Redox Reactions: Electron Transfer
(see H&S, 3rd Ed. Sect. 26.5, pp. 895-900)

**Inner Sphere:**

**Outer Sphere:**

**Inner sphere mechanism** – three distinct steps:

1) substitution to form a bridge between oxidant and reductant
2) actual electron transfer
3) separation of the products (often with transfer of the bridge ligand)

Taube’s classical 1953 experiment (Nobel Prize 1983):

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + [\text{Cr(H}_2\text{O)}_6\text{]}^{2+} + 5 \text{H}_2\text{O} \rightarrow
\]

\[
[\text{Co(H}_2\text{O)}_6\text{]}^{2+} + [\text{Cr(H}_2\text{O)}_5\text{Cl}]^{2+} + 5 \text{NH}_3
\]
Proceeds via the following steps:

1) \([\text{Co(NH}_3\text{)}\text{Cl}^{2+}] + [\text{Cr(H}_2\text{O)}^{2+}] \rightarrow [\text{(NH}_3\text{)}_5\text{Co(μ-Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O}\]

2) \([\text{(NH}_3\text{)}_5\text{Co(μ-Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} \rightarrow [\text{(NH}_3\text{)}_5\text{Co(μ-Cl)}\text{Cr(H}_2\text{O)}_5]^{4+}\]

3) \([\text{(NH}_3\text{)}_5\text{Co(μ-Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O} \rightarrow [\text{(NH}_3\text{)}_5\text{Co(H}_2\text{O)}]^{2+} + [\text{ClCr(H}_2\text{O)}_5]^{2+}\]

How do we know Cl does’t fall off before or after electron transfer?
It is possible for any of the three steps to be rate limiting depending on the particular ligand set and metal dⁿ count:

*Egs.*

Taube’s experiment has rate limiting electron transfer because Cr(II) (d⁴, Jahn Teller ion) is substitutionally labile but...

replace Cr(II) with V(II) (d³, inert) as [V(H₂O)₆]²⁺ makes the first step rate limiting.

What is the effect of the nature of X⁻ in [Co(NH₃)₅X]²⁺ likely to be if:

a) step 1 is rate limiting?

b) step 2 is rate limiting?
Electronic communication through the ligand is important:

\[
[\text{Fe(CN)}_5(\text{H}_2\text{O})]^{3-} + [\text{Co(NH}_3)_5(\text{L})]^{3+} \rightarrow \\
[\text{Fe(CN)}_5(\text{L})]^{2-} + [\text{Co(NH}_3)_5(\text{H}_2\text{O})]^{2+} \rightarrow 
\]

In general, single atoms, small conjugated units like CN\(^-\) or SCN\(^-\) and larger conjugated \(\pi\)-systems facilitate electron transfer.
Outer sphere mechanism

- complexes are usually kinetically inert
- quantum mechanical ‘tunneling’ of e⁻ between metals

Self-exchange outer sphere redox rates (from Table 26.9 text):

\[
\]

<table>
<thead>
<tr>
<th>M</th>
<th>n L</th>
<th>dⁿ, spin states</th>
<th>k (L mol⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>3 bipy</td>
<td>d⁵ ls, d⁶ ls</td>
<td>&gt;10⁶</td>
</tr>
<tr>
<td>Os</td>
<td>3 bipy</td>
<td>d⁵ ls, d⁶ ls</td>
<td>&gt;10⁶</td>
</tr>
<tr>
<td>Co</td>
<td>3 phen</td>
<td>d⁶ ls, d⁷ hs</td>
<td>40</td>
</tr>
<tr>
<td>Fe</td>
<td>6 H₂O</td>
<td>d⁵ hs, d⁶ hs</td>
<td>3</td>
</tr>
<tr>
<td>Co</td>
<td>3 en</td>
<td>d⁶ ls, d⁷ hs</td>
<td>10⁻⁴</td>
</tr>
<tr>
<td>Co</td>
<td>6 NH₃</td>
<td>d⁶ ls, d⁷ hs</td>
<td>10⁻⁶</td>
</tr>
</tbody>
</table>
Considerations in an outer sphere mechanism:

1) reactants must get close together for tunneling to occur

2) bond lengthening and shortening must occur

3) **Franck-Condon** principle must be obeyed
   - electronic transitions (and electron transfer) occur on a far shorter timescale than molecular vibrations (nuclear motion)
   - this means that electron transfer will only occur when the complexes are distorted to the appropriate geometry for the products – i.e., this imposes an electronic barrier on the rate of electron transfer
• as a result, the larger the bond length changes required, the larger the barrier and the slower the rate:

\[ \text{Eg. } [\text{Co(NH}_3)_6]^{2+/3+} \]

\[ \text{Eg. } [\text{Fe(bipy)}_3]^{2+/3+} \]

• \( \pi \)-bonding ligands have low lying empty MO’s that facilitate intermolecular electron transfer as well:

\[ \text{Eg. Compare } [\text{Co(phen)}_3]^{2+/3+} \text{ and } [\text{Co(NH}_3)_6]^{2+/3+} \]