Outer Sphere Electron transfer

- The mechanisms whereby electrons are transferred in redox reactions have been under intense scrutiny and have generated 2+ Nobel prizes.
- We will start with a discussion of “outer-sphere” degenerate electron transfers (those involving transfer between oxidized and reduced forms of the same couple). See Sec. 6.5 in text.

Transition state theory expression for the rate constant, $k$:

$$ k = \left( \frac{k_B T}{h c} \right) e^{-\Delta G^f/RT} = A e^{-\Delta G^*/RT} \quad c = \text{conc.} $$

or $\ln k = \ln A - \Delta G^*/RT \quad \left( \frac{k_B T}{h} \approx 6 \times 10^{12} \right)$
Some rate constants (M$^{-1}$ s$^{-1}$)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cr(H}_2\text{O)}_6\text{]}^{2+} + [\text{Cr(H}_2\text{O)}_6\text{]}^{3+} \rightarrow \text{Cr}^{\text{III}} + \text{Cr}^{\text{II}}$</td>
<td>$2 \times 10^{-5}$</td>
</tr>
<tr>
<td>$[\text{Ru(NH}_3\text{)}_6\text{]}^{2+} + [\text{Ru(NH}_3\text{)}_6\text{]}^{3+} \rightarrow \text{Ru}^{\text{III}} + \text{Ru}^{\text{II}}$</td>
<td>$8 \times 10^{2}$</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3\text{)}_6\text{]}^{2+} + [\text{Co(NH}_3\text{)}_6\text{]}^{3+} \rightarrow \text{Co}^{\text{III}} + \text{Co}^{\text{II}}$</td>
<td>$\sim 10^{-9}$</td>
</tr>
<tr>
<td>$[\text{Fe(bpy)}_3\text{]}^{2+} + [\text{Fe(bpy)}_3\text{]}^{3+} \rightarrow \text{Fe}^{\text{III}} + \text{Fe}^{\text{II}}$</td>
<td>$&gt; 10^{6}$</td>
</tr>
<tr>
<td>$[\text{IrCl}_6\text{]}^{3-} + [\text{IrCl}_6\text{]}^{2-} \rightarrow \text{Ir}^{\text{IV}} + \text{Ir}^{\text{III}}$</td>
<td>$&gt; 10^{9}$</td>
</tr>
<tr>
<td>$[\text{Co(H}_2\text{O)}_6\text{]}^{2+} + [\text{Co(H}_2\text{O)}_6\text{]}^{3+} \rightarrow \text{Co}^{\text{III}} + \text{Co}^{\text{II}}$</td>
<td>$\sim 5$</td>
</tr>
</tbody>
</table>

All but the last of these is “easily” explained!

Note: All these rxns involve at least one d$^6$ or d$^3$ (substitutionally inert) complex.
Marcus (Nobel, 1992) Theory

\[ \Delta G_{12}^\dagger \approx 0.5[\Delta G_{11}^\dagger + \Delta G_{22}^\dagger + \Delta G^0] \]

From absolute rate theory,

\[ k = A e^{-\Delta G^\dagger/RT} \] or \[ \ln k = \ln A - \frac{\Delta G^\dagger}{RT} \]

comparing to the first eqn:

\[ \ln k_{12} = \frac{1}{2}\{\ln f + \ln k_{11} + \ln k_{22} + \ln K_{eq}\} \]

\[ k_{12} = [f \times k_{11} \times k_{22} \times K_{eq}]^{1/2}; \]

\[ f \approx 1 \] (contains all the prefactors)
Inner Sphere Reactions

- Electron transfer between metal complexes sometimes involve more than tunneling of electrons from one complex to another.
- In 1953, Taube (Nobel 1983) performed classic experiments that unequivocally demonstrated cases electron transfer occurs through an intervening (shared) ligand.

Taube’s Experiments

\[ [\text{Co(NH}_3\text{)}_5\text{X}]^{2+} + [\text{Cr(H}_2\text{O)}_6]^{2+} + 5\text{H}_3\text{O}^+ \rightarrow [\text{Cr(H}_2\text{O)}_5\text{X}]^{2+} + [\text{Co(H}_2\text{O)}_6]^{2+} + 5\text{NH}_4^+ \]

\( \text{X} = \text{halides, SCN}^-, \text{N}_3^-, \text{RCOO}^-, \text{etc} \)

[Note: Both Co\text{II} (d^6) and Cr\text{II} (d^3) complexes undergo very slow ligand exchange reactions. In general, d^3, d^4 (low-spin), d^5 (low-spin), d^6 (low-spin) exchange ligands slowly (< 1 min\(^{-1}\)).]

Some rate constants (M\(^{-1}\) s\(^{-1}\))

\[ [\text{Co(NH}_3\text{)}_6]^{3+} + [\text{Cr(H}_2\text{O)}_6]^{2+} \rightarrow \text{Co}^{\text{II}} + \text{Cr}^{\text{III}} \]

\( k = 8 \times 10^{-5} \)

\[ [\text{CoX(NH}_3\text{)}_5]^{2+} + [\text{Cr(NH}_3\text{)}_6]^{3+} \rightarrow \text{Co}^{\text{II}} + \text{Cr}^{\text{III}} \]

\( X \)

\( F^- \)

\( 2.5 \times 10^5 \)

\( \text{Cl}^- \)

\( 6.0 \times 10^5 \)

\( I^- \)

\( 3.0 \times 10^6 \)

\( \text{NCS}^- \)

\( 19 \)

\( \text{SCN}^- \)

\( 1.9 \times 10^5 \)

\( \text{H}_2\text{O} \)

\( 0.1 \)
For alkali and alkaline earth, dissociative mechanism seems to hold throughout. Rates increase with ionic size.

- $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta V^\ddagger$
- How are each of these measured?
- For dissociative reactions, we expect that all of these will be $>0$. 

Mechanistic Clues

- Activation parameters: $\Delta H^\ddagger$, $\Delta S^\ddagger$, $\Delta V^\ddagger$
Trends for T.M.s

$V^{2+}, Ni^{2+} > Co^{2+} > Cr^{2+}, Cu^{2+} > Fe^{2+} > Mn^{2+}, Zn^{2+}$

Does this LFSE trend correlate
with exchange rates?

$\Delta V^{\ddagger} > 0$ for $Fe^{2+}, Co^{2+}, Ni^{2+}$

but, $\Delta V^{\ddagger} < 0$ for $V^{2+}, Mn^{2+}$

$Co^{3+}, Rh^{3+}, Ir^{3+}, Cr^{3+}$ all quite inert - all have high LFSE’s

Associative vs. Dissociative

$\Delta V^{\ddagger}$ measurements indicate mechanisms may differ in seemingly similar reactions:

$[Co(NH_{3})_{5}(H_{2}O)]^{3+} + Cl^{-} \rightarrow [Co(NH_{3})_{5}Cl]^{2+} + H_{2}O$

$\Delta V^{\ddagger} = 1.4 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$

$[Rh(NH_{3})_{5}(H_{2}O)]^{3+} + Cl^{-} \rightarrow [Rh(NH_{3})_{5}Cl]^{2+} + H_{2}O$

$\Delta V^{\ddagger} = 3.0 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$

$[Cr(NH_{3})_{5}(H_{2}O)]^{3+} + Cl^{-} \rightarrow [Cr(NH_{3})_{5}Cl]^{2+} + H_{2}O$

$\Delta V^{\ddagger} = -4.9 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$