In order to understand the rich reaction chemistry of transition metal and coordination complexes, you must have a good background in kinetics and thermodynamics. It is the interplay between kinetic and thermodynamics that makes inorganic reactions interesting.

A brief Review

Consider the reaction $A \rightarrow B$, what happens to $[A]$ and $[B]$ as the reaction proceeds? Naturally $[A]$ decreases and $[B]$ increases.

What about rate? Recall: $A \rightarrow B$ and $A \leftrightarrow B$, where $k$ is the rate constant. The rate constant is proportional to rate, and thus indicates how fast the reaction will proceed. Prior to equilibrium $k_f > k_r$ but at equilibrium $k_f = k_r$, implying that $A$ is converted into $B$ at the SAME RATE as $B$ is converted to $A$. This is the condition for a dynamic equilibrium.

Remember, also, that the order of the reaction also affects rate!
the previous kinetic argument tells us little about the energetics (or thermodynamics) of the reaction. We can surmise that if A is spontaneously converted to B under normal conditions then B is likely to be more stable than A (assuming this is not an entropy driven rxn). If B is indeed more stable then we can draw the corresponding Arrhenius plot. This plot represents the exothermic situation described thus the reaction enthalpy (ΔH) is negative, because energy is released in the formation of B. That is not the entire picture however before the reaction can proceed, some energy must be put into the system to reach the transition state. This is the activation energy. The rate of the reaction depends on $E_a$ directly.

It is common sense that a large $E_a$ would result in a slow reaction because few molecules would have high enough energy to overcome the transition state. This relationship was expressed in the equation:

$$k = A e^{-E_a/RT}$$

where $k$ is rate constant, $A$ is the Arrhenius factor, $E_a$ is the activation energy, $R$ is the gas constant and $T$ is the temperature. An important consequence of this relationship is that increasing temperature will increase the rate of both endothermic and exothermic reactions. This does not imply that increasing temperature will get you product. Recall Le Chatelier’s principle if the reaction is exothermic, increasing temp adds heat to the product and will shift the equilibrium back towards reactants.
In coordination chemistry, stability can have many meanings. In the literature, you will come across discussions of thermodynamic and kinetic stability. It is very important you know the difference!

Consider these situations:

In this process, A is converted to B through two mechanisms. While the ΔH remains the same, the lower energy pathway will happen more quickly and if the Ea values are far apart in energy, it may be the only pathway accessible at the reaction conditions.

In this process, the Ea for A* is lower, thus even though A* is thermodynamically less stable than A, the process A* → B will be kinetically favored over A → B due to the lower activation energy.

Taking this a step further, say one reactant can produce two different products; B + C and C is thermodynamically more stable than B. You might assume that C would be produced in a larger quantity due to its thermodynamic stability. You would be correct only if the activation energy was the same for both. If however, Ea is lower for A → B, you can produce a product composed mostly of B, this product is called the kinetic product. Recap: B - kinetic product    \[ \text{E}_a(B) < \text{E}_a(C) \]    C - thermodynamic product
Nothing discussed tells us definitively if a reaction will proceed spontaneously. We know intuitively, highly exothermic reactions are spontaneous (think bomb!)

Recall from gen chem the ΔH isn’t the whole story...

\[ ΔG = ΔH - TΔS \]

Gibbs Free Energy

When ΔG < 0 a reaction will be spontaneous. When ΔG > 0 the process will spontaneously reverse, and when ΔG = 0 the system is at equilibrium.

Recall for idealized gas phase reactions:

\[ ΔG = -RT \ln K_p + ΔG^\circ + RT \ln Q_p \]

\[ K_p = \frac{-ΔG}{RT} \]

K is the equilibrium constant!

(\( K \) is the rate constant - VERY DIFFERENT)

Combining these relationships we get a very important equation:

\[ ln K = -\frac{ΔH^\circ}{R} \left( \frac{1}{T} \right) + \frac{ΔS^\circ}{R} \]

(\( ln K \) form of Clausius Clapeyron)

This relates the equilibrium constant to temp, \( ΔH^\circ + ΔS^\circ \) and gives us a method for calculating \( ΔS^\circ \) and \( ΔH^\circ \) from values of \( K \) and \( T \), which are measurable.
Inorganic Reactions

Ligand Substitution  \[\rightarrow\]  redox catalyzed substitution

oxidative addition

Electron Transfer  \[\rightarrow\]  redox catalyzed insertion

This classification shows that the reaction types are interrelated and at times it is difficult to classify a reaction as a single category. Additionally, some metal complexes may be readily undergo ligand substitution but slow to react in electron transfer. This behavior is classified as labile or inert.

labile - rapidly undergo reaction < 1 min (mixing time)

inert  

- slow to react > 1 min

Kinetically robust

Unfortunately, this terminology does not distinguish between the thermodynamic and kinetic reasons behind why a particular complex is slow (or quick) to react. For example, a complex that is inert to a particular reaction may be so because it is thermodynamically stable relative to product or it is kinetically inert (high Ea). \[\left[\text{Fe(H}_2\text{O)}_5\text{F}^{2+}\right] \] is very stable (large k_eq) but is labile to substitution (small \(\Delta G^{\circ}\)). An example is:

\[
\left[\text{Co(NH}_3)_6\text{]}^{3+} + \text{H}_2\text{O}^+ \rightleftharpoons \left[\text{Co(OH}_2\text{)}_6\text{]}^{3+} + \text{NH}_4^+ \]  \(\Delta G^{\circ} < 0\)
Ligand Substitution

Ligand substitution commonly occurs in octahedral, tetrahedral and square planar coordination complexes. Substitution does occur in other geometries but it is not as well studied.

What is ligand substitution? When one ligand X is replaced by another Y

\[ ML_5X + Y \rightarrow ML_5Y + X \]

\[ K = \frac{[ML_5Y][X]}{[Y][ML_5X]} \]

Consider the substitution of the hexaaqua complex \( M(OH_2)_6^{2+} \) with neutral \( L \)

\[ M(OH_2)_6^{2+} + L \rightleftharpoons M(OH_2)_5L + H_2O \]

\[ K = \frac{[M(OH_2)_5L][H_2O]}{[M(OH_2)_6^{2+}][Y]} \]

or more commonly

\[ K = \frac{[ML]}{[L][M^{n+}]} \]

for a solvated metal ion.

This substitution can occur up to 6 times:

1.) \( M^{n+} + L \rightleftharpoons ML^{n+} \)

\[ K_{f1} = \frac{[ML]}{[M^{n+}][L]} \]

Typically:

\[ K_{f1} > K_{f2} > K_{f3} > K_{f4} > K_{f5} > K_{f6} \]

2.) \( ML^{n+} + L \rightleftharpoons ML_2^{n+} \)

\[ K_{f2} = \frac{[ML_2^{n+}]}{[ML^{n+}][L]} \]

3.) \( ML_2^{n+} + L \rightleftharpoons ML_3^{n+} \)

\[ K_{f3} = \frac{[ML_3^{n+}]}{[ML_2^{n+}][L]} \]

4.) \( ML_3^{n+} + L \rightleftharpoons ML_4^{n+} \)

\[ K_{f4} = \frac{[ML_4^{n+}]}{[ML_3^{n+}][L]} \]

5.) \( ML_4^{n+} + L \rightleftharpoons ML_5^{n+} \)

\[ K_{f5} = \frac{[ML_5^{n+}]}{[ML_4^{n+}][L]} \]

6.) \( ML_5^{n+} + L \rightleftharpoons ML_6^{n+} \)

\[ K_{f6} = \frac{[ML_6^{n+}]}{[ML_5^{n+}][L]} \]

\[ M^{n+} + 6L \rightleftharpoons ML_6^{n+} \]

\[ K_{overall} = \beta = \frac{[ML_6^{n+}]}{[M^{n+}][L]^6} \]
In substitution there are general rules for predicting whether a particular coordination complex will be inert or labile with respect to ligand substitution. Based on d<sup>n</sup> configuration:

<table>
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<tr>
<th>Inert</th>
<th>Intermediate</th>
<th>Labile</th>
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<tbody>
<tr>
<td>d&lt;sup&gt;8&lt;/sup&gt;</td>
<td>weak-field d&lt;sup&gt;8&lt;/sup&gt;</td>
<td>d&lt;sup&gt;1&lt;/sup&gt;, d&lt;sup&gt;2&lt;/sup&gt;</td>
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<tr>
<td>d&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>high-spin: d&lt;sup&gt;4&lt;/sup&gt;, d&lt;sup&gt;5&lt;/sup&gt;, d&lt;sup&gt;6&lt;/sup&gt;</td>
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<td>low-spin: d&lt;sup&gt;4&lt;/sup&gt;, d&lt;sup&gt;5&lt;/sup&gt;, d&lt;sup&gt;6&lt;/sup&gt;</td>
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<td>d&lt;sup&gt;7&lt;/sup&gt;, d&lt;sup&gt;8&lt;/sup&gt;, d&lt;sup&gt;9&lt;/sup&gt;, d&lt;sup&gt;10&lt;/sup&gt;</td>
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HIGH LFSE

These trends can generally be reasoned through by looking at the stability of the d<sup>n</sup> electron configuration.

Inert:

\[
\begin{align*}
\text{Inert:} & & \text{Inert:} \\
d^8 & = & d^9 \\
\pm tz_g^3 & = & \pm tz_g^4
\end{align*}
\]

These two configurations are recognizably inert to substitution because they are in an "especially stable" configuration.

Labile:

\[
\begin{align*}
\text{Labile:} & & \text{Labile:} \\
d^9 & = & d^{10} \\
\pm eg^2 & = & \pm eg^4 \\
\pm tz_g^4 & = & \pm tz_g^5
\end{align*}
\]

Analogously any complex with a high large LFSE is likely to be inert to substitution. Note also that all these configurations have occupied tzg (non-bonding) and empty eg (antibonding between M-L)

These config. have electrons in the M-L antibonding eg orbital. Populating this orbital will increase ligand lability.