{1}$</td>
<td>Forward reaction goes to completion; essentially no reverse reaction</td>
</tr>
<tr>
<td>-50</td>
<td>$6 \times 10^{8}$</td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>$3 \times 10^{17}$</td>
<td></td>
</tr>
<tr>
<td>-200</td>
<td>$1 \times 10^{35}$</td>
<td></td>
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</tbody>
</table>
Relationship between $\Delta G^\circ$ and $K$
Q: What do you think happens as the reaction proceeds until equilibrium is reached?

A: The reaction stops, therefore the voltage, or electrical potential, is zero (the battery is flat!)

In mathematic terms:

\[ E_{\text{obs}} = E^0 - \frac{0.0592}{n} \log(Q) = 0 \]

At eq'm Q=K

\[ E^0 = \frac{0.0592}{n} \log(K) \]

So the equilibrium constant determines the cell potential!

Large K \Rightarrow \text{products favoured} \Rightarrow \text{large cell potential}, E
Let's examine the relationship between $E^0$ and $K$...
Interrelationship of $\Delta G^0$, $E^0$, and $K$

$\Delta G^0 = -nF E_{\text{cell}}$

$E_{\text{cell}} = \frac{RT}{nF} \ln K$

<table>
<thead>
<tr>
<th>$\Delta G^0$</th>
<th>$K$</th>
<th>$E_{\text{cell}}^0$</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>
Q: A voltaic cell consisting of a Ni/Ni$^{2+}$ half-cell and Co/Co$^{2+}$ half-cell is constructed with the following initial concentrations:  \([\text{Ni}^{2+}] = 0.80\text{M}; \ [\text{Co}^{2+}] = 0.2\text{M}\).

a) What is the initial \(E_{\text{cell}}\)?

b) What is the \([\text{Ni}^{2+}]\) when the voltage reaches 0.025V?

c) What are the equilibrium concentrations of the ions?

Given:  \(E^0 (\text{Ni}^{2+}|\text{Ni}) = -0.25 \text{ V}; \ E^0 (\text{Co}^{2+}|\text{Co}) = -0.28 \text{ V}\)
Example question

a) $\text{Co(s)} + \text{Ni}^{2+}(\text{aq}) \rightleftharpoons \text{Co}^{2+}(\text{aq}) + \text{Ni(s)} \quad E^0 = 0.03 \text{ V}$
Example question

b) \[ E_{\text{cell}} = E^0 - \frac{0.0592}{n} \log(Q) \]

\[ \text{Co}(s) + \text{Ni}^{2+}(aq) \rightleftharpoons \text{Co}^{2+}(aq) + \text{Ni}(s) \]

So when \( E_{\text{cell}} = 0.025 \) V

\[ [\text{Co}^{2+}] = \]

\[ [\text{Ni}^{2+}] = \]
Example question

c) \[ E^0 = \frac{0.0592}{n} \log(K) \]

\[ \text{Co(s) + Ni}^{2+}(aq) \rightleftharpoons \text{Co}^{2+}(aq) + \text{Ni(s)} \]

So at equilibrium,

\[ [\text{Co}^{2+}] = \]
\[ [\text{Ni}^{2+}] = \]
Concentration cells

- If the electrochemical potential is a function of concentration (as in the Nernst eq’n), then can we build a voltaic cell using the same half-reaction, but with different concentrations in each half-cell?

How does this work?

Afterall:

\[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \quad E^0 = -0.34 \]
\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad E^0 = +0.34 \]

???? \quad E = 0.0V
Concentration cells

A Concentration Cell

**Oxidation half-reaction**

Cu (s) $\rightarrow$ Cu$^{2+}$ (aq, 0.10 M) + 2e$^-$

**Reduction half-reaction**

Cu$^{2+}$ (aq, 0.10 M) + 2e$^-$ $\rightarrow$ Cu (s)

**Overall (cell) reaction**

Cu$^{2+}$ (aq, 1.0 M) $\rightarrow$ Cu$^{2+}$ (aq, 0.10 M)
Concentration cells

- It works because the standard half-cell potential are based on 1.0 M concentrations. Even though in this experiment $E^0 = 0$, the potential for $Q \neq 1$ is non-zero.
- The measured cell potential in our experiment was ____
- Let’s work out what the $[Cu^{2+}]$ was in the beaker:

Cu $\rightarrow$ $Cu^{2+}$ (y M) + 2e$^-$
Cu$^{2+}$ (1.0M) + 2e$^-$ $\rightarrow$ Cu

$Cu^{2+}$ (1.0M) $\rightarrow$ $Cu^{2+}$ (y M)

$E_{cell} = ____$ V

$E_{cell} = E^0 - \frac{0.0592}{n} \log(Q) = 0.0 - 0.0296 \times \log\left(\frac{y}{1.0}\right) = ____$ V

Solve for y: ____________________________
Standard Electrodes

- For routine measurements, it is nice to have one half-reaction that we use all the time, and just change the other half-cell.
- Several choices:
  - Standard hydrogen electrode (SHE), $E^0 = 0.00$ V
  - Standard calomel electrode (SCE), $E^0 = 0.28$ V
  - Silver/Silver chloride, $E^0 = 0.22$ V

Calomel:  $\text{Hg}_2\text{Cl}_2(s) + 2e^- \rightarrow 2\text{Hg}(l) + 2\text{Cl}^-(aq)$

Q: In lecture 31 we measured the Zn/Zn$^{2+}$ potential relative to the SHE (about +0.76 V). What would be the observed cell potential for the Zn/Zn$^{2+}$ couple when measured using the SCE as a reference?

Ans: ____________________________

So to get $E^0$ using the SCE, subtract 0.28 V from the reading
Applications of concentration cells

Consider the following concentration cell:

\[
\begin{align*}
H_2(g) &\rightarrow 2H^+(aq, \text{unknown}) + 2e^- \\
2H^+(aq, 1M) + 2e^- &\rightarrow H_2(g) \\
2H^+(1M) &\rightarrow 2H^+(\text{unknown})
\end{align*}
\]

\[E_{\text{cell}} = ?\]

\[
E_{\text{cell}} = E^0 - \frac{0.0592}{n} \log(Q) = -0.0296 \times \log\left(\frac{[H^+]^2}{1.0}\right) = -0.0592 \log[H^+]
\]

\[\text{pH} \equiv -\log[H^+]\]

\[E_{\text{cell}} = 0.0592 \times \text{pH}\]

i.e. measurement of the cell potential provides pH directly!

pH meter
Applications of concentration cells

Concentration cells are used all around us, e.g.

- nerve signalling
  - concentration gradients produce electrical current
- ion pumps across cell membranes
- Na⁺ / K⁺ pump, Ca²⁺ pump
- energy production and storage in cells
  - ATP

- pH meters
  - these usually use a silver/silver chloride reference rather than SHE
- ion selective electrodes
  - different choice of reference can then be specific to specific ions.
Other applications of voltaic cells

- **Batteries (lecture 35)**
  
  Refs: Most General Chemistry texts have good sections on batteries, e.g.
  - Silberberg, pp.923-5
  - McMurray and Fay, pp.781-6
  - Petrucci, Harwood and Herring, pp.844-848
  - However, Housecroft and Constable does not(!)

- **Corrosion (lecture 35)**
  
  Ref: Most General Chemistry texts also have a section on corrosion:
  - Silberberg, pp.926-8
  - McMurray and Fay, pp.786-9
  - Petrucci, Harwood and Herring, pp.849-50
  - Again, Housecroft and Constable does not(!)
Step 1: Determine the half-reactions.

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

Step 2: Balance the atoms and charges in each half reaction:

- Balance atoms other than O and H
- Balance O by adding H\textsubscript{2}O
- Balance H by adding H\textsuperscript{+}
- Balance charge by adding e\textsuperscript{-}
Balancing Redox Reactions

- Step 2: Balance the atoms and charges in each half reaction:

  \[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} \]

  - Balance atoms other than O and H
    \[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]
  
  - Balance O by adding H\(_2\)O
    \[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
  
  - Balance H by adding H\(^+\)
    \[ 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

  - Balance charge by adding e\(^-\)
    \[ 6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
Balancing Redox Reactions

- Step 2: Balance the atoms and charges in each half reaction:

  \[ I^- \rightarrow I_2 \]

  - Balance atoms other than O and H

  \[ 2I^- \rightarrow I_2 \]

  - Balance charge by adding e^-

  \[ 2I^- \rightarrow I_2 + 2e^- \] Oxidation
Balancing Redox Reactions

- **Step 3:** Multiply each half reaction by an integer so that the number of \( e^- \) in each reaction are the same.

\[
6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \\
(2I^- \rightarrow I_2 + 2e^-) \times 3
\]

- **Step 4:** Add the balanced half reactions and include the states of matter.

\[
6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \\
6I^- \rightarrow 3I_2 + 6e^-
\]

\[
6I^-_{(aq)} + 14H^+_{(aq)} + Cr_2O_7^{2-}_{(aq)} \rightarrow 3I_2(s) + 7H_2O_{(l)} + 2Cr^{3+}_{(aq)}
\]

- **Step 5:** Check the atoms and charges are balanced.
Reactants (6I, 14H, 2Cr, 7O; 6+) → Products (6I, 14H, 2Cr, 7O; 6+)
Balancing Redox Reactions in Basic Solutions

- Balance the following reaction as a basic reaction:
  \[ \text{MnO}_4^{-} \text{(aq)} + \text{C}_2\text{O}_4^{2-} \text{(aq)} \rightarrow \text{MnO}_2(s) + \text{CO}_3^{2-} \text{(aq)} \]

- Initially balance the reaction as an acidic reaction

  \[
  \begin{align*}
  \text{C}_2\text{O}_4^{2-} & \rightarrow \text{CO}_3^{2-} & \text{Identify } \frac{1}{2} \text{ Eqn} \\
  \text{C}_2\text{O}_4^{2-} & \rightarrow 2\text{CO}_3^{2-} & \text{Balance C} \\
  \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} & \rightarrow 2\text{CO}_3^{2-} & \text{Balance O} \\
  \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} & \rightarrow 2\text{CO}_3^{2-} + 4\text{H}^+ & \text{Balance H} \\
  \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} & \rightarrow 2\text{CO}_3^{2-} + 4\text{H}^+ + 2\text{e}^- & \text{Balance e}^- \\
  \text{Loss of electrons} = \text{OXIDATION}
  \end{align*}
  \]

  \[
  \begin{align*}
  \text{MnO}_4^{-} & \rightarrow \text{MnO}_2 & \text{Identify } \frac{1}{2} \text{ Eqn} \\
  \text{MnO}_4^{-} & \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} & \text{Balance O} \\
  \text{MnO}_4^{-} + 4\text{H}^+ & \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} & \text{Balance H} \\
  \text{MnO}_4^{-} + 4\text{H}^+ + 3\text{e}^- & \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} & \text{Balance e}^- \\
  \text{Gain of electrons} = \text{REDUCTION}
  \end{align*}
  \]
Balancing Redox Reactions in Basic Solutions

STEP 3

- $\text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_3^{2-} + 4\text{H}^+ + 2\text{e}^- \times 3$
- $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \times 2$
- $3\text{C}_2\text{O}_4^{2-} + 6\text{H}_2\text{O} \rightarrow 6\text{CO}_3^{2-} + 12\text{H}^+ + 6\text{e}^-$
- $2\text{MnO}_4^- + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{MnO}_2 + 4\text{H}_2\text{O}$

STEP 4

- $3\text{C}_2\text{O}_4^{2-} + 6\text{H}_2\text{O} \rightarrow 6\text{CO}_3^{2-} + 12\text{H}^+ + 6\text{e}^-$
- $2\text{MnO}_4^- + 8\text{H}^+ + 6\text{e}^- \rightarrow 2\text{MnO}_2 + 4\text{H}_2\text{O}$
- $2\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{MnO}_2 + 6\text{CO}_3^{2-} + 4\text{H}^+$
One additional step is necessary at Step 4.

The acidic result would be:

$$2\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{MnO}_2 + 6\text{CO}_3^{2-} + 4\text{H}^+$$

Add $\text{OH}^-$ to each side to cancel the $\text{H}^+$, therefore add $4\text{OH}^-$.

$$2\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{C}_2\text{O}_4^{2-} + 4\text{OH}^- \rightarrow 2\text{MnO}_2 + 6\text{CO}_3^{2-} + (4\text{H}^+ + 4\text{OH}^-)$$

Balancing Redox Reactions in Basic Solutions

$$2\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{C}_2\text{O}_4^{2-} + 4\text{OH}^- \rightarrow 2\text{MnO}_2 + 6\text{CO}_3^{2-} + 4\text{H}_2\text{O}$$

$$2\text{MnO}_4^-_{(aq)} + 3\text{C}_2\text{O}_4^{2-}_{(aq)} + 4\text{OH}^-_{(aq)} \rightarrow 2\text{MnO}_2_{(s)} + 6\text{CO}_3^{2-}_{(aq)} + 2\text{H}_2\text{O}_{(l)}$$