Inorganic reaction mechanisms

Substitution reactions

Thermodynamic factors

Kinetic factors
Energy profile

Activated Complex

$E_a, \Delta H^#, \Delta S^#$

Reactants

$Y + M \rightarrow X$

Products

$M - Y + X$

Kinetics

Thermodynamics

REACTION COORDINATE
Thermodynamics

Both kinetics and thermodynamics are important in the assessment of a reaction.

This is because some thermodynamically feasible reactions may be kinetically hindered

Ligand substitution reactions will be used to illustrate these concepts:

Consider the reaction: \( Y + M \rightarrow X \rightarrow M - Y + X \)

This is a typical substitution reaction

\( Y = \) entering group

\( X = \) leaving group

The simplest illustration is a complex formation reaction:

\( \text{e.g. } [\text{Co(H}_2\text{O)}_6]^{2+} + \text{Cl}^- \rightarrow [\text{CoCl(H}_2\text{O)}_5]^+ + \text{H}_2\text{O} \)
**Aquo complexes**

Fundamentally metal ions dissolved in water are complexed \( \rightarrow \) Aquo complexes \( \rightarrow [M(H_2O)_x]^n+ \)

Formation of coordination compounds from an aqueous medium \( \rightarrow \) requires displacement of aquo ligands by other ligands.

\( \rightarrow \) Several geometries are possible: Typical examples of aquo compounds \( \rightarrow \) e.g. Co(II)

\[ [\text{Co}(\text{H}_2\text{O})_6]^{2+} \quad \text{Octahedral} \quad [\text{Co}(\text{H}_2\text{O})_4]^{2+} \quad \text{Terahedral} \]

In reality the value of \( x \) varies \( \rightarrow \) due to extensive hydrogen bonding around the coordination sphere of \( M \)

Spectra and magnetic properties \( \rightarrow \) similar to hydrated salts of non-coordinating anions \( \rightarrow \) Co(ClO\(_4\))\(_2\).6H\(_2\)O; Co(NO\(_3\))\(_2\).6H\(_2\)O
Aquo complexes

Predominantly \([\text{Co}(\text{H}_2\text{O})_6]^{2+}\) \(\rightarrow\) octahedral

Also general for the 1st transition series \(\rightarrow\) \([\text{M}(\text{H}_2\text{O})_x]^{n+}\); \(n=+2\) or \(+3\)

Note: \(\text{Cr(II)}\); \(\text{Mn(III)}\) and \(\text{Cu(II)}\) show distortions in the octahedral geometry due to Jahn-Teller effects

2nd and 3rd TS are much less certain \(\rightarrow\) octahedral probably \(\rightarrow\) higher coordination also possible

Most \(\text{M}(\text{H}_2\text{O})_6\) exchange rapidly \(\rightarrow\) can easily be demonstrated by isotopic labeling with \(^{18}\text{O}\) enriched \(\text{H}_2\text{O}\).

Aqua ions are more or less acidic \(\rightarrow\) dissociate as follows:

\[
[M(\text{H}_2\text{O})_x]^{n+} \rightarrow [M(\text{H}_2\text{O})_{x-1}(\text{OH})]^{n-1} + \text{H}^+
\]
e.g. \([\text{Co}((\text{NH}_3)_5(\text{H}_2\text{O}))]^{3+} \rightarrow [\text{M}((\text{NH}_3)_5(\text{OH}))]^{2+} + \text{H}^+\)
Formation constants

**Formation constant:** the strength of a ligand relative to the strength of the solvent molecules (usually H₂O) as a ligand.

\[ [\text{Fe(OH}_2\text{)}_6]^{3+}(\text{aq}) + \text{SCN}^- (\text{aq}) \rightleftharpoons [\text{Fe(SCN)(OH}_2\text{)}_5]^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \]

In dilute solutions \([\text{H}_2\text{O}] \Rightarrow \text{constant}; \]

\[ K_f = \frac{[\text{Fe(SCN)(OH}_2\text{)}_5]^{2+}}{[\text{Fe(OH}_2\text{)}_6]^{3+}[\text{SCN}^-]} \]

**Step-wise formation constant:** formation constant of each solvent replacement stage.

\[ K_{f1} ; K_{f2} \ldots \ldots \ldots K_{fn} \]

**Overall formation constant:** product of the step-wise formation constants.

\[ \beta_n = K_{f1} K_{f2} \ldots \ldots \ldots K_{fn} \]
Successive formation constants

\[
\begin{align*}
M + L & \rightleftharpoons ML \quad K_{f1} = \frac{[ML]}{[M][L]} \\
ML + L & \rightleftharpoons ML_2 \quad K_{f2} = \frac{[ML_2]}{[ML][L]} \\
ML_{n-1} + L & \rightleftharpoons ML_n \quad K_{f_n} = \frac{[ML_n]}{[ML_{n-1}][L]} \\
M + nL & \rightleftharpoons ML_n \quad \beta_n = \frac{[ML_n]}{[M][L]^n}
\end{align*}
\]

The inverse of each \(K_f\) is the dissociation constant \(K_d\): 
\[
M + L \rightleftharpoons ML \quad K_{d1} = \frac{[M][L]}{[ML]} = \frac{1}{K_{f1}}
\]
Trends in successive formation constants

The general trend \( K_{f1} > K_{f2} \)

\[ \cdots \ K_{fn-1} > K_{fn} \]

This trend is a result of the sequential decrease in number of \( H_2O \) to be replaced.

Situations do arise where \( K_{fn} > K_{fn-1} \)

Generally there are 2 reasons to account for anomalies in the trends of successive \( K_f \) values:

1 \( \Rightarrow \) due to a major change in electronic structure of the complex, e.g. moving from a high spin (due to weak field \( H_2O \)) to a low spin complex.

2 \( \Rightarrow \) due to a major structural change e.g. from an octahedral to a tetrahedral or square planar geometry \( \Rightarrow \) characteristic of some halo complexes.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( K_f )</th>
<th>( \frac{K_n}{K_{n-1}} )</th>
<th>( \frac{K_n}{K_{n-1}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>148</td>
<td>0.28</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>45.7</td>
<td>0.31</td>
<td>0.53</td>
</tr>
<tr>
<td>4</td>
<td>13.2</td>
<td>0.29</td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>4.7</td>
<td>0.35</td>
<td>0.53</td>
</tr>
<tr>
<td>6</td>
<td>1.1</td>
<td>0.20</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Q. Consider the formation constants of the following Fe(II) complexes: Justify the observed trend?

\[ \text{[Fe(bipy)(H}_2\text{O})_4]^{2+}: \quad K_{f1}: 4.2 \]
\[ \text{[Fe(bipy)}_2(\text{H}_2\text{O})_2]^{2+}: \quad K_{f2}: 3.7 \]
\[ \text{[Fe(bipy)}_3]^{2+}: \quad K_{f3}: 9.3 \]

\( K_{f3}: [\text{Fe(bipy)}_3]^{2+} \gg K_{f2}: [\text{Fe(bipy)}_2(\text{H}_2\text{O})_2]^{2+}: \)

The reason is due to a major electronic shift ➔

from a high spin (due to weak field \( \text{H}_2\text{O} \)) \( t_{2g}^4e_g^2 \) (LFSE \( \Delta_o = 0.4 \)) config ➔

to a low spin \( t_{2g}^6 \) config (LFSE \( \Delta_o = 2.4 \)). Large increase \( \Delta_o \).

Therefore \([\text{Fe(bipy)}_3]^{2+}\) is more stable than \([\text{Fe(bipy)}_2(\text{H}_2\text{O})_2]^{2+}\)
Q. Justify the following observation in the successive formation constants for complexes of cadmium with Br⁻:

\[
\begin{align*}
[Cd(Br)(H_2O)_5]^+ : & \quad K_{f1} : 36.3 \\
[Cd(Br)_2(H_2O)_4]^- : & \quad K_{f2} : 3.47 \\
[Cd(Br)_3(H_2O)_3]^- : & \quad K_{f3} : 1.15 \\
[Cd(Br)_4]^{2-} : & \quad K_{f4} : 2.34
\end{align*}
\]

The anomaly here is that \( K_{f4} > K_{f3} \):

The reason may not be electronic since both H₂O and Br⁻ are considered weak field ligands.

The reason is due to a major structural shift from an octahedral \([Cd(Br)_3(H_2O)_3]^-\) configuration to a tetrahedral \([Cd(Br)_4]^{2-}\) geometry with the simultaneous expulsion of 3 molecules of water from a restricted geometry.

Most halo complexes of M²⁺ have tetrahedral or square geometry.
Irving-Williams series

The Irving-Williams series summarises the relative stabilities of complexes formed by $M^{2+}$ ions. The series reflect a combination of electrostatic effects and LFSE. For the series $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$ the observed trend is purely electrostatic. For the TMs in addition to electrostatic effects, the high values of $K_f$ is due to additional stability from LFSE.

In terms of ionic radii ➔
$\text{Mn}^{2+} > \text{Fe}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$.

But,

Generally for strong field ligands the observed order is:
$\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$.

The additional stability of $d^9$ Cu(II) is due to the influence of Jahn-Teller distortion ➔ results in the strong binding of the 4 planar ligands in tetragonally distorted Cu(II) complexes ➔ higher $K_f$ values.

RECALL: $\Delta_o$ is highest at $d^3$ and $d^8$
Other thermodynamic factors

In addition to the foregone discussion the following thermodynamic factors are also important to the stability of TM complexes:

**The chelate effect:** this is largely an entropy effect → represents the greater stability of a complex containing a chelated polydentate ligand compared with the equivalent complex with an analogous monodentate ligands.

![Chelate Effect Diagram](image)

**Steric Effect:** The size of ligands are important in determining the most stable configuration → e.g. octahedral vs. tetrahedral

**Electron delocalisation:** This is important in complexes containing chelated ring structures. The empty ring $\pi^*$ orbitals act as electron sinks that drain electrons from the full metal $t_{2g}$ non-bonding orbitals.
**Labile and non-labile complexes**

The rate at which one complex inter-converts into another is determined by the height of the activation barrier between the two:

**Labile complexes:** A complex with a half life of the order of milliseconds; e.g. \([\text{Ni(H}_2\text{O)}_6]^{2+}\) is said to be labile

**Non-labile or inert** complex has half-life of the order of minutes; e.g \([\text{Co(HH}_3)_5(H_2\text{O})]^3+\)

**Factors affecting lability of complexes:**
Complexes with no stabilising LFSE or chelate effects are very labile
Complexes of small metal ions are less labile due to greater M-L bonds
Complexes of M(III) ions are less labile than those of M(II) ions
Complexes of d\(^3\) and low spin d\(^6\) config are non-labile ➔ high LFSE
Chelate complexes of metal ions with high LFSE (e.g. \([\text{Fe(phen)}_3]^{2+}\)) are very stable
Complexes of d\(^{10}\) ions (zero LFSE: Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\)) are generally labile
Classification of mechanisms

Associative (A);

Dissociative (D);

Interchange (Ia or Id)
Classification of mechanisms

Dissociative:
5-coordinate intermediate
D

ML_nX + Y → ML_nY + X

Energy profile for Dissociative mechanism: Intermediate has lower coordination number than reactant.

Interchange
I_d or I_a

Energy profile for Interchange mechanism: Reaction proceeds with no change in coordination number.

Associative:
7-coordinate intermediate
A

ML_nY + X → ML_nX + Y

Energy profile for Associative mechanism: Intermediate has higher coordination number than reactant.
Classification of mechanisms

No intermediate

ENERGY

ENERGY

Transition state occurs at an E maximum

Intermediate occurs at a local E minimum

Transition state occurs at an E maximum

Intermediate may be isolated

Transition state cannot be isolated
Interchange I

In most TM substitution reactions \( \rightarrow \) bond formation between  \( M + Y \) happens concurrently with bond cleavage between  \( M + X \) \( \rightarrow \)

**Interchange mechanism:**

\[
ML_nX + Y \quad \longrightarrow \quad Y \ldots \ldots ML_n \ldots \ldots X \quad \longrightarrow \quad ML_nY + X
\]

For an **interchange mechanism** \( \rightarrow \) there is **no intermediate formed**, but **various TS may be possible:**

Hence there are 2 types of I:

- **Dissociative Id**: bond breakage dominates over formation and
- **Associative Ia**: bond formation dominates over breakage

It is often difficult to distinguish between:

- A and Ia
- D and Id
- Ia and Id
Substitution reactions in square planar complexes

- Referring to complexes of $d^8$ ion TM
- Under a large crystal field:

  \[
  \text{Rh(I)  Ir(I)  Pt(II)  Pd(II)  Au(III)}
  \]
Steric Effects

Remember 4-coord. Ni(II) can be tetrahedral or sq planar (why?)

Nucleophilic subst. in sq. planar complexes ⇒ usually A or Ia ⇒
the rate of the reaction is dependent on the nature of the entering
group Y

But steric crowding at the reaction centre by bulky groups ⇒
usually inhibits A or Ia reactions ⇒ results in D or Id mechanism

$k$ values for $\text{cis-}[\text{PtCl}_2\text{L(PEt}_3\text{)}_2]\ + \text{H}_2\text{O} \rightarrow \text{cis-}[\text{Pt(H}_2\text{O)}\text{L(PEt}_3\text{)}_2]$

$L = \begin{array}{ccc}
\text{pyridine} & \text{2-Mepy} & \text{2,6-diMepy} \\
8 \times 10^{-2} & 2 \times 10^{-4} & 1 \times 10^{-6}
\end{array}$

The rate ↓ with ↑ in steric bulk around N→M bond
⇒ The Me groups hinder the attack by H$_2$O
Stereochemistry

Substitution reactions at square complexes are stereospecific ➔ the original geometry of the complex is preserved:

- cis reactants lead to cis products
- trans reactants lead to trans products
- most of these are 16 electron complexes ➔ useful in catalysis ➔ oxidative addition-reductive elimination (16 e↔18 e) chemistry
The kinetic *trans*-effect and thermodynamic *trans*-influence

Since the substitution reactions of sq. planar TM complexes are usually A or Ia, what factors determine the nature of the TS and

Why a 5 coordinate (trigonal bipyramidal or square pyramidal) TS?

Which ligand leaves is determined by the ligand trans to it ➔ *trans* influence ➔ *trans* effect

**σ-donor ligands** ➔ Ligands capable of contributing more electron density to the shared orbital between itself and the *trans* ligand, thereby weakening the bond to the leaving group ➔ *trans* influence

**π-acceptor ligands** ➔ drain away electrons in A or Ia substitution reactions ➔ TS characterised by high electron density at the metal center due to a 5-coordinate intermediate ➔ *trans* effect
The kinetic *trans*-effect and thermodynamic *trans*-influence

*trans* influence and *trans*-effect are related \(\Rightarrow\) weakening the bond to the *trans*-ligand and increasing the rate of substitution,

**Note:** there is NO close correlation between the relative magnitudes of the two phenomena

Why a 5 coordinate (trigonal bipyramidal or square pyramidal) TS?

The leaving group (X), the entering group (Y) and the *trans* ligand L₃ all lie in the same plane. **The TS is stabilised if L₃ is a good π acceptor** ligand such as CO. The three are able to communicate electronically via the π-bonding orbitals.

Remember the influence of π bonding on the **crystal field splitting** \(\Delta\)
The kinetic \textit{trans}-effect and thermodynamic \textit{trans}-influence

- **Peyrane's Reaction (1845)**

\[
2K^+ \left[ \begin{array}{c} \text{Cl} \\ \text{Cl} \\ \text{Pt} \\ \text{Cl} \\ \text{Cl} \end{array} \right]^{-2} \rightarrow \text{NH}_3 \rightarrow \left[ \begin{array}{c} \text{Cl} \\ \text{Cl} \\ \text{Pt} \\ \text{NH}_3 \\ \text{Cl} \end{array} \right]^{-} \rightarrow \text{NH}_3 \rightarrow \left[ \begin{array}{c} \text{Cl} \\ \text{Cl} \\ \text{Pt} \\ \text{NH}_3 \\ \text{Cl} \end{array} \right]^{-}
\]

- **Jorgensen's Reaction (1886)**

\[
\left[ \begin{array}{c} \text{H}_3\text{N} \\ \text{H}_3\text{N} \\ \text{Pt} \\ \text{NH}_3 \\ \text{NH}_3 \end{array} \right]^{+2} \rightarrow \text{HCl} \rightarrow \left[ \begin{array}{c} \text{Cl} \\ \text{H}_3\text{N} \\ \text{Pt} \\ \text{NH}_3 \\ \text{NH}_3 \end{array} \right]^{+} \rightarrow \text{HCl} \rightarrow \left[ \begin{array}{c} \text{Cl} \\ \text{H}_3\text{N} \\ \text{Pt} \\ \text{NH}_3 \\ \text{Cl} \end{array} \right]
\]


The *trans* effect

The trans effect states that the bond holding a group *trans* to an electronegative group is weakened. This *trans* group is the first to be removed in a substitution reaction.

Chloride is a better trans-labilizer than ammonia or pyridine.

Ethylene is a better trans-labilizer than chloride.
Kinetic Studies to determine *trans*-effect of ligands

![Chemical structure](image)

<table>
<thead>
<tr>
<th>L</th>
<th>k (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4, \text{CO})</td>
<td>too fast</td>
</tr>
<tr>
<td>(\text{P(OMe)}_3)</td>
<td>10.3</td>
</tr>
<tr>
<td>(\text{PEt}_3)</td>
<td>6.6</td>
</tr>
<tr>
<td>(\text{PPh}_3)</td>
<td>3.1</td>
</tr>
<tr>
<td>(\text{Me}_2\text{SO})</td>
<td>0.0082</td>
</tr>
<tr>
<td>(\text{Et}_2\text{S})</td>
<td>0.0024</td>
</tr>
<tr>
<td>(\text{Me}_2\text{S})</td>
<td>0.0015</td>
</tr>
<tr>
<td>(\text{NH}_3)</td>
<td>(6.3\times10^{-6})</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>(8.0\times10^{-8})</td>
</tr>
</tbody>
</table>
Trans-influence from x-ray crystallography
Trans-influence from vibrational spectroscopy

<table>
<thead>
<tr>
<th>L</th>
<th>ν Pt-Cl (cm⁻¹)</th>
<th>L</th>
<th>ν Pt-Cl (cm⁻¹)</th>
<th>L</th>
<th>ν Pd-Cl (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>322</td>
<td>py</td>
<td>336</td>
<td>py</td>
<td>342</td>
</tr>
<tr>
<td>SMe₂</td>
<td>310</td>
<td>SMé₂</td>
<td>336</td>
<td>Cl</td>
<td>330</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>309</td>
<td>COD</td>
<td>327</td>
<td>NH₃</td>
<td>327</td>
</tr>
<tr>
<td>SEt₂</td>
<td>307</td>
<td>SEt₂</td>
<td>324</td>
<td>EtSCH₂CH₂SEt</td>
<td>323</td>
</tr>
<tr>
<td>PPh₃</td>
<td>279</td>
<td>NH₃</td>
<td>321</td>
<td>H₂NCH₂CH₂NH₂</td>
<td>307</td>
</tr>
<tr>
<td>PEt₃</td>
<td>271</td>
<td>PPh₃</td>
<td>305</td>
<td>PEt₃</td>
<td>297</td>
</tr>
</tbody>
</table>

- Ligands with high trans-influence have high trans-effect.
- Exceptions to this rule include CO, C₂H₄, and DMSO.
- Frequency order for Rh(III)-Cl: H⁻ > PR₃ > Me⁻ > CO > I⁻ > Br⁻ > Cl⁻.
- For octahedral complexes, trans-influence parallels trans-effect.
**Trans effect vs. trans influence**

- The trans effect is the influence of a ligand (L) on the rate of substitution of the ligand trans to it (X). It is a kinetic effect (ground and transition states).

\[
\text{H}^- = \text{CH}_3^- = \text{CN}^- = \text{C}_2\text{H}_4 = \text{CO} \gg \text{PR}_3 = \text{SR}_2 > \text{NO}_2 = \text{SCN}^- = \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{RNH}_2 = \text{NH}_3 > \text{OH}^- > \text{H}_2\text{O}
\]

- The trans influence is the extent to which a ligand (L) weakens the bond that is trans to itself. It is a thermodynamic effect (ground state). Apply primarily to the leaving group.

\[
\text{R}_3\text{Si}^- = \text{R}^- = \text{H}^- > \text{PEt}_3 > \text{PMe}_2\text{Ph} > \text{PPh}_3 > \text{P(OPh)}_3 = \text{CN}^- > \text{SEt}_2 > \text{Et}_2\text{NH} > \text{py} > \text{OSMe}_2 = \text{C}_2\text{H}_4 = \text{CO} > \text{Cl}^-
\]

- The trans effect is often the manifestation of the trans influence although there are some ligands (DMSO, CO, C₂H₄) which do not show significant trans-influences yet show strong effects.
Theory on *trans* influence

- Grinberg Polarization Theory (1935): M→L and then L→M induced dipole results in repulsion of electrons in X ➔ weakening of M-X bond.

- Chatt/Orgel theory of back-bonding: Stabilisation of a 5 coordinate (trigonal bipyramidal) activated complex.
Q. Does back-bonding generally indicate stronger *trans* effect?

**YES**

- The trend holds for olefins, CO, and DMSO...

- Phosphorus donors...

- And sulfur donors to a lesser extent...


But, metal alkyl and metal hydrides have large trans effects and no back-bonding.

\[ \text{H}_2\text{PtCl}_2 \rightarrow \text{H}_2\text{PtI}_2 \]


\[ \left[ \begin{array}{c} \text{NH}_3 \\ \text{Rh} \\ \text{NH}_3 \\ \text{H}_3\text{N} \\ \text{NH}_3 \end{array} \right]^{2+} \rightarrow \left[ \begin{array}{c} \text{NH}_3 \\ \text{Rh} \\ \text{OH}_2 \\ \text{H}_3\text{N} \\ \text{NH}_3 \end{array} \right]^{2+} \]

Rates of aquation: H > Et > CF₂CF₂H >> Cl

Q. Given $\text{Pt(NH}_3\text{)}_4^{2+}$, $[\text{PtCl}_4]^{-2}$, HCl and NH$_3$ suggest synthetic routes to

a) cis-$[\text{PtCl}_2(\text{NH}_3)_2]$  
b) trans-$[\text{PtCl}_2(\text{NH}_3)_2]$