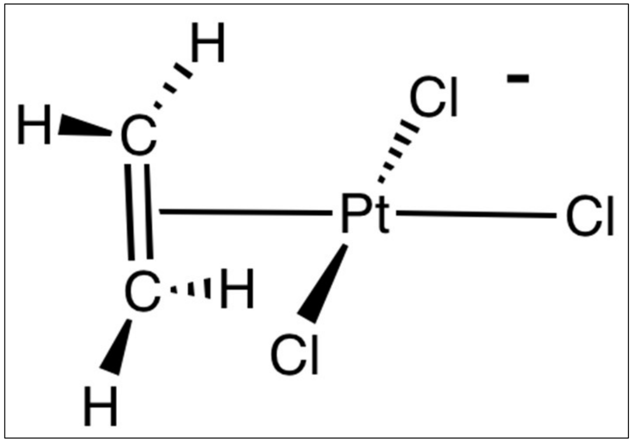
Ligands and Metals

In inorganic and organometallic compounds, the metal is the most important thing.

A “ligand” is a chemical species (“moiety”) somehow bonded to the metal:

- Organometallic compounds have at least one carbon-metal bond
- Inorganic compounds don’t have any



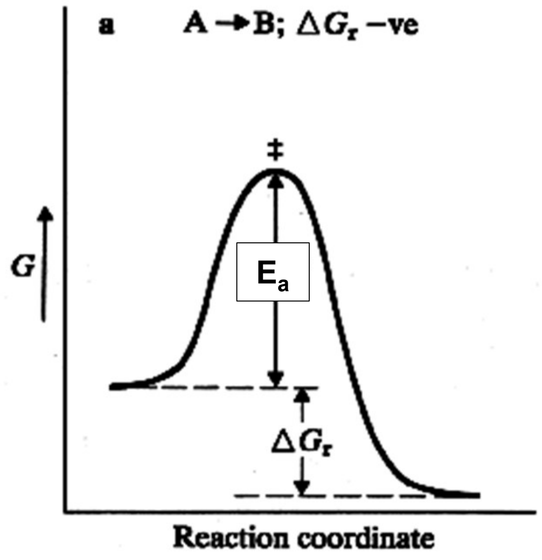
Zeise’s salt: this compound is organometallic, and it was one of the first prepared ever prepared.

It indicates a lot of issues we will talk about.

Zeise, W. C. "Von der Wirkung zwischen Platinchlorid und Alkohol, und von den dabei entstehenden neuen Substanzen" [On the reaction between platinum chloride and alcohol, and its resulting new substances]. *Ann. Phys. Chem*. **1831**, 97, 497. doi:10.1002/andp.18310970402.

Activation Energy

The reaction coordinate is an energy diagram where the x-axis represents how far along the chemical is.



In this case, A → B goes through an intermediate A‡. A‡ is the transition state, and is at a higher energy than the reactants or products.

Not that this diagram shows a thermodynamically favoured reaction, where ΔG_r is negative. The reverse reaction is thermodynamically unfavourable.

Arrhenius Equation

The activation energy can be measured from the reactants to the transition state and demonstrate the necessary energy to “be allowed” to go to products.

$$k = Ae^{\frac{-E_a}{RT}}$$

It’s straightforward to approximate the activation energy from knowing the rate and time from a reaction. Rearrange the Arrenius equation to a y = mx + b form:

$$\ln(k) = \frac{-E_a}{R}\frac{1}{T} + \ln(\mathrm{A})$$

y = ln(k), x = 1/T, and:

$$m = \frac{-E_a}{R} = \frac{\partial(\ln(k))}{\partial\left(\frac{1}{T}\right)} \qquad E_a = -R\,\frac{\partial(\ln(k))}{\partial\left(\frac{1}{T}\right)} \sim -R\,\frac{\Delta(\ln(k))}{\Delta\left(\frac{1}{T}\right)}$$

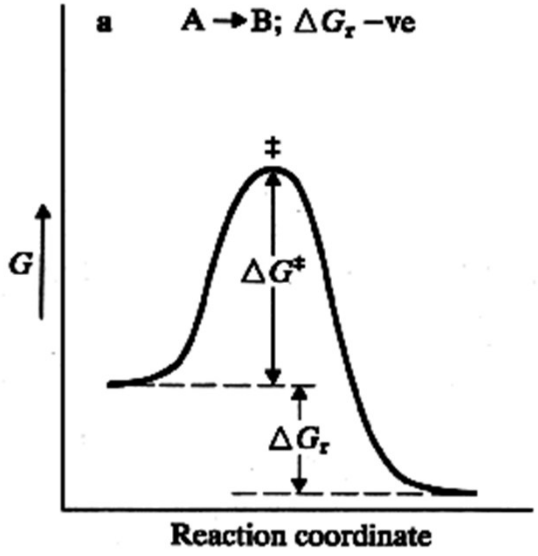
Transition State Theory

The Eyring equation from Transition State Theory can be written in the form of the Arrehnius equation:

$$k = Ae^{\frac{-E_a}{RT}} \qquad k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

This relates the transition Gibbs free energy to Boltzmann's (k_b) and Planck's (h) constants.

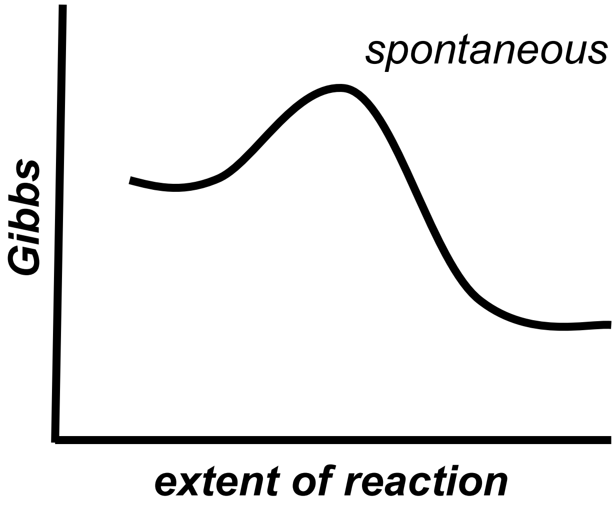
Linearization of the Eyring equation can solve $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

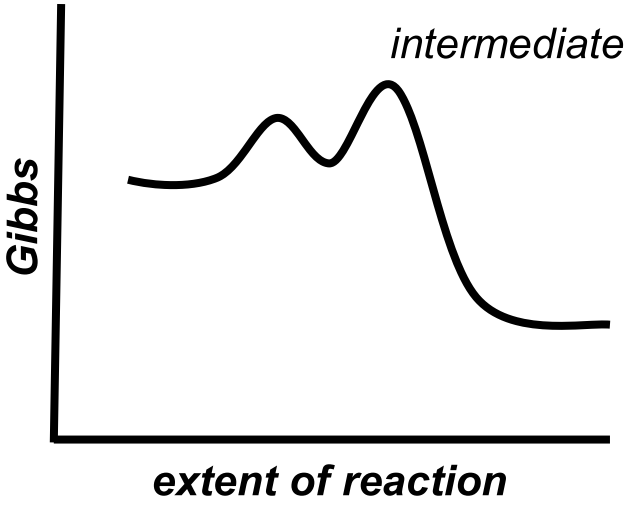


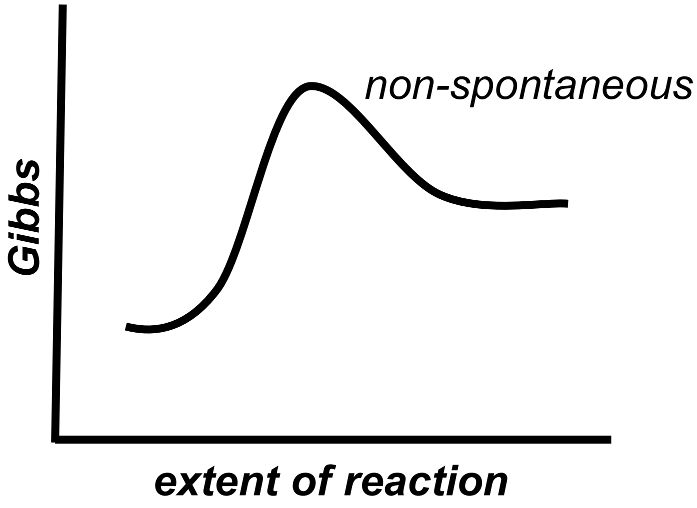
A derivation of Eyring can be found here:

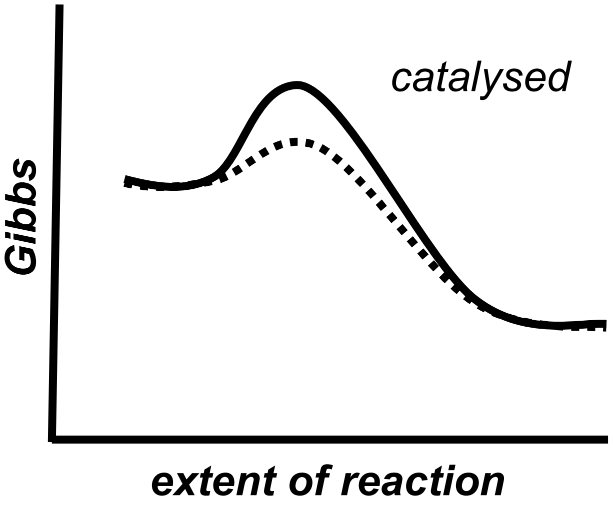
http://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Kinetics/Modeling_Reaction_Kinetics/Transition_State_Theory/Eyring_equation

Different Reaction Coordinates


spontaneous


intermediate


non-spontaneous


catalysed

Substitution Reaction

This is obviously replacing one ligand with another:

$$\underbrace{Cu(H_2O)_6^{2+} + 4\ NH_3\ (aq)}_{} \rightarrow Cu(NH_3)_4(H_2O)_2^{2+} + 4\ H_2O$$

$$Cu(H_2O)_6^{2+} + \underset{\textit{nucleophile}}{4\ NH_3\ (aq)} \rightarrow Cu(NH_3)_4(H_2O)_2^{2+} + \underset{\textit{leaving group}}{4\ H_2O}$$

Other ligands not directly involved in substitution process are called "spectator ligands".

Two classes of complexes:

- Inert – React very slowly (more robust)
- Labile – React very quickly (half-life ≤ 1 min)

Not the same as "stable" and "unstable"
(thermodynamic terms)

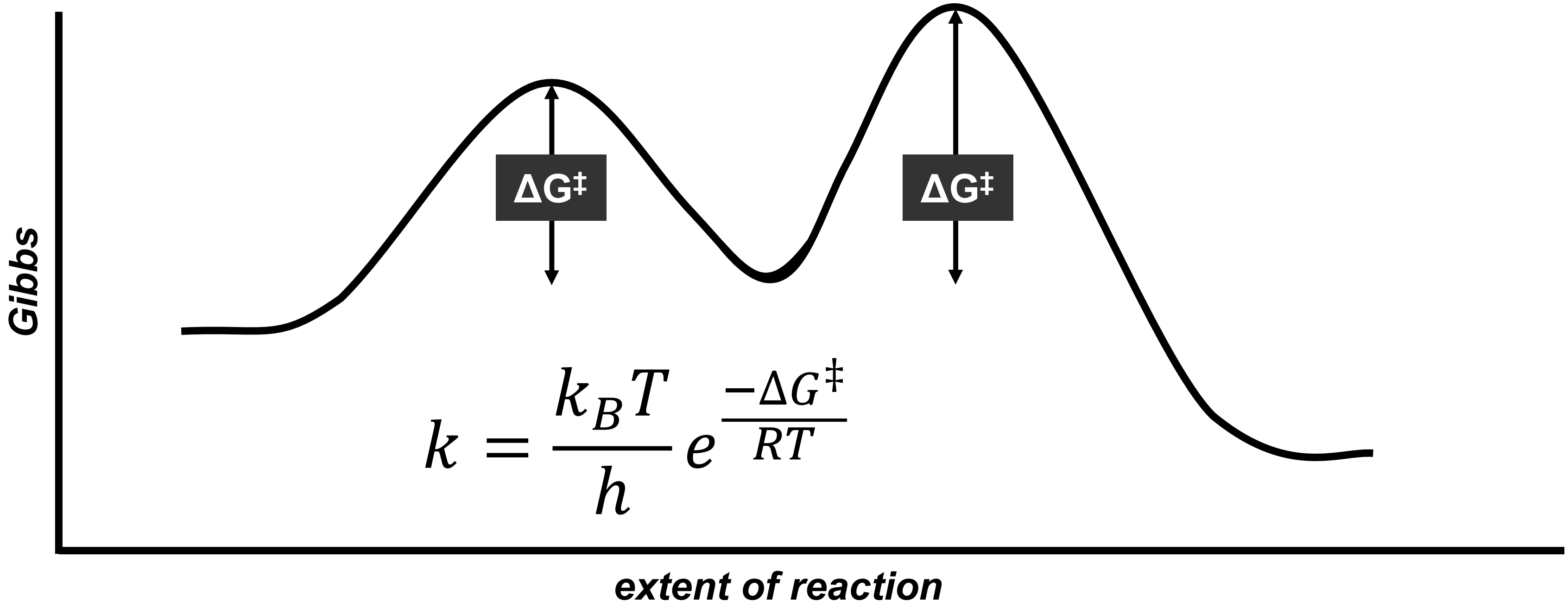
Thermodynamic vs. Kinetic Product

A thermodynamic product has the lower product energy. Given all the time and energy needed, this is where the system ends up.

- The thermodynamic product takes time to get to, and is the endpoint of the reaction

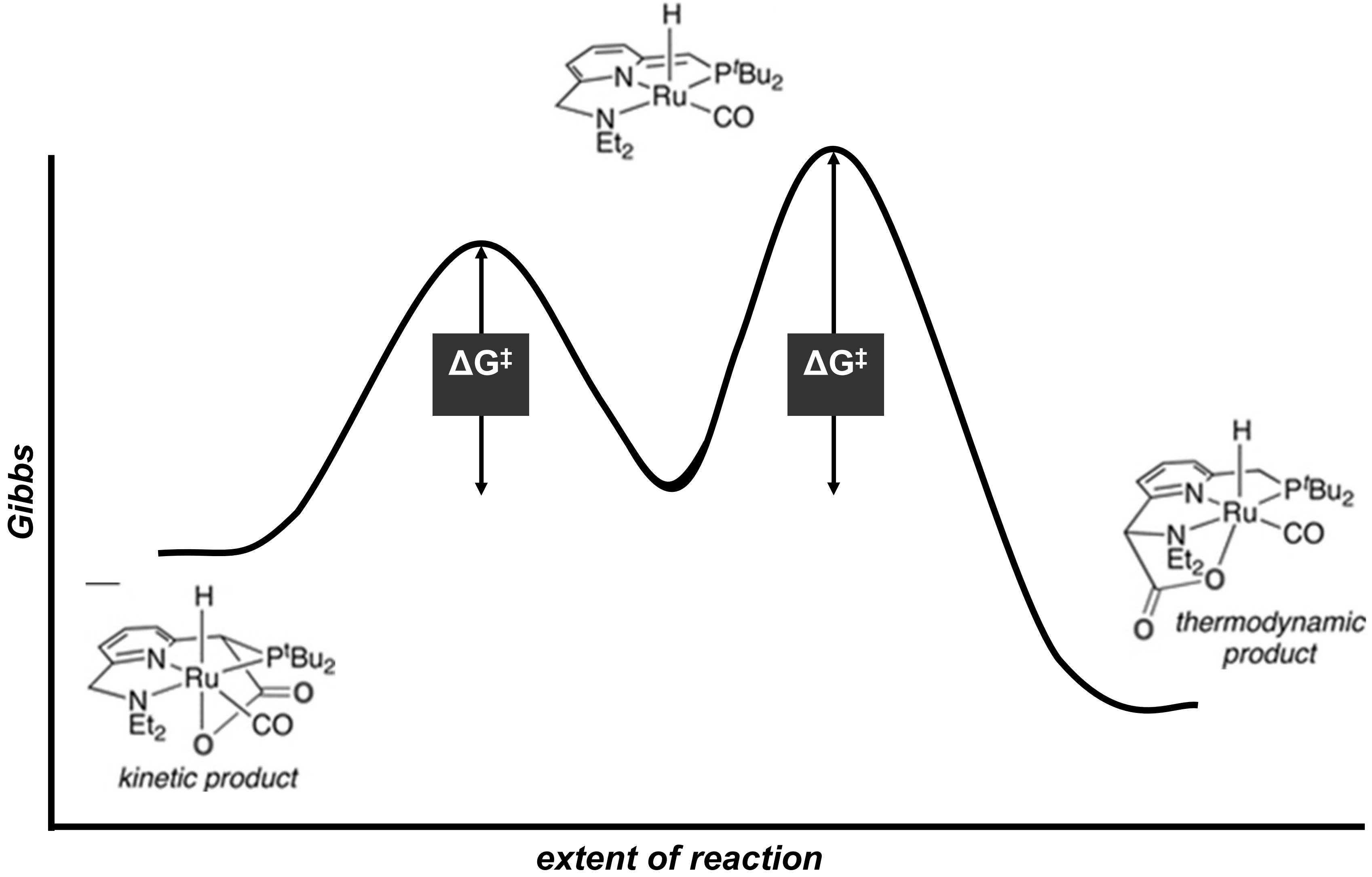
The kinetic product has a lower activation energy , and so (according to Eyring), the faster rate.

- The kinetic product happens quickly, but is not the endpoint.



$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

Kinetic vs. Thermodynamic



Hickman, A. J.; Sanford, M. S. *Nature* **2012**, *484*, 177–185.

Effects of Kinetic vs. Thermodynamic Products

This type of reactivity can determine the outcome of a chemical transformation (usually as an isomerization).

1

Here the example is:

1. Association/Dissociation Substitution
2. Nucleophilic attack
3. Anti-Markovnikov vs. Markovnikov substitution

2

3

Timokhin, V. I.; Stahl, S. S.
J. Am. Chem. Soc. **2005**, *127*, 17888–17893.

Labile vs. Inert Substitutions

Substitution of water from a metal cation is generally fast

- rates can vary by 15 orders of magnitude

Generally, low-spin (high field) d^3-d^6 systems are inert, as well as strong filed square planar complexes.

- maybe inaccessible e_g levels are to blame

d_1, d_2 and high-spin (weak field) d^4-d^6 systems are labile.

$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$

Enthalpy of Activation:

- Bonds are weakened before new bonds are formed
- Included inner and outer spheres
- Usually, $\Delta H^{\ddagger} > 0$

Entropy of Activation:

- Bringing molecules together in an activated state increases order, $\therefore$ $\Delta S^{\ddagger} < 0$ (association)
- If a bond breaks in the activated state, that leads to greater disorder, $\therefore \Delta S^{\ddagger} > 0$ (dissociation)

These terms can help us to determine the mechanism of a substitution reaction.

Linearization of Eyring Equation

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta G^{\ddagger}}{RT} + ln\left(\frac{k_B}{h}\right)$$

$$\ln\left(\frac{k}{T}\right) = \frac{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})}{RT} + ln\left(\frac{k_B}{h}\right)$$

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + ln\left(\frac{k_B}{h}\right)$$

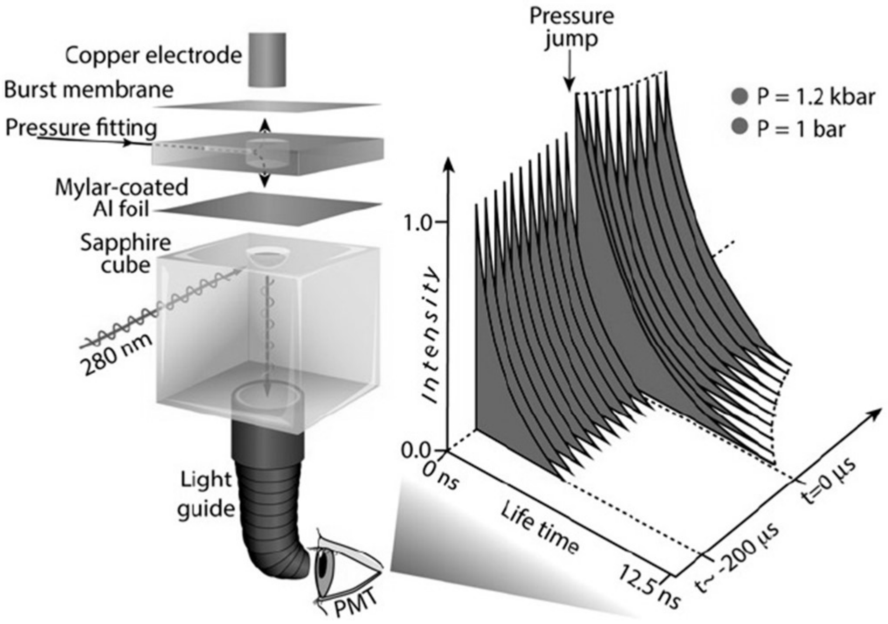
Volume of Activation V‡

$$\frac{d(\ln(k))}{dp} = \frac{\Delta V^{\ddagger}}{RT}$$

The volume of activation is good to use when there's no change in complex charge in the activated state. It is an easy to measure state variable that can distinguish I and D:

- If $\Delta V^{\ddagger} < 0$, molecules are brought together in the activated state (association)
- If $\Delta V^{\ddagger} > 0$, a molecule is broken apart in the activated state (dissociation)

Pressure Jump Experiments



Somewhat unrelated to organometallic chemistry, pressure “jump” experiments seem to mainly be used to observe protein folding.

The concept is simple: pressure is changed instantly by bursting a membrane, and the shift in the rate can be converted into a change in the volume of the transition state (indicating associative or dissociative mechanisms)

$$\frac{d(\ln(k))}{dp} = \frac{\Delta V^{\ddagger}}{RT}$$

Types of Substitutions

Dissociative (*D*): Departing ligand leaves and an intermediate with a lower coordination number is formed. Then the new ligand is added.

Associative (*A*): Incoming ligand adds to the complex and an intermediate is formed with an increased coordination number. Then the departing ligand leaves.

Interchange (I, I_d, I_a): Anything in between these two extremes. Incoming ligand assists in the reaction but no intermediates are detectable. These can be labeled $\mathrm{I_d}$ and $\mathrm{I_a}$.

Dissociate Substitution

$ML_6 \rightarrow ML_5 + L$

(rate limiting step)

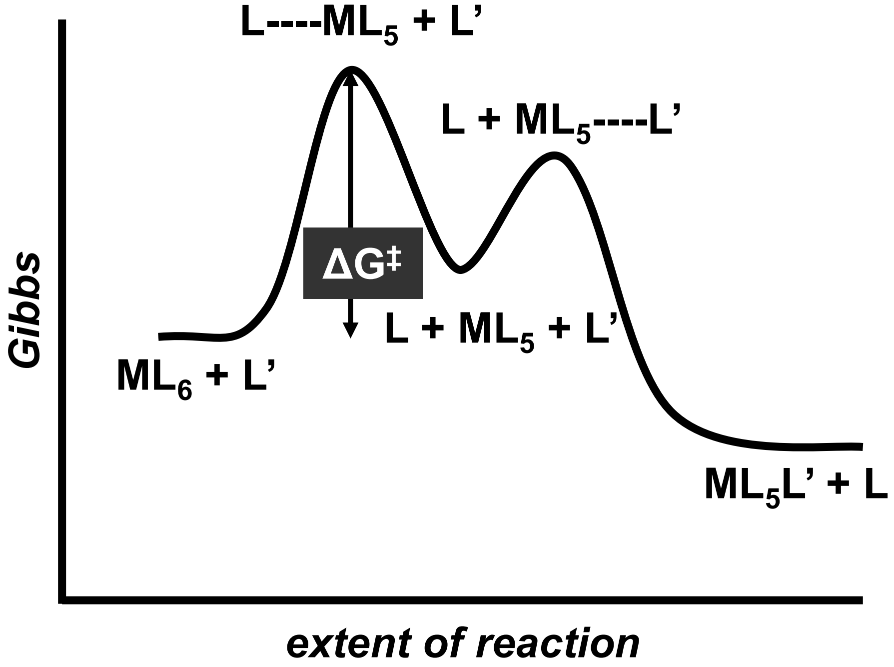
$ML_5 + L' \rightarrow ML_5L'$

(fast)

Rate Law

$$\frac{-d[ML_6]}{dt} = k[ML_6]$$

This is independent of L’



Associative Mechanism

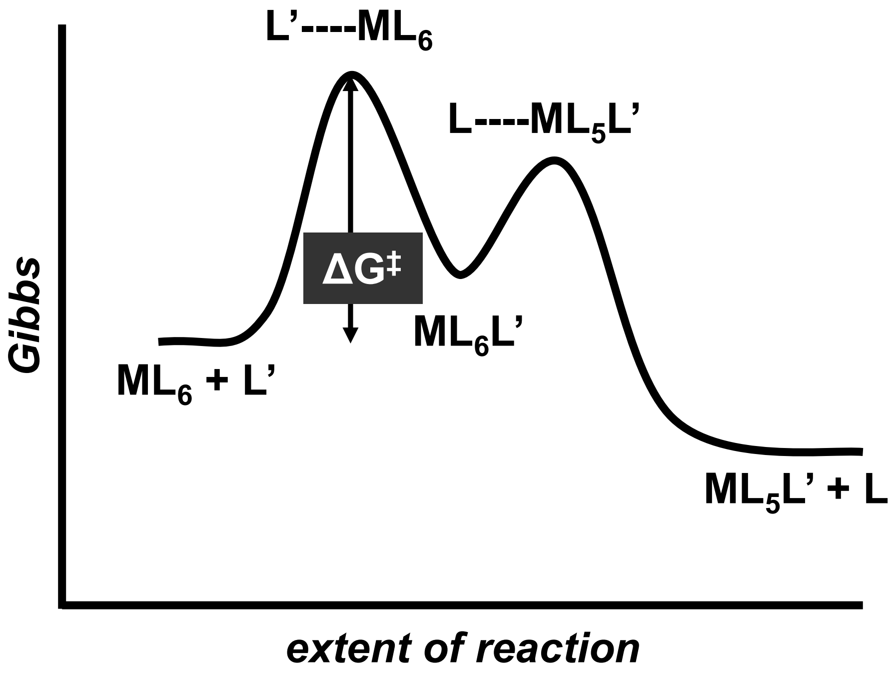
$L' + ML_6 \rightarrow ML_6L'$

(rate limiting step)

$ML_6L' \rightarrow L'ML_5 + L$

Rate Law:

$$-\frac{d[ML_6]}{dt} = k[ML_6][L']$$



This is dependent on L’, usually independent of leaving group

Intermediate Mechanism

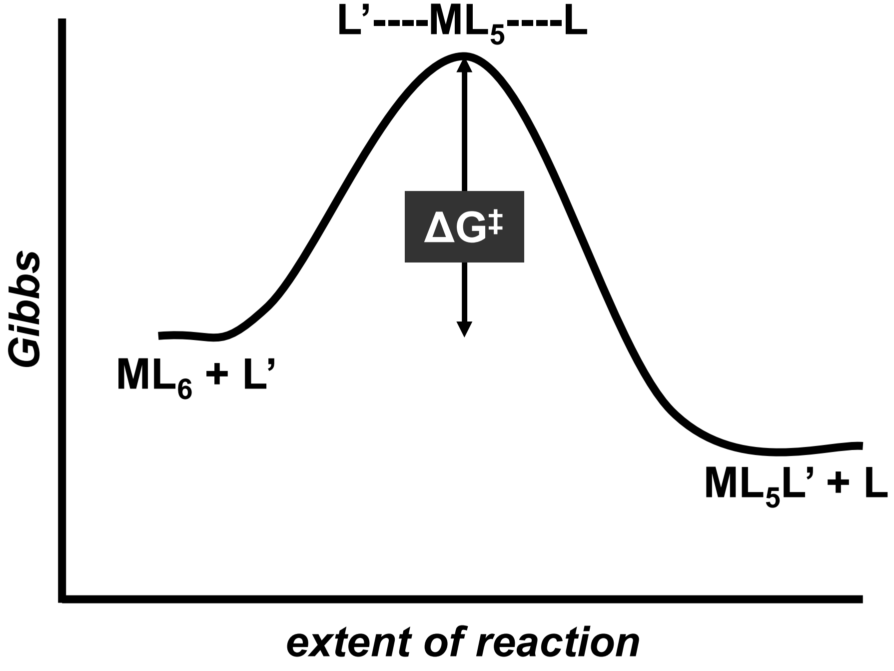
In between *A* and *D* mechanisms:

L' + M-L → [L'---M----L] → L'M + L
(Bond formation) (Bond breaking)

No detectable intermediates, and further divided into I_a and I_d.

Rate Law:

$$-\frac{d[ML_6]}{dt} = k[ML_6][L']$$



Stoichiometric vs. Intimate Mechanisms

Many reactions are described as I_d or I_a rather than *D* or *A*. This means that the kinetic data points to an association or a dissociation, but detection of intermediate species is not possible.

Stoichiometric Mechanisms: I_d, I_a ,*D*, *A*.

- deals with the rate laws entirely

Intimate Mechanisms: Dissociative and Associative

- deals with the nature of the activated state

Dissociative (D or I_d)

from experiment

1. Rate of reaction changes only slightly or not at all with changes in the incoming ligand
    - Aquation (incoming ligand is water) and anation (incoming ligand is an anion) are similar

2. Increasing positive charge on complex decreases the rate of substitution

3. Steric crowding from other ligands increases rate of substitution

4. Rate of reaction correlates with metal-ligand bond strength (i.e. it has a linear free energy relationship)

5. Activation energies, entropies and volumes are consistent with dissociation

O_h Substitution

For most 6-coordinate complexes, steric hindrance usually prevents expansion to 7-coordinate intermediate. Thus the mechanism is typically dominated by bond breakage:

- Primarily I_d mechanism

Exceptions occur with large ions (e.g lanthanides) or with empty t_{2g} orbital sets:

- Large enough to allow for expansion
- Space for extra electrons
- Primarily I_a mechanism

From O_h to Square Pyramidal

Considering only ligand field stabilization energy (LFSE) change from octahedral to square pyramidal, the ligand field activation energy can be calculated.

high spin, weak field

octahedral *square pyramidal*

electrons	**LFSE (O_h)**	**LFSE (SqPy)**	**LFAE**
0, 10	0.00	0.00	0.00
1, 6	-0.400	-0.457	-0.057
2, 7	-0.800	-0.914	-0.114
3, 8	**-1.200**	**-1.000**	**0.200**
4, 9	-0.600	-0.914	-0.314
5	0.00	0.00	0.00

Calculating the d^7 Case

Considering only ligand field stabilization energy (LFSE) change from octahedral to square pyramidal, the ligand field activation energy can be calculated.

high spin, weak field

octahedral

square pyramidal

electrons	**LFSE (O_h)**	**LFSE (SqPy)**	**LFAE**
0, 10	0.00	0.00	0.00
1, 6	-0.400	-0.457	-0.057
2, 7	-0.800	-0.914	-0.114
3, 8	**-1.200**	**-1.000**	**0.200**
4, 9	-0.600	-0.914	-0.314
5	0.00	0.00	0.00

From O_h to Square Pyramidal

Considering only ligand field stabilization energy (LFSE) change from octahedral to square planar, the ligand field activation energy can be calculated.

low spin, strong field

electrons	LFSE (O_h)	LFSE (SqPy)	LFAE
0, 10	0.00	0.00	0.00
1	-0.400	-0.457	-0.57
2	-0.800	-0.914	-1.14
3	**-1.200**	**-1.000**	**2.00**
4	**-1.600**	**-0.914**	**0.686**
5	**-2.00**	**-1.371**	**0.629**
6	**-2.400**	**-1.828**	**0.572**
7	-1.800	-1.914	-0.114
8	-1.200	-1.828	-0.628
9	-0.600	-0.914	-0.314

octahedral *square pyramidal*

Calculating the d^7 Case

Considering only ligand field stabilization energy (LFSE) change from octahedral to square planar, the ligand field activation energy can be calculated.

low spin, strong field

octahedral *square pyramidal*

electrons	**LFSE (O_h)**	**LFSE (SqPy)**	**LFAE**
0, 10	0.00	0.00	0.00
1	-0.400	-0.457	-0.57
2	-0.800	-0.914	-1.14
3	**-1.200**	**-1.000**	**2.00**
4	**-1.600**	**-0.914**	**0.686**
5	**-2.00**	**-1.371**	**0.629**
6	**-2.400**	**-1.828**	**0.572**
7	-1.800	-1.914	-0.114
8	-1.200	-1.828	-0.628
9	-0.600	-0.914	-0.314

Electronic and Steric Trends

Size of M^{n+}

- Smaller metal (higher charge density) = stronger bonds

$[Sr(H_2O)_6]^{2+}$ (more likely than) $[Ca(H_2O)_6]^{2+}$ (more likely than) $[Mg(H_2O)_6]^{2+}$
112 pm 99 pm 66 pm

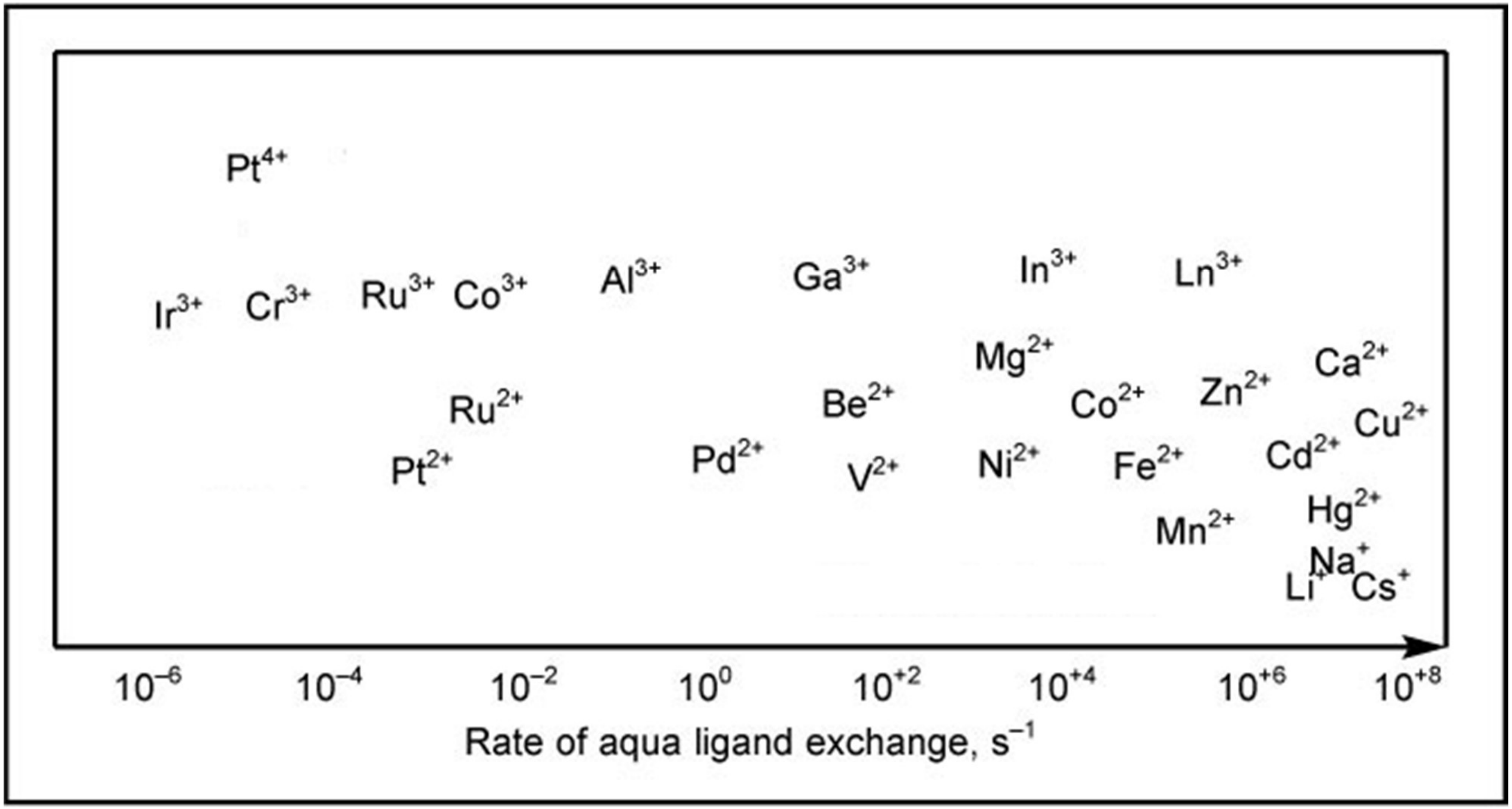
Charge (oxidation state) and Z_{eff}

- Higher charge/ oxidation state / Z_{eff} = stronger bonds

$[Na(H_2O)_6]^{2+}$ (more likely than) $[Mg(H_2O)_6]^{2+}$ (more likely than) $[Al(H_2O)_6]^{2+}$
1+ 2+ 3+

Stronger bonds = higher activation barrier
Higher activation barrier = slower exchange rate

A Variety of Aquation Rates



Base Hydrolysis Mechanism

Conjugate Base Mechanism

If a ligand can be constructed to be converted from “L” to “X^-”, then it can add stabilization to the metal centre.

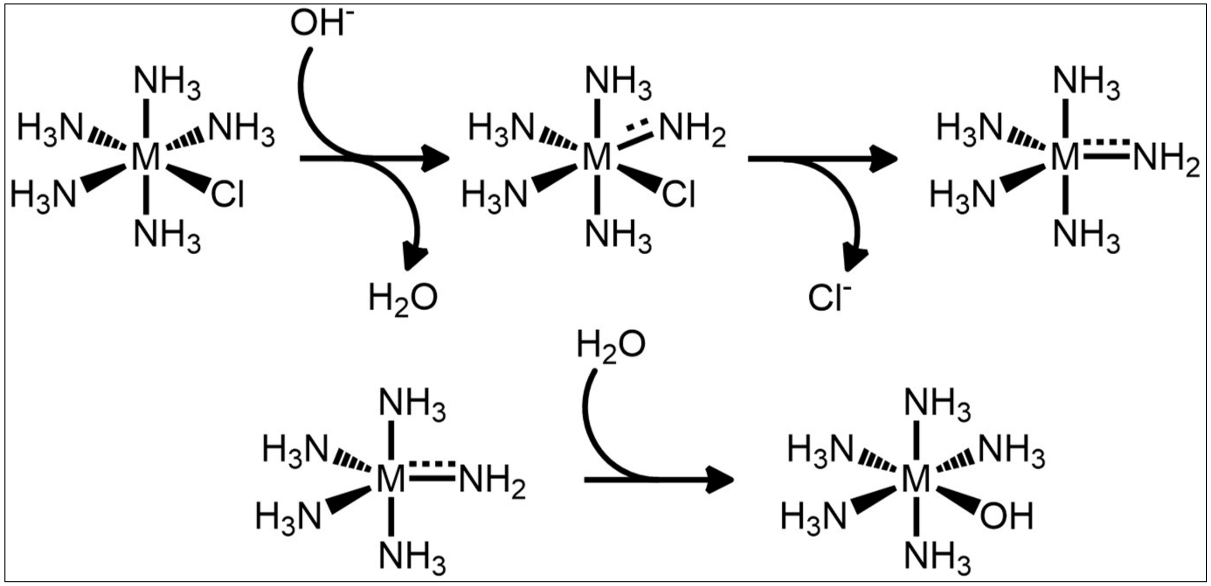
This can accelerate a reaction rate by a factor of up to 10^8

In the case of ammonia, it can be deprotonated to amido:

$$NH_3 + OH^- \rightarrow NH_2^- + H_2O$$

- Amido ligand (NH_2^-) is a strong π-donor ligand that stabilizes the 5-coordinate intermediate

Ammonia to Conjugate Base



1. $[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_4(NH_2)Cl]^{+} + H_2O$
2. $[Co(NH_3)_4(NH_2)Cl]^{+} \rightarrow [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$
3. $[Co(NH_3)_4(NH_2)]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH)]^{2+} + NH_3$

Association (A or I_a)

Experimental Evidence

1. This is less likely for octahedral complex, more likely for square planar because of steric considerations.
2. The rates of reaction are quite affected by changes in the entering group.
3. Steric crowding interferes with incoming ligand and slows the reaction.
4. Activation energies, entropies and volumes are consistent with association.

D_{4h} Substitution

$ML_3X + Y \rightarrow ML_3Y + X$

Associative Reaction mechanism:
There can be two contributing pathways.

The rate equation is:

Rate = $k_1[MX]_4 + k_2[MX_4][Y]$

This can be simplified in practice by using a pseudo-first order reaction (i.e., an excess of Y):

Rate = $k'[MX]_4$, where $k' = k_1+k_2[Y]$

Determining Rate Constants

Pseudo-first order reaction (i.e., an excess of Y):

Rate = $k'[MX]_4$, where $k' = k_1 + k_2[Y]$

If you graph the observed rate constant with [Y], the slope will be k_2 and the y-intercept will be k_1.

Here, $[PtCl_2py_2]$ shows different substitution rates in methanol

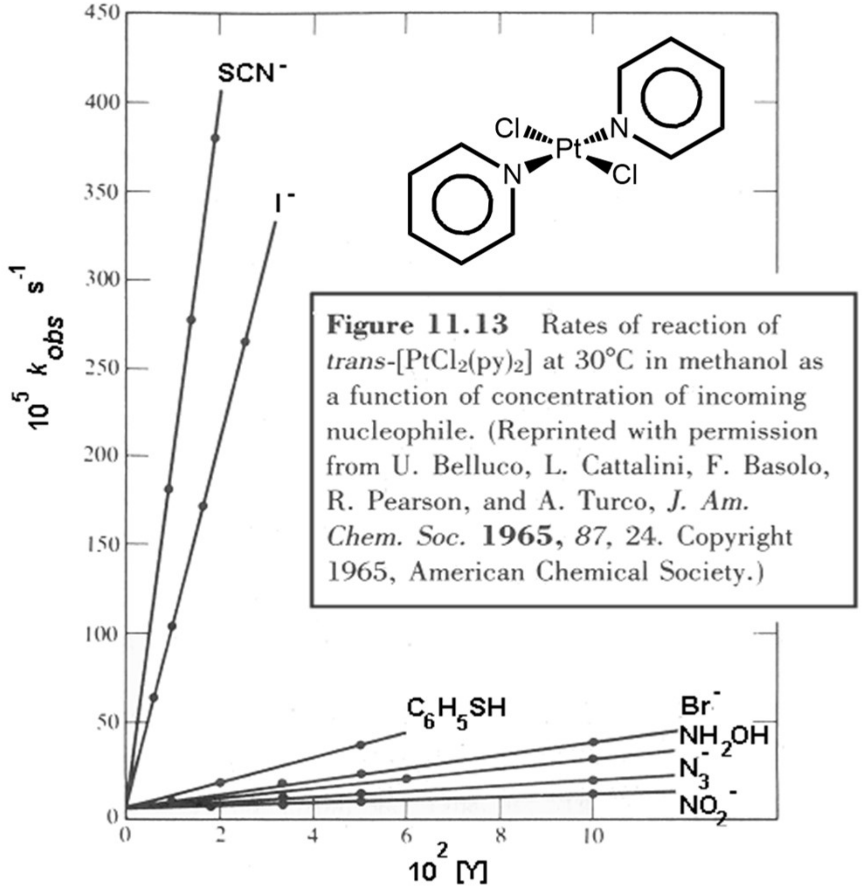
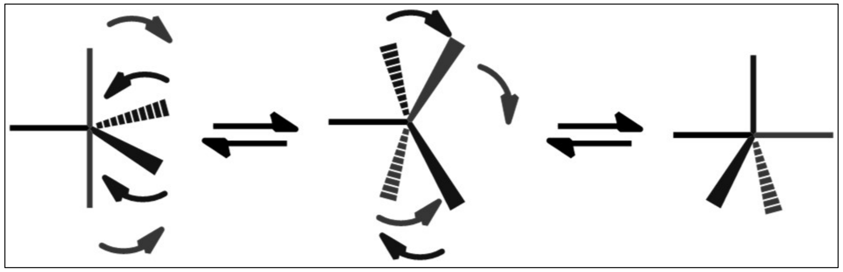


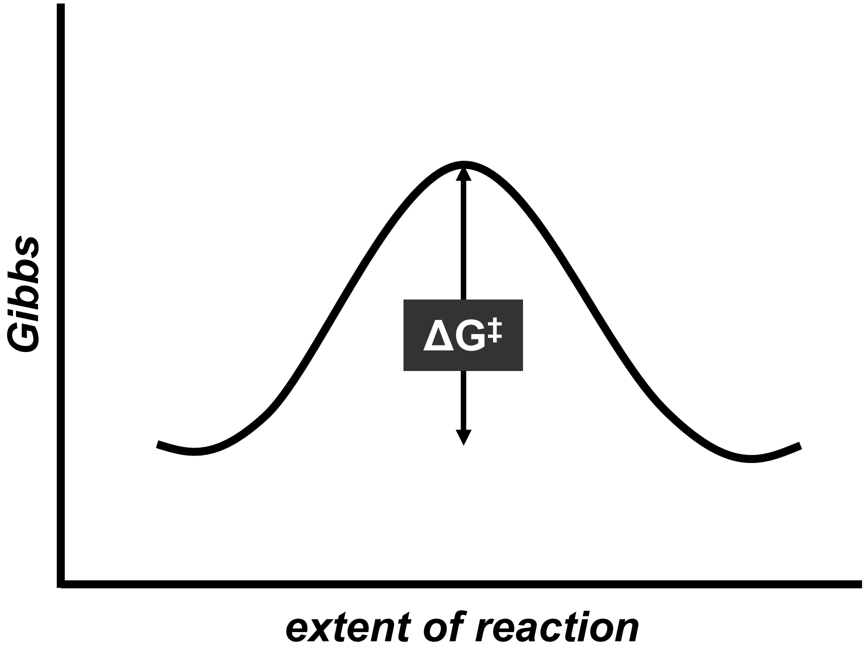
Figure 11.13 Rates of reaction of *trans*-$[PtCl_2(py)_2]$ at 30°C in methanol as a function of concentration of incoming nucleophile. (Reprinted with permission from U. Belluco, L. Cattalini, F. Basolo, R. Pearson, and A. Turco, *J. Am. Chem. Soc.* **1965,** *87*, 24. Copyright 1965, American Chemical Society.)

Berry Pseudo-Rotation



The interconversion of a square-based pyramid to a trigonal bipyramid is called the Berry pseudorotation.

This is important because it allows the axial and equatorial positions to scramble.

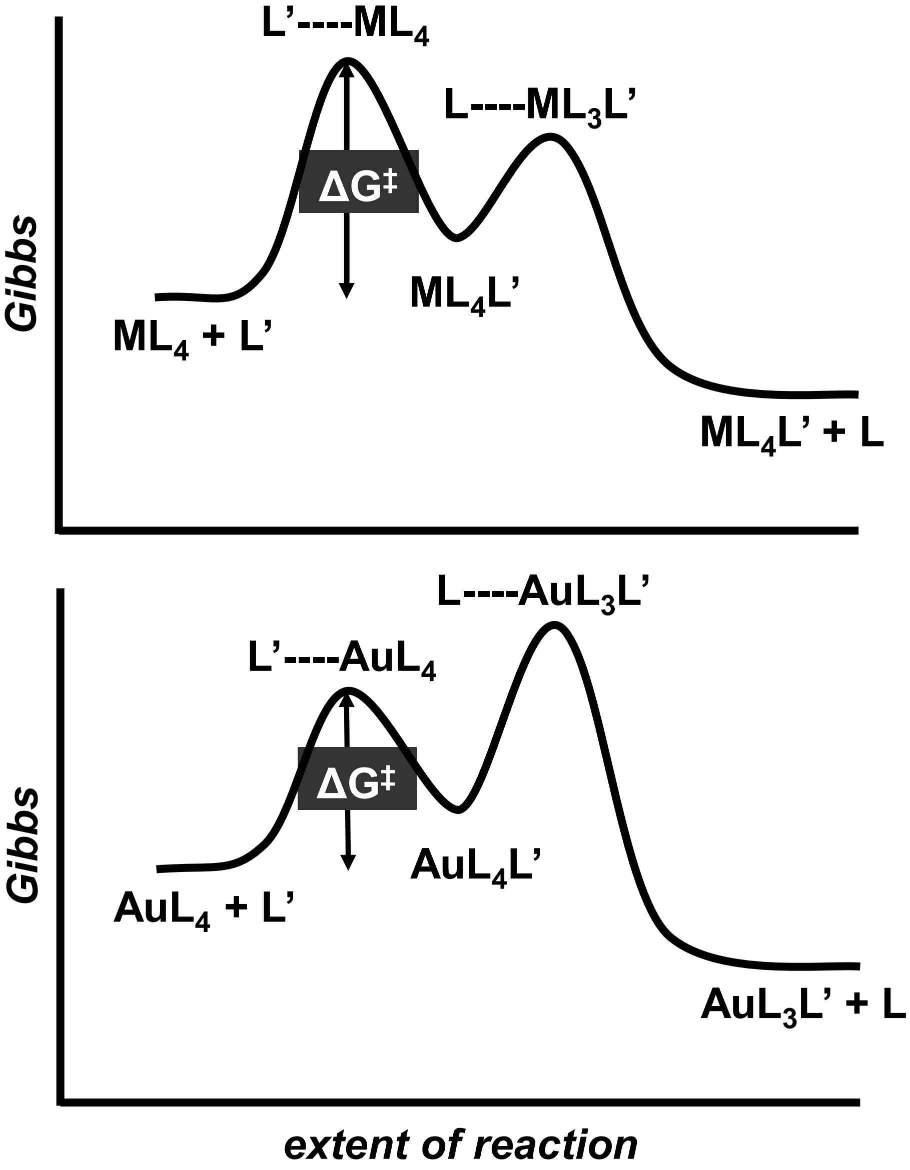


Pt/Pd vs. Au

For ligand substitution in Au(III) complexes (associative mechanism), the nature of the leaving group is important.

Why the difference between Pt(II)/Pd(II) and Au(III) potential energy diagrams?

- Higher oxidation state
- Stronger bond
- Harder to remove leaving group
- Higher activation barrier



Trans Effect

square planar Pt(II) complexes

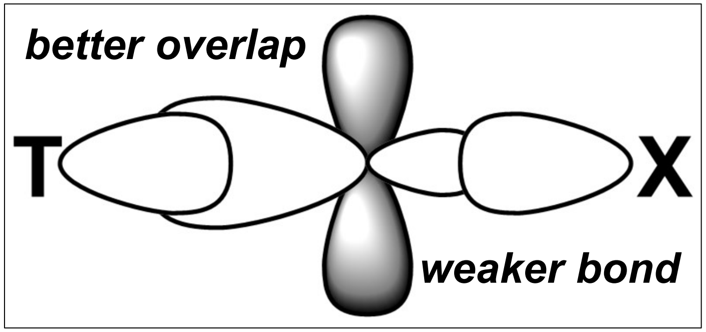
A strong "trans effect" ligand greatly accelerates the rate of substitution of the ligand that is *trans* (180°) to it.

This ability depends on both σ and π properties.

The greater the overlap of ligand's σ or π symmetry p-orbitals with the metal d orbitals (e.g. Pt^{2+}), the stronger the trans effect is.

- Weaken the Pt-X bond
- Stabilize the 5-coordinate intermediate

Explaining the Trans Effect



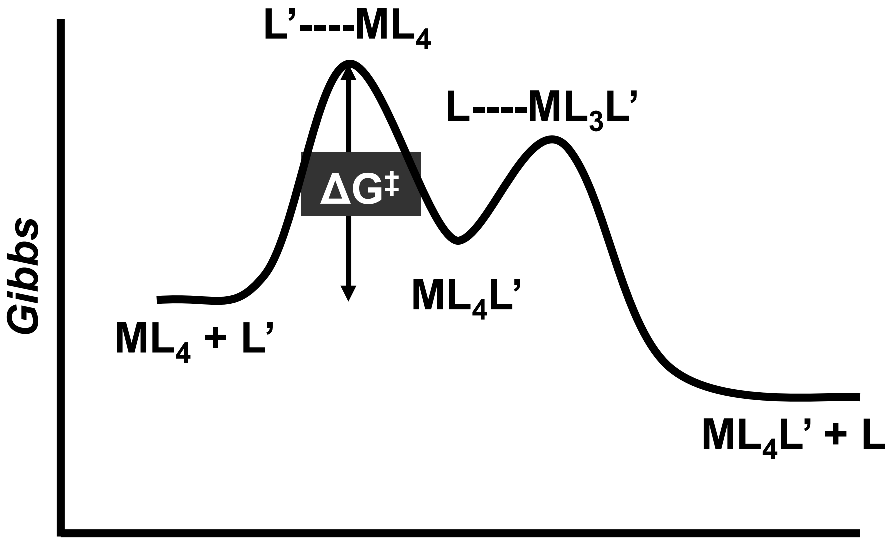
σ-donation:

- Pt-X bond is influenced
  by Pt-T bond
  (T = trans effect ligand)
- they both use the Pt p_x or d_{x2-y2} orbitals, which weakens the ground state

π-acceptor:

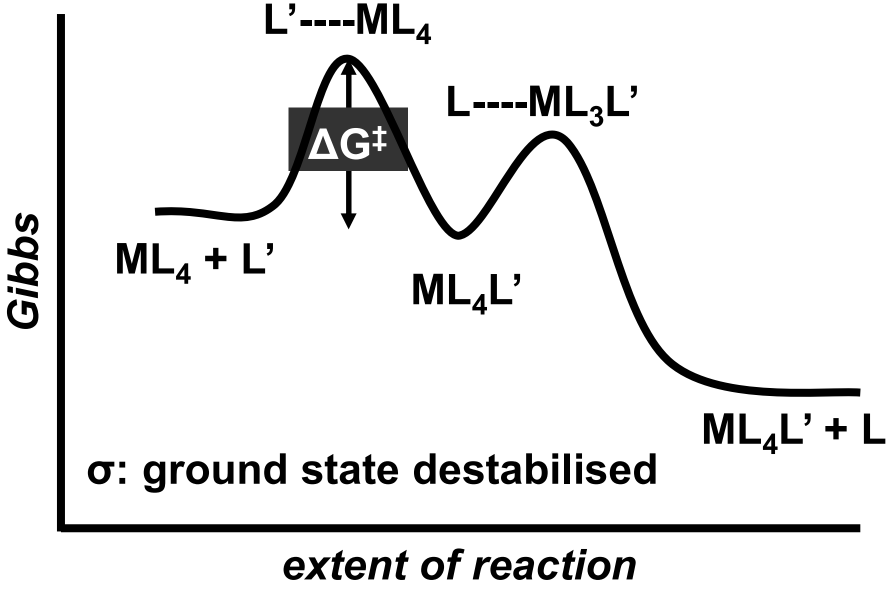
- A strong π-acceptor will pull electron density away from the metal (not shown)
- This makes it easier for another ligand to enter and so this stabilizes the intermediate

Trans Effect on Reaction Coordinate

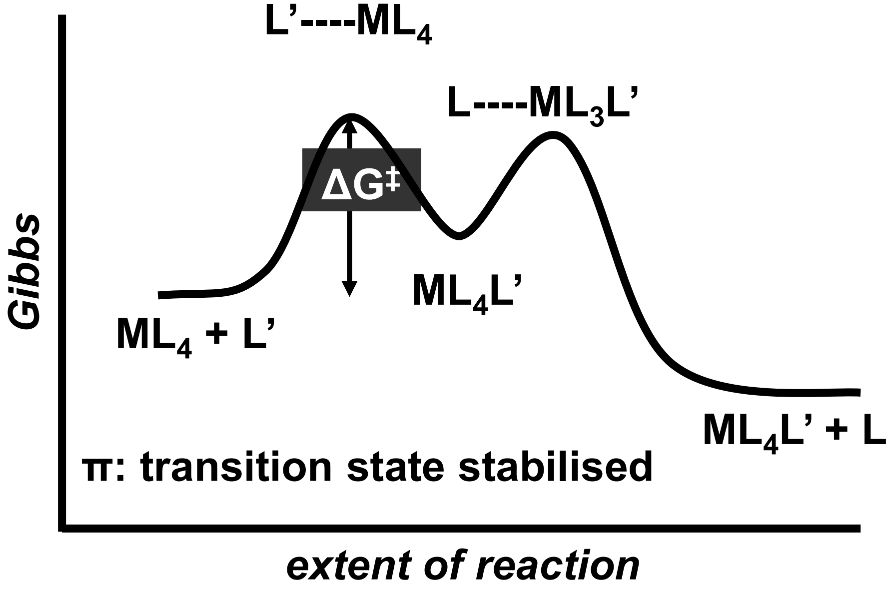


Stronger to weaker trans effectors:

$CO \approx CN \approx C_2H_4 > PR_3$
$\approx H^- > CH_3^- > NO_2^- \approx SCN^-$
$\approx I^- > Br^- > Cl^- > py \approx NH_3$
$\approx OH^- \approx H_2O$



σ: ground state destabilised



π: transition state stabilised

Trans Effect in Synthesis: Trans

Cl^- is more trans directing than NH_3, so we can substitute two chlorides on $[Pt(NH_3)_4]^{2+}$

- First chloro substitutes anywhere
- Second chloro will replace “trans” to the chloro

Stronger to weaker:

$CO \approx CN \approx C_2H_4 > PR_3 \approx H^- > CH_3^- > NO_2^- \approx SCN^- \approx I^- > Br^- >$ ***Cl^-*** $> py \approx$ ***NH_3*** $\approx OH^- \approx H_2O$

Trans Effect in Synthesis: Cis

Cl^- is more trans directing than NH_3, so we can substitute two chlorides on $[PtCl_4]^{2-}$

- First ammonia substitutes anywhere
- Second ammonia will replace "trans" to a chloro

Stronger to weaker:

CO ≈ CN ≈ C_2H_4 > PR_3 ≈ H^- > CH_3^- >NO_2^- ≈ SCN^- ≈ I^- > Br^- > ***Cl^-*** > py ≈ ***NH_3*** ≈ OH^- ≈ H_2O