Reactivity of Transition Metal Complexes
(H&S 3rd Ed., Chpt. 26)

Four main types of reactivity:

1) Substitution reactions: $ML_n + L' \rightarrow ML_{n-1}L' + L$

\[ [\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3 \text{acac}^- \rightarrow \text{Fe(acac)}_3 + 6 \text{H}_2\text{O} \]

\[ [\text{Cu}(\text{H}_2\text{O})_6]\text{SO}_4 + 4 \text{NH}_3 \rightarrow [\text{Cu(NH}_3)_4(\text{H}_2\text{O})_2]\text{SO}_4 \]

2) Addition (dissociation) reactions: $ML_n + L' \rightarrow ML_nL'$

\[ [\text{Cu(acac)}_2] + \text{py} \rightleftharpoons [\text{Cu(acac)}_2(\text{py})] \]

Td $\rightleftharpoons$ SqPy

dissociation (the reverse reaction) usually requires heat or light to occur:

\[ [\text{NiCl}_2\text{py}_4] \xrightarrow{180 \ ^\circ\text{C}} [\text{NiCl}_2\text{py}_2] \xrightarrow{220 \ ^\circ\text{C}} - 2 \text{py} \]

\[ 220 \ ^\circ\text{C} \]

\[ [\text{NiCl}_2\text{py}] \xrightarrow{350 \ ^\circ\text{C}} [\text{NiCl}_2] \xrightarrow{350 \ ^\circ\text{C}} - \text{py} \]
3) Redox (e\textsuperscript{-} transfer) reactions: \( ML_n^{x+} \rightarrow ML_n^{(x+1)^+} + e^- \)

eg. \([\text{Ru(NH}_3\text{)}_6]^{2+} \rightarrow [\text{Run(NH}_3\text{)}_6]^{3+} + e^-\)

also includes \textit{oxidative-addition} (and its reverse: \textit{reductive-elimination}), especially of SqP complexes

\[
\begin{align*}
\text{L} \quad \text{M} \quad \text{L} \quad + \quad \text{X-Y} \quad & \iff \quad \text{L} \quad \text{M} \quad \text{X} \\
\text{L} \quad \text{M} \quad \text{L} \quad + \quad \text{H-H} \quad & \iff \quad \text{L} \quad \text{M} \quad \text{H} \quad \text{Cl}
\end{align*}
\]

\( L = \text{PPh}_3 \)

Wilkinson's catalyst

4) Reactions at coordinated ligands (many variants here)

\[
\begin{align*}
\text{H} \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{H} \\
\text{O} \quad \text{O} \quad \text{H} \quad \text{N} \quad \text{N} \\
\text{R} \quad \text{N} \quad \text{H} \quad \text{N} \quad \text{R}
\end{align*}
\]

\(-2 \text{H}_2\text{O} \quad + \quad \text{RNH}_2 \quad \rightarrow \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{H} \quad \text{R}
\]

a template reaction
Substitution Reactions

General mechanistic considerations

Four recognized mechanisms for ligand substitution in inorganic chemistry:

1) Associative (A)
2) Dissociative (D)
3) Associative Interchange (I_A)
4) Dissociative Interchange (I_D)

Associative and Dissociative differ from I_A and I_D respectively in that there is a discrete intermediate of higher or lower coordination number:

Associative mechanism:

\[
\text{ML}_n + L' \overset{\text{slow}}{\rightarrow} \text{ML}_nL' \overset{\text{fast}}{\rightarrow} \text{ML}_{n-1}L' + L
\]
A mechanism (cont.):

- rates depends on starting complex and incoming ligand concentration
- sensitive to nature of L’ (but solvent effects can sometimes mask this)
- more likely for low coordination number complexes

Dissociative mechanism:

\[
\begin{align*}
ML_n & \quad \xrightleftharpoons{\text{slow}} \quad ML_{n-1} + L \quad \xrightleftharpoons{\text{fast}} \quad ML_{n-1}L' \\
+L' & \\
\end{align*}
\]

- equivalent to a S_N1 reaction in organic chemistry
- rates depend only on concentration of starting complex \(ML_n\)
- insensitive to nature of incoming ligand L’
- more common for high coordination number complexes and those containing very bulky ligands L
Interchange mechanisms: concerted reaction with no discrete intermediate of higher or lower coordination number

- more common than true A or D mechanisms
- based on the Eigen-Wilkins ‘encounter complex’ model
- $I_A$ has both leaving and entering ligands strongly bound in the TS and shows sensitivity to the nature and concentration of $L'$
- $I_D$ has both leaving and entering ligands weakly bound in the TS and shows little sensitivity to the identity or concentration of $L'$
Eigen-Wilkins ‘encounter complex’

Solvent cage containing starting octahedral complex, [M(H₂O)₆]²⁺

outer-sphere complex

‘Encounter complex’

No M-H₂O or M-X bonding

weak M-H₂O and M-X bonding

strong M-H₂O and M-X bonding

Dissociative

Interchange

Associative

\[ k_f = \frac{k_{-w}k_x}{k_w[H_2O] + k_x[X]} \]

\[ k_f = K_{diff}k_{-w} \]

\[ k_f = K_{diff} \frac{k_{-w}k_x}{k_x + k_{-w}} \]
Substitution in Octahedral Complexes

- mechanism generally found to be $I_D$ (there are of course exceptions); true $D$ mechanism is rare

- water exchange rates vary enormously across the d-block:

(water exchange rates are simply representative of general exchange kinetics for the d-block metals but they are very useful to know since much chemistry is done in water and they have been extensively studied as a result)

How can we rationalize these widely varying rates?
1) Non-d-block metals show decreasing k with increasing Q/r

- since this is a dissociative mechanism, weakening the M-OH₂ bond should increase rate and the strength of ion-dipole interaction depends on Q/r

- no directional (crystal field) effects associated with spherical ions

2) Even though there isn’t an obvious Q/r trend for the d-block metals, there is some influence of charge
egs.

Fe²⁺ and Ru²⁺ are about 10⁴ x faster in water exchange than Fe³⁺ and Ru³⁺, respectively

BUT V²⁺ is about 10 x SLOWER than V³⁺ so the trend is not perfect

However, within a charge series the Q/r ratio doesn’t hold:

V²⁺ has one of the lowest Q/r and yet has one of the slowest rates and Cr²⁺ and Cu²⁺ are very different in size but almost the same in rate
3) Jahn-Teller ions show exceptional fast water exchange:

waters in the coordination sphere of $\text{Cr}^{2+}$ ($d^4$) and $\text{Cu}^{2+}$ ($d^9$) have an average residence time of *less than a nanosecond!!*

- Jahn-Teller ions already show elongation of two (or four) M-OH$_2$ bonds so it is not too surprising that these waters are less tightly bound and more easily lost in an I$_D$ mechanism

4) Besides the Jahn-Teller ions, water exchange rates are also significantly influenced by the d$^n$ count for other d-block ions

- even though the true mechanism is probably I$_D$ not D, it is useful to think about changes in CFSE going from an Oh ground state to a square pyramidal intermediate (or transition state):
  - a net gain in CFSE is a stabilizing influence on the intermediate, lowering $\Delta G^*$ and increasing the rate
  - a net loss in CFSE is a destabilizing influence on the intermediate, increasing $\Delta G^*$ and decreasing the rate
Does this actually work? Let’s look at the change in CFSE (square pyramidal – octahedral) for various d counts:

<table>
<thead>
<tr>
<th>d^n</th>
<th>ΔCFSE (high spin)</th>
<th>ΔCFSE (low spin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+0.06</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>+0.11</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>+0.31</td>
<td>-0.14</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>-0.09</td>
</tr>
<tr>
<td>6</td>
<td>+0.06</td>
<td>-0.40</td>
</tr>
<tr>
<td>7</td>
<td>+0.11</td>
<td>+0.11</td>
</tr>
<tr>
<td>8</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>+0.31</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

So, as long as we stay within a particular ionic charge group we do pretty well:

For first row 3+ ions:

\[ \text{Cr}^{3+} (d^3) \Delta \text{CFSE} = -0.20 \] is in fact substitution inert

followed in increasing order of lability by:

\[ \text{Fe}^{3+} (d^5) \Delta \text{CFSE} = 0 \]
\[ \text{V}^{3+} (d^2) \Delta \text{CFSE} = +0.11 \]
\[ \text{Ti}^{3+} (d^1) \Delta \text{CFSE} = +0.06 \]
For first row 2+ ions:

\[ V^{2+} (d^3) \Delta \text{CFSE} = -0.20 \] is quite slow (87 s\(^{-1}\))

\[ \text{Ni}^{2+} (d^8) \Delta \text{CFSE} = -0.20 \] is labile but \( 2^{nd} \) slowest overall (10\(^4\) s\(^{-1}\))

\[ \text{Co}^{2+} (d^7) \Delta \text{CFSE} = +0.11; \text{Fe}^{2+} (d^6) \Delta \text{CFSE} = +0.06; \text{Mn}^{2+} (d^5) \Delta \text{CFSE} = 0; \text{Zn}^{2+} (d^{10}) \Delta \text{CFSE} = 0 \] are very close in lability to one another and fast exchanging (10\(^7\) s\(^{-1}\))

\[ \text{Cr}^{2+} (d^4) \Delta \text{CFSE} = +0.31; \text{Cu}^{2+} (d^9) \Delta \text{CFSE} = +0.31 \] are both Jahn-Teller distorted ions and have large changes in CFSE as well. Their exchange rates are among the fastest known for any ions at >10\(^9\) s\(^{-1}\)

Second and third row metals

- generally less labile
- partly due to less favourable \( \Delta \text{CFSE} \) for these low spin metals (remember \( \Delta_{\text{oct}} \) is larger for these metals so the CFSE corresponds to a greater energy in general)

- note that the especially unfavourable \( \Delta \text{CFSE} \) of -0.40 for low spin d\(^6\) ions leads to substitution inert octahedral Rh\(^{3+}\) and Ir\(^{3+}\) complexes