Reaction kinetics and mechanisms in coordination compounds

The kinetics of inorganic reaction mechanism

The mechanism of a chemical reaction is understood from transition state theory. The course of a chemical reaction involves collision of reactants sufficiently energetic to form the **activated complex** or **transition state**.

Along the path from reactants to products kinetic energy is converted into potential energy by bond stretching, partial bond formation, angular distortions etc.

The transition state is the species of maximum potential energy resulting from these motions. All energetically unfavourable processes have occurred by the time a transition state is reached.

Activation energy: The energy required for the reactant to reach the transition state from ground state is called the activation energy.

After the transition state, the collection of atoms rearranges toward more stable species: old bonds are fully broken, new bonds are fully made, and geometric rearrangement toward a more stable configuration (Relaxation) occurs.

In multistep reactions a new transition state is reached for each distinguishable step. Plots can be made of the energy of a reacting system as a function of relative atomic positions.

Consider the reaction,

$$H_2 + F \rightarrow HF + H$$
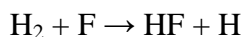
When all reactants are confined to a straight line, the distances between atoms are r_{H-H} and r_{H-F} describes relative atomic positions.

The path which involves changes in both r_{H-H} and r_{H-F} is called reaction coordinate.

A plot of energy verses two variable is three dimensional.

Principle of microscopic reversibility

Whether any reaction proceeds forward or backward, it follows the reaction coordinate. Atomic positions simply reverse themselves as the reaction is reversed, like a film shown backwards. This is a statement of the principle of microscopic reversibility.

1. The principle of microscopic reversibility is extremely important and it requires that at equilibrium both forward and reverse reactions proceed at equal rates along the reaction coordinate.
2. The study of exchange reactions where leaving and entering groups X are the same, the entry for the new ligand must be just the reverse of that for loss of the leaving ligand. The energy profile diagram is shown in Fig.1, where a saddle point is observed.
3. If some other entering ligand Y resembles the leaving one X, the principle of microscopic reversibility places limitations on the possible mechanisms for replacement of X by Y. this if true for each separate step of a multistep reaction. Instead of a saddle point, some potential surfaces have a potential well or depression corresponding to a slightly stable configuration of reaction atoms, known as intermediate. Slightly stable means the intermediate can persist for some small length of time. Then it eventually follows the reaction coordinate down into a valley as shown in Fig.2. Several successive intermediates are also possible in multistep reactions.
4. A steeply sloping and narrow valley is associated with very negative entropy of activation involving constriction of the reactant atomic motions.

5. A wide valley is associated with relative freedom in the motion and orientation of the reactants (more positive entropy)

Lability, inertness and stability and unstability

Stable (Stability) and Unstable (Unstability) are **Thermodynamic terms** and Labile (Lability) and Inert **(Inertness) Kinetic terms.**

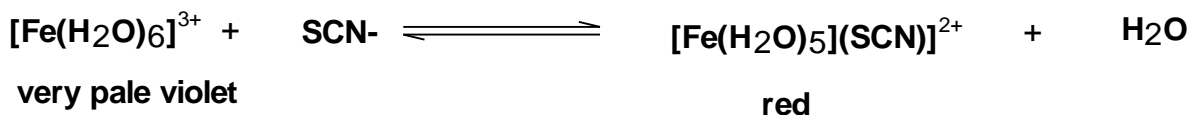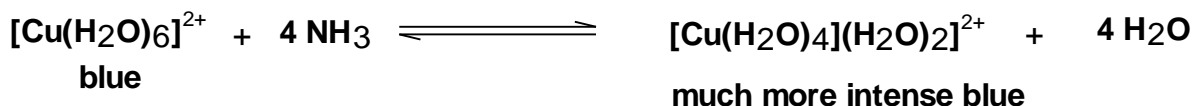Stable/Unstable and Labile/Inert

- "Stable" and "unstable" refer to the thermodynamics of complex formation (e.g., K, β).
- "Labile" and "inert" refer to the kinetics of complex formation.
- A complex whose formation equilibria are established rapidly is labile.
- A complex whose formation equilibria are established slowly is inert.
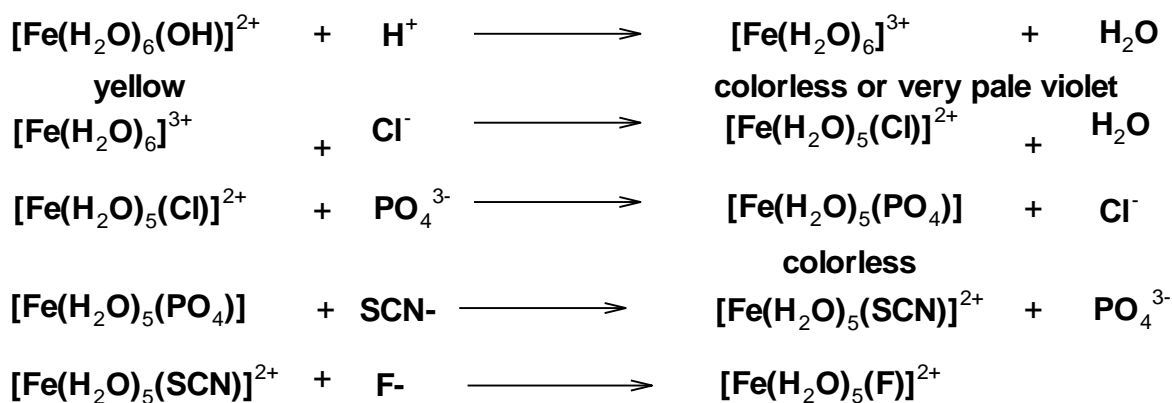
Inert and labile compounds:

Compounds such as those that react rapidly are called **labile**. In many reactions exchange of one ligand for another can take place in the time of mixing the solutions. Taube suggested a reaction of half-life (the time of disappearance of half the initial compound) of one minute or less as the criterion for Lability.

Many synthetic reactions require substitution, or replacement of one ligand by another, that is particularly true when the starting material is in aqueous solution, where the metal ion is likely to be in the form $[M(H_2O)_m]^{n+}$. Some simpler reactions of this type produce coloured products that can be used to identify metal ions. Formation of blue purple $[Cu(NH_3)_4]^{2+}$ which happens within seconds;

$$[Cu(H_2O)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(H_2O)_4](H_2O)_2]^{2+} + 4\,H_2O$$

blue   much more intense blue

$$[Fe(H_2O)_6]^{3+} + SCN\text{-} \rightleftharpoons [Fe(H_2O)_5](SCN)]^{2+} + H_2O$$

very pale violet   red

Some reactions are very fast and form species (products) that can undergo a variety of reactions that are also very fast. Addition of HNO_3 (H^+), NaCl (Cl^-), H_3PO_4 (PO_4^{3-}), KSCN (SCN^-) and NaF (F^-) successfully to a solution of $Fe(NO_3)_3 \cdot 9H_2O$ shows this very clearly. The initial solution is yellow because of the presence of $[Fe(H_2O)_5(OH)]^{2+}$ and other hydrolysed species containing both water and hydroxide ion. Although the exact species formed in this series depend on solution concentrations, the products in the reactions given here are representative:

$$[Fe(H_2O)_6(OH)]^{2+} \quad + \quad H^+ \quad \longrightarrow \quad [Fe(H_2O)_6]^{3+} \quad + \quad H_2O$$

<center>yellow   colorless or very pale violet</center>

$$[Fe(H_2O)_6]^{3+} \quad + \quad Cl^- \quad \longrightarrow \quad [Fe(H_2O)_5(Cl)]^{2+} \quad + \quad H_2O$$

$$[Fe(H_2O)_5(Cl)]^{2+} \quad + \quad PO_4^{3-} \quad \longrightarrow \quad [Fe(H_2O)_5(PO_4)] \quad + \quad Cl^-$$

<center>colorless</center>

$$[Fe(H_2O)_5(PO_4)] \quad + \quad SCN- \quad \longrightarrow \quad [Fe(H_2O)_5(SCN)]^{2+} \quad + \quad PO_4^{3-}$$

$$[Fe(H_2O)_5(SCN)]^{2+} \quad + \quad F- \quad \longrightarrow \quad [Fe(H_2O)_5(F)]^{2+}$$

Compounds that react more slowly are called **inert or robust** (a term used less often) compounds. An inert compound is not inert in the usual sense that no reaction can take place; it is simply slower to react.

*These kinetic terms must also be distinguished from the thermodynamic terms **stable** and **unstable**.*

A species such as $[Fe(H_2O)_5(F)]^{2+}$ is very stable (has a large equilibrium constant for formation), but it is also labile. On the other hand, hexaaminocobalt(3+) is thermodynamically unstable in acid and can decompose to the equilibrium mixture on the right, Substitution of water on $[Co(NH_3)_6]^{3+}$ takes years.

$$[Co(NH_3)_6]^{3+} \quad + \quad 6\,H_3O^+ \quad \longrightarrow \quad [Co(H_2O)_6]^{3+} \quad + \quad 6\,NH_4^+ \quad \Delta G^0 < 0$$
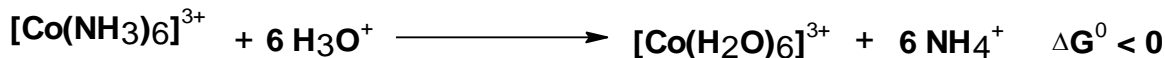
But it reacts very slowly (has a very high activation energy) and is therefore called **inert** or **robus**t. The possible confusion of terms is unfortunate, but no other terminology has gained general acceptance. One possibility is to call the compounds **kinetically labile or inert**, but these terms are not in general use at this time.

Werner studied cobalt(III), chromium(III), platinum(II), and platinum(IV) compounds because they are inert and can be more readily characterised than labile compounds. This tendency has continued, and much of the discussion in this chapter is based on inert compounds because they can be more easily crystallised from solution and their structures determined. Labile compounds have been studied extensively, but their study requires techniques capable of dealing with very short times; stopped flow or relaxation methods, for ex. temp or pressure jump, nuclear magnetic resonance.

Although there exceptions, general rules can be given for inert and labile electronic structures. Inert octahedral complexes are generally those with high ligand field stabilisation energies (LFSE), specifically those with d^3 or low spin d^4 through d^6 electronic structures. Complexes with d^8 configurations generally react somewhat faster, but slower than the d^7, d^9 or d^{10} compounds. With strong field ligands d^8 atoms form square planar complexes, many are inert. Compounds with any other electronic structures tend to be labile.

Slow Reactions (Inert)	Intermediate	Fast Reactions (Labile)
d^3, low spin d^4, d^4, and d^6		d^1, d^2, high spin d^4, d^5 and d^6
Strong field d^8 (square planar)	weak field d^8	d^7, d^9, d^{10}
$[Cr(CN)_6]^{3-}$, $t_{1/2} = 24$ days	$[Mn(CN)_6]^{3-}$, $t_{1/2} = 1.0$ h	$[Ni(CN)_4]^{2-}$, $t_{1/2} = 30$ sec

All these complexes are thermodynamically highly stable. Kinetically they are different.

The 1st Order rate constants for the substitution of inner sphere water in transition and non-transition metal complexes fall over 10-orders of magnitude.

General Comments
- The rate constants of a given ion are approximately constant, no matter what the nature of the entering group. (evidence for dissociative activation)
- The substitution rates divide the metal ions into 4-distinct groups:

Taube classified metal ions into 4 categories based on the rate of exchange of coordinated water. For large metals, a large ΔV is seen because they are more accessible. Also low non-bonding d count. Hence, tend towards I$_a$.

Class I:
- The exchange of water is extremely fast.
- The first order rate constants are in the order of k $>10^8$ s-1, which may approaches the maximum possible rate constants (calculated to be 10^9 to 10^{11} s^{-1} for a diffusion controlled reaction).
- The complexes are bound by the essentially electrostatic forces and includes the complexes of the alkali metals and larger alkaline earth metals (Group 1 and 2 ions except Be^{2+} and Mg^{2+}), Group 12 except Zn^{2+}, and Cr^{2+} and Cu^{2+}.
- The metal ions are characterised by low charge and larger size, z^2/r rations up to about $10 \times 10^{-28} C^2 m^{-1}$.
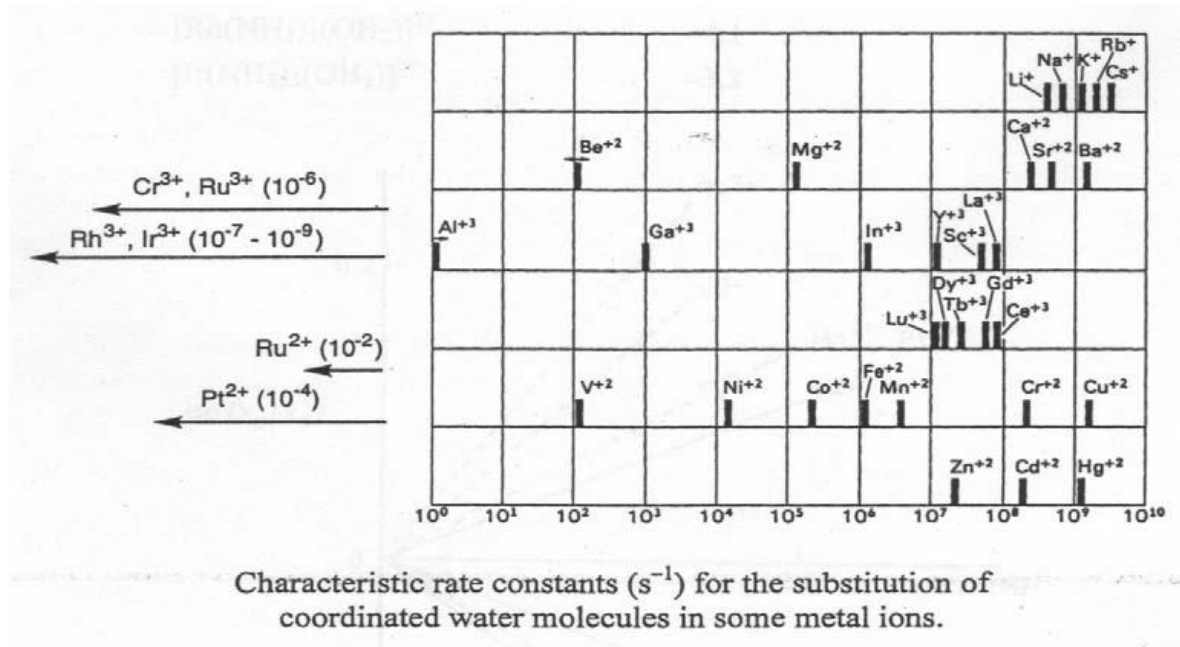
Class II:
- The exchange of water is fast.
- First order rate constants range from 10^5 to 10^8 s^{-1}.
- Metal ions belonging to this group are the dipositive transition metals, Mg^{2+}, and tripositive lanthanides.
- These ions form complexes in which the bonding is somewhat stronger than in those of class I ions, but LFSE are relatively small. The z^2/r values for ions in this category range from about 10 to 36-28 $C^2 m^{-1}$. This includes Mg^{2+}, the tripositive lanthanides (Ln^{3+}) cations, and most of the of divalent first row transition metal ions (except for V^{2+}, and that in Class 1).

Class III:
- The exchange of water is relatively slow compared with classes I and II, although fast on an absolute scale, with first order rate constants of 1 to 10^4 s^{-1}.
- The metal ions of this category are most of the first row trivalent transition metal ions, stabilised to some extent by LFSE, and two very small ions Be^{2+} and Al^{3+}. The z^2/r ratios greater than about $30 \times 10^{-28} C^2/m$. Other examples are Be^{2+}, Al^{3+}, V^{2+}.

Class IV:
- The exchange of water is slow.
- These are the only inert complexes.
- First order rate constants range from 10^{-1} to 10^{-9} s^{-1}.
- These ions are comparable in size to class III ions and exhibit considerable LFSE: Cr^{3+} (d^3), Ru(III) (low spin d^5), Pt^{2+} (low spin d^8). Best estimates for Co^{3+}, which oxidises water and is therefore unstable in aqueous solution, also place it in this class.

Characteristic rate constants (s^{-1}) for the substitution of coordinated water molecules in some metal ions.

Methods for studying exchange reactions of class I to IV:

- ^{17}O-NMR line-broadening experiments are the technique of choice for determining rate constants of water exchange of paramagnetic ions when the values of k lie between 10^3 and 10^9 s^{-1}.

 The process that is studied is,

  $$[M(H_2O)_y]^{z+} \ + \ n\, H_2^{17}O \longrightarrow [M(H_2^{17}O)_y]^{z+} \ + \ y\, H_2^{17}O$$
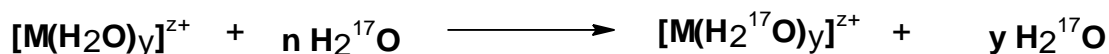
- Chemical shifts of bulk and coordinated water differ and as a result the line width at half-height can be used to calculate the rate of chemical exchange. If reactions are slow, NMR methods can be used directly to determine reaction rates since one need only follow the isotopic enrichment of a complex.
- Relaxation techniques based on ultrasonic have been widely used to obtain rate constants for reactions. In this technique a system at equilibrium perturbed by the passage of a sound wave, which induces pressure and temperature variations? Although relaxation rates ranging from 10^5 to 10^{10} s^{-1} can be measured, interpretations of results can be difficult and the range of substances that can be studied is limited.
- Rate constants greater than 10^8 s^{-1} are frequently obtained indirectly from formation reactions involving multidentate ligands.

  Comparison of dipositive with tripositive species is difficult because the reaction rate is affected by the charge on the central metal ion, higher charge strengthening the M-L bonds and reducing lability. In the fig. the Ru(III) is less labile than Ru(II), just as Fe(III) is less labile than Fe(II). However note that V(III) is more labile than V(II). When isoelctronic pairs, such as V^{2+}/Cr^{3+} or Mn^{2+}/Fe^{3+} are considered, evaluation of charge effects is more straightforward. Charge effects are

also seen very clearly in the non-transition metal series in which the lability decreases in the order shown with $[SF_6]$ exceptionally inert.

$$[AlF_6]^{3-} > [SiF_6]^{2-} > [PF_6]^- > [SF_6]$$
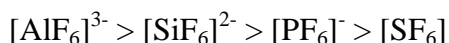
Ligand field effects and Reaction rates: Techniques to study the exchange reactions for Class I, II, III and IV metal ions:

- The complexes of metal ions in Class IV are typically stabilised to great extent by LFSE: Co^{3+} (2.4 Δ_0, low spin) and Cr^{3+} (1.2 Δ_0).
- For tripositive metal ions, lability for low spin complexes is expected to increase in the order Co(III) < Cr(III) < Mn(III) < Fe(III) < Ti(III) < V(III). Similar considerations lead us to predict less lability for V(II) and Ni(II) than for Co(II), Fe(II), Cr(II) and Mn(II).
- The difference in lability between complexes of isoelectronic metal ions within the same group, such as those of Ni(II) and Pt(II), can be related to effects of ligand fields as well. Ni(II) is a Class II metal, whereas Pt(II) belongs to Class IV. Both ions possess an empty nonbonding a_{2u} (p_z) orbital available for occupancy by a fifth group. Loss of LFSE (negative values of LFSE hence destabilisation of complex) for the heavier Pt(II) will be proportionately greater than for Ni(II). It is generally observed that Lability decreases for an analogues series of compounds in descending order within a group.
- d^3 and low spin d^4, d^5, and d^6. The configuration is border line. The octahedral d^8 complexes encountered are weak field complexes of Ni(II).
- Strong field complexes of d^8 ions,
- Rh(I), Ir(I), Ni(II), Pd(II), Pt(II) and Au(III) are square planar and low spin.
- The weak field complexes of Ni(II) usually react more rapidly than those of d^3 or d^6 ions. But slower than those of labile Cu(II), Co(II), Zn(II) complexes.

Table: Change in LFSE upon changing from 6 coordinate to 5 coordinate or 7 coordinate complexes; units are Dq or $\Delta/10$

Systems	High spin		Low spin	
	CN = 5	CN = 7	CN = 5	CN = 7
d0	0	0	0	0
d1	0.57	1.28	0.57	1.28
d2	1.14	2.56	1.14	2.56
d3	-2.00	-4.26	-2.00	-4.26
d4	3.14	-1.07	-1.43	-2.98
d5	0	0	-0.86	-1.70
d6	0.57	1.28	-4.00	-8.52
d7	1.14	2.56	1.14	-5.34
d8	-2.00	-4.26	-2.00	-4.26
d9	3.14	-1.07	3.14	-1.07
d10	0	0	0	0

Introduction to ligand substitution reactions:

Substitution reactions in inorganic chemistry have been divided into 2 classes based on the bond breaking and bond making in the rate determining step. The factors which control this is:

- The activation energy (E_a) require to breaking of the bond to the leaving group (Dissociative) or making of the bond to the entering group (Associative).
- The sequence of elementary steps leading from reactants to the products is.
- Langford and Gray labelled these as **intimate** and **stoichiometric** mechanisms.

Mechanisms of General Substitution Reactions of Octahedral Complexes

Langford and Gray classified substitution reaction Mechanisms as follows:

	Stoichiometric mechanism	
	Dissociative	Associative
Intimate Mechanism	5-Coordinate Transition State for octahedral Reactants	7-Ccoordinate Transition State for octahedral Reactants
Dissociative activation	D I_d	
Associative activation	I_a	A
	Alternative Labels	
SN1 lim (limiting first order nucleophilic substitution)		SN2 lim (limiting second order nucleophilic substitution)

Dissociation (D) and Association (A) (Intimate mechanisms):

Dissociation, D: The departing ligand leaves and a discernible intermediate with a lower coordination number is formed, a mechanism labelled D for dissociation.

Association, A: The incoming ligand adds to the complex and an intermediate to the complex and an intermediate with an increased coordination number (discernible either by kinetic or analytical methods) is formed in a mechanism labelled A for association.
These are called **intimate mechanisms.**

**Interchange I mechanism: (Stoichiometric mechanisms)**

Between the two extremes is interchange mechanism in which the incoming ligand is presumed to assist in the reaction but no detectable intermediates appear.

- **Interchange dissociative (I_d):** When the degree of assistance is small and the reaction is primarily dissociative, it is called **dissociative interchange (I_d)** mechanism.

- **Interchange associative (I_a):** When the incoming ligand begins forming a bond to the central atom before the departing ligand bond is weakened appreciably, it is called **association interchange (I_a)** mechanism.

The energy profile for associative and dissociative reactions:

The energy profile for associative and dissociative reactions is shown in fig. The clear separation of these two mechanisms should not be taken as an indication that the distinction is easily made. In many cases there is no clear cut evidence to distinguish them.
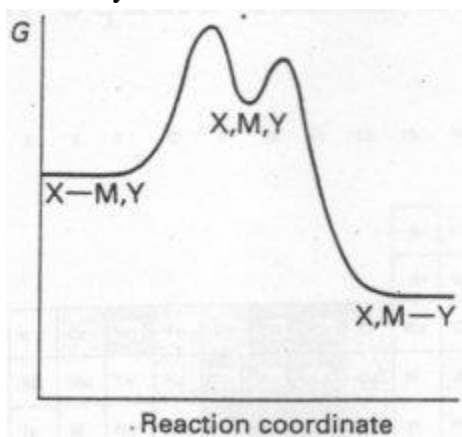
Dissociative mechanism,
The intermediate has a lower CN than reactant
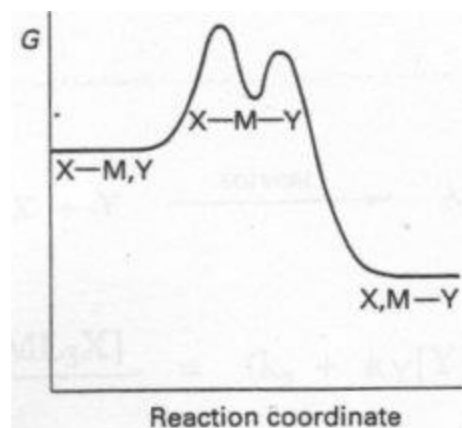
Associative mechanism,
The intermediate higher CN than reactant

Kinetics of substitution reactions in octahedral complexes and the derivation rate expressions

Derivation of rate expression for D mechanism:

The activation energy is determined primarily by the energy required to break the bond to the leaving group. This is called dissociative (D) mechanism. In a dissociative (D) reaction loss of a ligand to form an intermediate with a lower coordination number is followed by addition of a new ligand to the intermediate:

Consider a ligand substitution reaction in an octahedral complex, where, L is the ligand; M is the metal; X is the leaving ligand; Y is the entering ligand.

$$[L_5MX] + [Y] \longrightarrow [L_5MY] + [X]$$
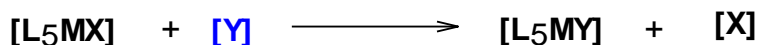
Two elementary steps are possible / detectable:

$$[L_5MX] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [L_5M] + [X]$$

$$[L_5M] + [Y] \overset{k_2}{\longrightarrow} [L_5MY]$$
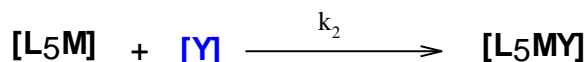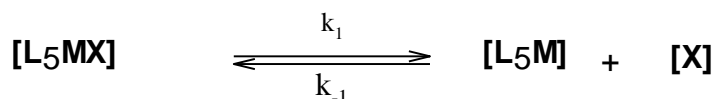
The complex accumulates enough energy to break completely the bond M-X, leaving a 5-coordinate intermediate. Then this intermediate reacts with Y (this may be solvent also) from the second coordination sphere. This is called **D** mechanism.

The rate law for D mechanism by applying the **Steady-State Approximation** to a very small concentration of [L$_5$M], the rates of formation and reaction of the intermediate must be equal. This requires that the rate of change of [L$_5$M], be zero during much of the reaction. Any reaction to precede this mechanism L$_5$M must have a sufficiently long lifetime to be experimentally detectable.

$$\frac{d[ML_5]}{dt} = k_1[ML_5X] - k_{-1}[ML_5][L] - k_2[ML_5][Y] = 0$$

Solving for [ML$_5$],

$$[ML_5] = \frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]}$$

And substituting into the rate law for formation of the product,

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5][Y]$$

Leads to the rate law:

$$\frac{d[ML_5Y]}{dt} = \frac{k_2 k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

One criterion for this mechanism is that the intermediate ML$_5$ be detectable during the reaction. Direct detection at low concentration expected is a very difficult experimental challenge, and there are very few clear cut dissociative reactions.

Derivation of rate expression for Interchange (I) mechanism

Consider a ligand substitution reaction in an octahedral complex, Where, L is the ligand; M is the metal; X is the leaving ligand; Y is the entering ligand.

$$[L_5MX] + [Y] \longrightarrow [L_5MY] + [X]$$
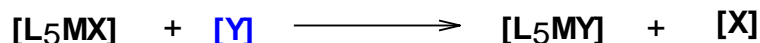
When L$_5$M does not have an appreciable lifetime, the I$_d$ mechanism is followed. In an interchange (I) mechanism a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combinations. This species which is not described as having an increased coordination number and is not directly detectable, then reacts to form the product and release the initial ligand.

The complex **[L$_5$MX]** accumulates enough energy to the bond **M-X** to vibrate and to begin to break the bond. Before it can be broken fully, **M** begin to break to form a bond with whatever species **Y** happens to be in a suitable geometric position. The possible mechanism is as follows.
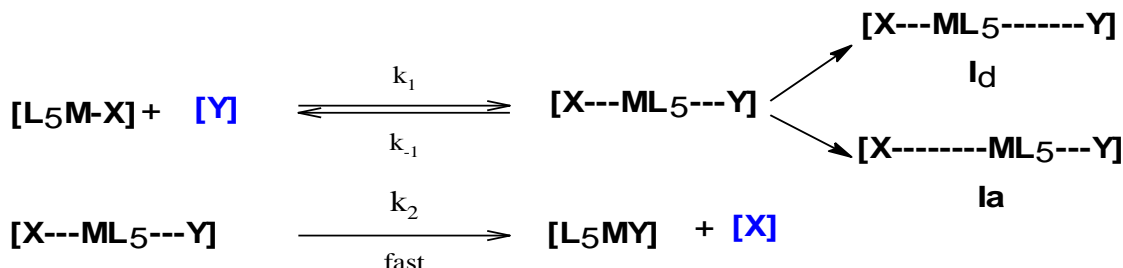
When $k_2 \lll k_{-1}$, the reverse reaction of the first step is fast enough that this step is independent of the second step, and the first step is an equilibrium with $K_1 = k_1/k_{-1}$.

$$\frac{d[ML_5X-Y]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5X-Y][L] - k_2[X-Y] = 0$$

If [Y] is large compared with $[ML_5X]$ (a common experimental condition), the concentration of the unstable transition species may be large enough to significantly change the concentration of the $[ML_5X]$, but not that of Y. For this reason we must solve for this species in terms of the total initial reactant concentration of $[ML_5X]$ and Y, which we will call $[M]_0$ and $[Y]_0$

$$[M]_0 = [ML_5X] + [ML_5X-Y]$$

Assuming that the concentration of the final product $[ML_5Y]$, is too small to change the concentration of Y significantly, then,

$$[Y]_0 \equiv [Y]$$

From the stationary state equation,

$$k_1[M]_0 - [ML_5X-Y][Y]_0 - k_{-1}[ML_5X-Y] - k_2[ML_5X-Y] = 0$$

The final rate equation then becomes

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5X-Y][Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + k_2/k_{-1}} \equiv \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

K_1 can be measured experimentally in some cases and estimated theoretically in others from calculation of the electrostatic energy of the interaction, with fair agreement in case in which both methods have been used.

Two variations on the interchange mechanism are I_d (dissociative interchange) and I_a (associative interchange). The difference between them is in the degree of bond formation in the first step of the mechanism. If bonding between the incoming ligand and the metal is more important, it is an I_a mechanism. If breaking the bond between the leaving ligand and the metal is more important it is an I_d mechanism. The distinction between them is subtle, and careful experimental design is required to determine which description fits a given reaction.

As can be seen from these equations both D and I mechanisms have the same mathematical form for their rate laws. (If both the numerator and the denominator of the D rate law are divided by k-1/k-1, the equations have the similar forms shown here).

$$\text{Rate} = \frac{k[M][Y])}{[X] + k^1[Y]} \qquad\qquad \text{Rate} = \frac{k[M]_0[Y]_0}{1 + k^1[Y]_0}$$

As low [Y], the denominator simplifies to [X] for the dissociative and to 1 for the interchange equation. Both then are secong order (first order in M and Y, rate $= k[M]_0[Y]_0$ or $\frac{k[M]_0[Y]_0}{[X]}$, with the rate of the dissociative reaction showing as more free X is formed.

At high [Y], a common condition in kinetic experiments the second term in the denominatore is larger, $[X] + k1[Y] = k^1[Y]$ and $1+ k_1[Y]_0 = k1[Y]_0$ and [Y] cancels, making the reaction first order in complex and zero in Y (rate $= k/k^1[M]_0$)
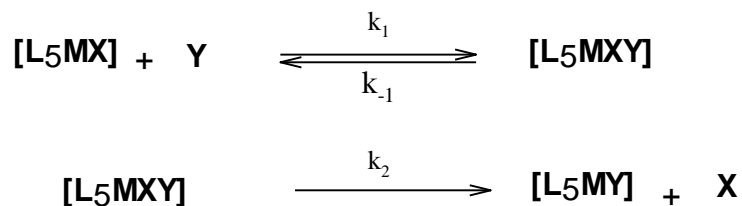
The change from one rate law to the other depends on the specific values of the rate constants. The similarity of the rate laws limits their usefulness in determining the mechanism and requires other means of distinguishing between different mechanisms.

This is a limiting case as the intermediate's lifetime becomes progressively shorter, and finally it does not survive long enough to be detectable. Otherwise no 5-coordinate intermediate has formed. The energy necessary for bond breaking mainly determines the activation energy and hence the rate. Therefore this is called dissociative interchange ($\mathbf{I_d}$) mechanism.

The accessible parameters are the initial concentration of Y and of the reactant complex, $[L_5MX]_0$, which in a solution exists partly in the form of the outer sphere complex.

Derivation of rate expression for Association (A) Mechanism:

In an association reaction, the first step forming an intermediate with an increased coordination number, is the rate determining step. It is followed by a faster reaction in which the leaving ligand is lost:

$$[\mathbf{L_5MX}] + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathbf{L_5MXY}]$$

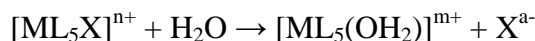$$[\mathbf{L_5MXY}] \xrightarrow{k_2} [\mathbf{L_5MY}] + X$$

The same stationary state approach used in the rate laws results in the rate law

$$\frac{d[ML_5Y]}{dt} = \frac{k_2 k_1 [ML_5X][Y]_0}{k_{-1}[Y]_0 + k_2} = k[ML_5X][Y]$$

This is a second order equation regardless of the concentration of Y.

Kinetics of Hydrolysis under Acid and Alkaline Conditions

The hydrolysis reaction:

$$[ML_5X]^{n+} + H_2O \rightarrow [ML_5(OH_2)]^{m+} + X^{a-}$$

This is often called aquation. The rate law for such a reaction is commonly of the form:

$$\text{Rate} = k_A [ML_5X] + k_B[ML_5X][^-OH]$$

Water as the entering ligand (55.5 M) does not appear in the rate law. This reaction has been studied extensively for Co^{3+} complexes. The second term occurs when there are ionisable protons in the complex. In general, k_B (for base hydrolysis) is about 10^4 times k_A (for acid hydrolysis).

Acid Hydrolysis –

Data for Co^{3+} complexes indicate an I_d mechanism very close to the D limit.

- For $[Co(NH_3)_5X]^{n+}$ the rates correlate well with the stability of the complexes, indicating that Co-X bond breaking in important in the rate limiting step.
- For a series of $[Co(NH_3)_5(RCO_2)]^{n+}$ complexes there was a correlation with the basicity of the carboxylate.
- For a series of substituted bidentate amines, the rate increases with increasing bulk of substituents on the chelating ligand (e.g. Me_2en faster than en), indicating a dissociative mechanism.
- ΔV for X=Cl was close to the molar volume of water, indicating an I_d mechanism close to the D limit.

**Conjugate base mechanism: SN$_1$CB mechanism** *(Base Hydrolysis)*

Substitution nucleophilic unimolecular conjugate base mechanism. These reactions depend on amine, or aqua ligands that can lose protons to form amido or hydroxo species that are then more likely to lose one of the other ligands. If the structure allows it, the ligand trans to the amido or hydroxo group is frequently the one lost. As mentioned earlier the rates of substitution of octahedral complexes are not sensitive to the nature of the entering group-with one exception. In basic media Co(III) complexes having ligands of the type NH_3, RNH_2, R_2NH are sensitive to the nature of the entering group. The base catalysed reactions are generally much more rapid than anation or hydrolyses in acid solution.

The agreed mechanism, involves the removal of a proton from the amine ligand. This step is generally very fast, (10^5 faster), and represents rapid pre-equilibrium to the rate determining loss of leaving group.

$$[Co(NH_3)_5(X)]^{2+} + OH^- \xrightarrow{\text{Equilibrium}} [Co(NH_3)_4(NH_2X)]^+ + H_2O$$

$$[Co(NH_3)_4(NH_2X)]^+ \xrightarrow{\text{Slow}} [Co(NH_3)_4(NH_2)]^{2+} + X^-$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{Fast}} [Co(NH_3)_4(NH_2)]^{2+}$$

$$[Co(NH_3)_5(X)]^{2+} + OH^- \xrightarrow{\text{Overall}} [Co(NH_3)_4(NH_2)]^{2+} + X^-$$

12
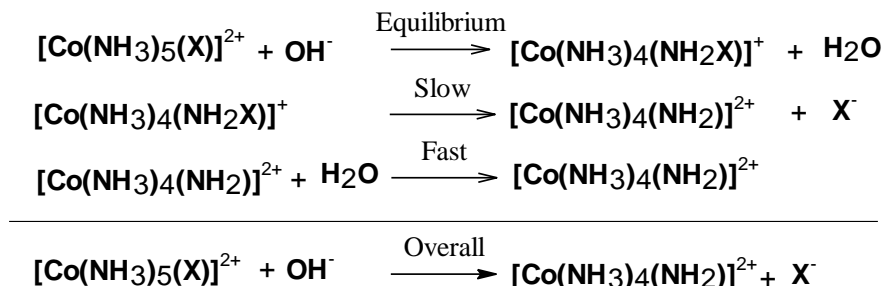
$$\frac{-d[\text{complex}]}{dt} = k_{obs}[\text{complex}][OH^-]$$

The second order rate law for base hydrolysis of complexes with ionisable protons on the ligands does not arise from direct attack of –OH on the complex in an A mechanism. The reaction is generally accepted to occur via the conjugate base of the complex like so:
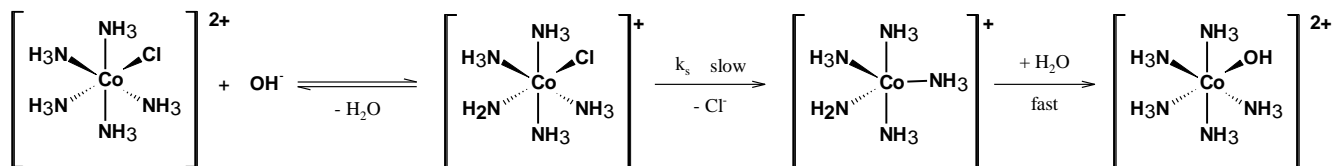
$$\frac{-d[\text{complex}]}{dt} = \frac{k_2 K[\text{complex}][OH^-]}{1 + K[OH^-]}$$

If, however, K is quite small (it is in the range 0.01-0.2 for Pt(IV) complexes) so that K[OH] << 1, the rate law would reduce to that experimental observed.

- Base catalysed exchange of hydrogen from the amine groups takes place under the same conditions as these reactions.
- The isotope ratio ($^{18}O/^{16}O$) in the product in ^{18}O-enriched water is the same as that in the water regardless of the leaving group ($X^- = Cl^-$, Br^-, NO^-). If an incoming water molecule had a large influence (an associative mechanism), a higher concentration of ^{18}O should be in the product, because the equilibrium constant K = 1.040 for the reaction,

$$H_2{}^{16}O + {}^{18}OH^- \rightleftharpoons H_2{}^{18}O + {}^{16}OH^-$$
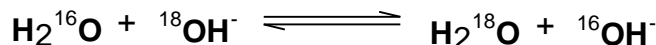
- RNH_2 compounds (R = alkyl) react faster than NH_3 compounds, possibly because steric crowding favours the 5-coordinate intermediate formed in **Step 2**.
- The rate constants and dissociation constants for these compounds form a linear free energy relationship (LFER), in which a plot of $\ln k_{OH}$ vs. $\ln K_{OH}$ is linear.
- When substituted amines are used, and there are no protons on the nitroigen available for ionisation, the reaction is very slow or nonexistent.
- The rate of H/D exchange for the coordinated ammonia is 10^5 times faster than the hydrolysis reaction, consistent with the rapid pre-equilibrium between the complex and its conjugate base.
- The rate in the presence of the HOO- ion, which is a weaker base but stronger nucleophile than –OH, is slower.
- The acidity of coordinated ammonia is low, so the equilibrium concentration of the conjugate base is low, and the actual rate acceleration by the amide group is $> 10^6$.
- The proposed trigonal bipyramidal structure of the conjugate could result in stereochemical change.

Another factor which should be considered here, as well as those above for Water Exchange, is vacancy in the non-bonding orbitals. This is because the amide created in the base hydrolysis above is now a very strong π-donor, and the electrons it donates must enter low energy nonbonding orbitals in order to increase the rate. In fact, if the t2g is full, the rate will decrease due to the destabilising influence. This influence is worse when large splittings are involved, e.g. from strong field ligands or 4d/5d orbitals.

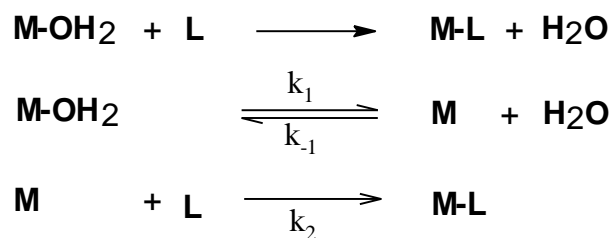**The main difference between the D and I_d mechanisms is;**

- The intimate mechanism in both the cases is dissociative (D).
- The formation intermediate with reduced coordination number to be detected experimentally.
- When the 5-coordinate intermediate is detectable, the stoichiometric mechanism is D (dissociative), the other case is I_d (dissociative interchange).
- Differing in the sequences of elementary steps, different stoichiometric mechanisms.
- These are related with the stoichiometric mechanism SN1 in organic chemistry.

Factors Favouring A or D (or Ia or Id)

- **Sterics**-Bulky ligands clearly will obstruct the nucleophile, so favouring the D mechanism over A.
- **Large Metal Ion** favours A (easy attack by Y).
- **Good Leaving Group** favours D.
- **Nucleophilicity** highly favours A. I- is good for soft metals, F- good for hard metals.
- **Spectator ligands** – no trans effect present for octahedral. However, strength of ligand matters. A good σ-donor increases e-density on the metal, so M-X breaks more easily. They may also stabilise low coordination number activated complex after the dissociation.

Mechanisms of Substitution of water (H_2O) by other ligandsin Octahedral Complexes:

Substitution reactions in octahedral complexes may proceed by D, I_d, I_a or A mechanisms and it is often difficult to distinguish between them because the rate law by itself does not allow the distinction to be made. Consider the replacement of water by ligand L under neutral conditions. If this reaction proceeds by a dissociative (D) mechanism, the first step is breaking of metal-water bond, followed by formation of the metal-L bond:

$$\text{M-OH}_2 \ + \ \text{L} \ \longrightarrow \ \text{M-L} \ + \ \text{H}_2\text{O}$$

$$\text{M-OH}_2 \ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \ \text{M} \ + \ \text{H}_2\text{O}$$

$$\text{M} \ + \ \text{L} \ \overset{k_2}{\longrightarrow} \ \text{M-L}$$

The rate law obtained from these reactions shows a dependence on [L], even though it is derived for a dissociative mechanism:

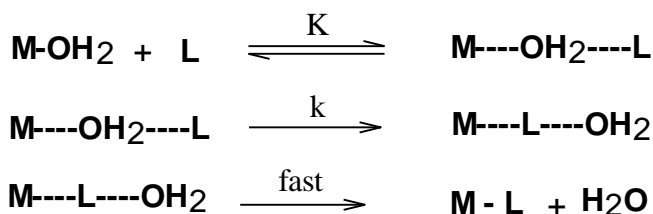$$\text{rate} = -\frac{d[M-OH_2]}{dt} = \frac{k_1 k_2 [M-OH_2][L]}{k_{-1}[H_2O] + k_2[L]}$$

At high concentrations of L, $k_2[L] > k_{-1}[H_2O]$ and above equation simplifies to a form independent of [L]:

$$\text{rate} = k_{obs}[M-OH_2]$$

At lower concentrations of L however, both and H_2O compete for M and the rate shows a dependence on [L]. For example, the reaction of SCN- with a Co(III) hematoporphyrin complex can be described by above eqns. A plot of kobs vs. [SCN-] shows the expected dependence of the rate on [SCN-] for lower concentrations of SCN-.

[SCN-] M
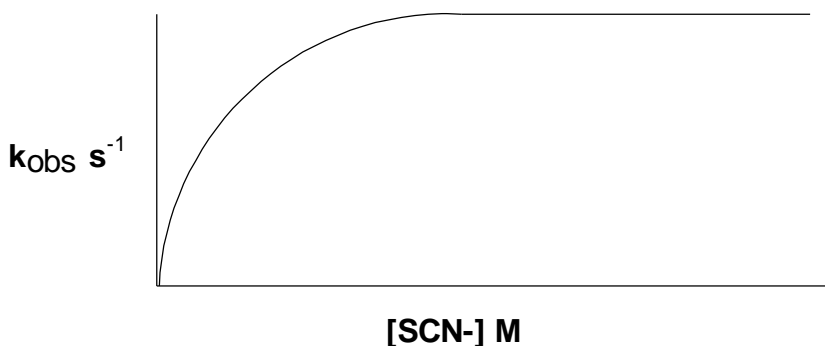
     If some M-L bond making takes place before the M-OH$_2$ bond is completely broken (I$_d$), the process can be described in three steps:

$$M\text{-}OH_2 \; + \; L \; \xrightleftharpoons{K} \; M\text{----}OH_2\text{----}L$$

$$M\text{----}OH_2\text{----}L \; \xrightarrow{k} \; M\text{----}L\text{----}OH_2$$

$$M\text{----}L\text{----}OH_2 \; \xrightarrow{fast} \; M\text{-}L \; + \; H_2O$$

The rate law derived from these reactions takes a form similar to that of for rate for a D mechanism:

$$rate = \frac{kK[M-OH_2][L]}{1 + K[L]}$$

This eqn. also simplifies to: $rate = k_{obs}\,[M-OH_2],$

     Where $k_{obs} = kK[L]$ under pseudo first order conditions.

     Furthermore the form of the rate law does not change if bond making becomes more important than bond breaking (I$_a$). Since rate laws for D, I$_d$ and I$_a$ cannot be distinguished with certainly (knowledge of rate and equilibrium constants for individual reaction steps may provide clarification), it is not surprising that there have been considerable debate and controversy over the mechanistic details of many octahedral substitution reactions. Few reactions appear to fit into the limiting D and A categories; thus most discussion centres around the I$_d$ and I$_a$ mechanisms.

     Because of the inertness of the Co(III) and Cr(III) complexes their substitution reactions were the first among those of octahedral complexes to be extensively studied. Most evidence supports the I$_d$ mechanism for substitution in Co(III) complexes. First there is little dependence of reaction rates on the nature of the incoming ligand. If bond making were of significant importance, the opposite would be expected. Data are presented in table for the anation of pentammineaquacobalt(III):

$$[Co(NH_3)_5(H_2O)]^{3+} \; + \; X^{n-} \longrightarrow [Co(NH_3)_5(X)]^{m+} \; + \; H_2O$$
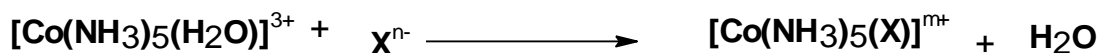
Rate constants for the reaction of $[Co(NH_3)_5(H_2O)]^{3+}$ with X^{n-} in water at 45^0C		Rate constants for the reaction of $[Co(NH_3)_5(X)]^{m+}$ with H_2O in water at 45^0C	
X^{n-}	$k\,(M^{-1}\,s^{-1})$	**X^{n-}**	$k\,(M^{-1}\,s^{-1})$
NCS$^-$	1.3×10^{-6}	NCS$^-$	5.0×10^{-10}
$H_2PO_4^-$	1.3×10^{-6}	$H_2PO_4^-$	2.6×10^{-7}
Cl$^-$	1.3×10^{-6}	Cl$^-$	1.7×10^{-6}
NO$_3^-$	1.3×10^{-6}	NO$_3^-$	2.7×10^{-5}
SO$_4^{2-}$	1.3×10^{-5}	SO$_4^{2-}$	1.2×10^{-5}

     We see a small variation in rate constants for a variety of anionic X^{n-} ligands. It is instructive to also consider the reverse reaction of above eqn. aquation of the Co(III) complex. If this is an I$_d$

reaction, M-X bond strength should correlates with reaction rate since most of the activation energy would be associated with bond breaking. In the above table satisfies our expectation that the reaction rate depends on the kind of the M-X bond being broken. The entering group and leaving group data provide constrict arguments. The reaction in water replaces Cl- in $[Co(NMeH_2)_5(Cl)]^{2+}$ takes place 22 times faster than the same reaction for $[Co(NH_3)_5(Cl)]^{2+}$. The greater steric requirements of methylamine encourage dissociation of the Cl$^-$ ligand. If the reaction proceeds by an I_a or A pathway, the order of rates would be expected to slow the reaction. Finally, it should be noted that the absence of a trans effect (so important in square planar substitution) for Co(III) complexes is consistent with a dissociative mechanism.

There is growing evidence that substitution reactions in Co(III) complexes may not be typical of octahedral transition metal complexes. Early studies of substitution reactions for Cr(III) complexes revealed a rather strong dependence of reaction rate on the nature of the entering group, which supported the I_a mechanism. More recently high pressure oxygen-17 NMR spectroscopy has come into widespread use for obtaining mechanistic details about facts reactions and as a result many water stable transition metal complexes ions have been investigated. The parameter of interest that is yielded by these experiments is volume of activation. $\Delta V^{\ddagger}$, which is a measure of the change in compressibility that occurs as the reaction proceeds from the ground state to the transition state. The data in table obtained for the solvent exchange with $[M(NH_3)_5(H_2O)]^{3+}$ complexes, show a positive $\Delta V^{\ddagger}$ for Co^{3+} but negative values for Cr^{3+}, Rh^{3+}, and Ir^{3+} suggesting an Id mechanism for the cobalt ion but Ia for chromium, Rh, and Ir ions. Data for water exchange reactions of first row hexa aqua tripositive ions are shown in table. We see a general increase in volumes of activation as we move across the periodic table from Ti(III) to Fe(III). In fact the value for Ti(III) approaches that predicted for an A mechanism. The trend may be viewed as a gradual change from strongly associative to moderately associative. Similar NMR studies of solvent exchange reactions also have been carried out for divalent transition metal ions, $[M(H_2O)_6]^{2+}$. In these experiments volumes of activation indicate a change from Ia to Id across the first row; the dissociative mechanism is more important for Ni(II) than for Fe(II). Since pretation is not always straightforward, and some believe that the power of the method has been overstated. For ex. Langford and swaddle have presented opposing views on this matter. Undoubtedly the Ia pathway is more common for octahedral substitution than once thought.

Factors which control the rate of H₂O Substitution:

➢ For **Class 1**, ionic size, and ionic charge are clearly the important ones. As the ion becomes smaller the substitution rate slows. Reflecting importance of orbital overlap between metal ion and departing ligand. Group 2 and 12 show similar trend, (Be^{2+} is anomalous due to complex hydrolysis reactions).

➢ For T.M. metals the correlation of rate with size is not obeyed, e.g. Cr^{2+}, Ni^{2+}, and Cu^{2+} have identical radii.

➢ *Mechanism* – activation parameters have been determined for many water exchange reactions, and they support I_d (Eigen-Wilkins) for ions of Groups 1, 2, 12, 13 and the lanthanides (typically ΔS_a and $\Delta V_a > 0$).

➢ However, other data indicates that associative activation is also possible. This is particularly seen for early transition metal ions, but it changes to dissociative (I_d) across the 1st row.

➢ 2nd /3rd row transition metal ions and more highly charged 1st row ions tend to follow the I_a mechanism.

Studies on octahedral complexes have largely been limited to two types of reaction:

1. **Substitution or Replacement of coordinated solvent (e.g. water):** Perhaps the most thoroughly studied replacement reactions of this type is the formation of a complex ion from a hydrated metal ion in solution.
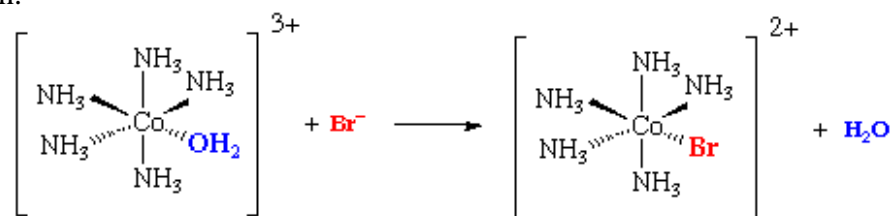
2. **Anation**: When the entering group is an ion the reaction is called anation.
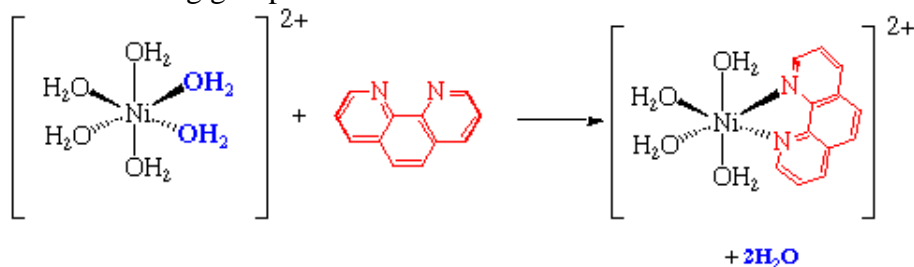
3. **Solvolysis**. Since the majority of such reactions have been carried out in aqueous solution, hydrolysis is a more appropriate term. Hydrolysis reactions have been done under acidic or basic conditions.
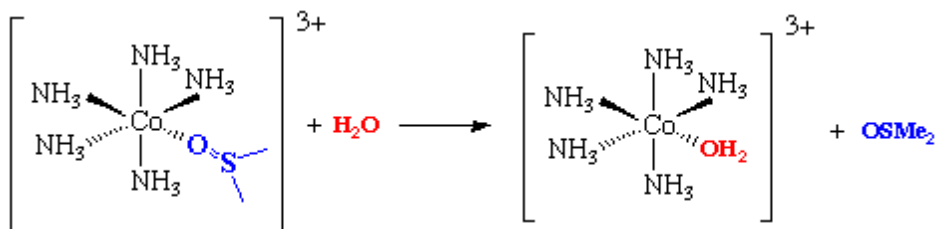
Observations / Implications

> Rates quite similar to water exchange rates (H_2O dissociation important factor)
> Rate increases with charge on anion ("Outer Sphere" Complex)
> Rate unaffected by nucleophilicity, basicity, etc... (A and I_a paths thus unlikely)
> Rate strongly dependent on M (suggests D or I_d mechanism)
> Kinetics 2nd order (does not eliminate any mechanism)
> Intermediates not detected (very few cases, e.g. $[Co(CN)_5H_2O]^{2-}$)
> ΔV^{++} +ve, generally

All this generally suggests an I_d mechanism.

The rationalisation for the substitution of water (H_2O) ligand by other is as follows:

- For ions following the I_d mechanism, bond breaking is important in the rate limiting step and therefore one key factor must be the strength of the M-O interaction. We expect rate to increase as ionic radius increases and charge decreases. This is clearly the case for Groups 1, 2 and 13, and most of the lanthanides. Hence Be^{2+} and Al^{3+} undergo slow water substitution.

- For transition metals the correlation between rate and size is not always obeyed, e.g. Cr^{2+}, Ni^{2+} and Cu^{2+} have the same ionic radii. Octahedral Cr^{2+} (HS d^4) and Cu^{2+} (d^9) are susceptible to Jahn-Teller distortions which lengthen two of the M-O bonds, which will facilitate substitution by a dissociative mechanism (breaking a weaker bond).

- Group 2 vs. Group 13: Ca^{2+}/Zn^{2+} and Sr^{2+}/Cd^{2+} are as expected. Hg^{2+} faster than expected. Perhaps due to 2-short/four long $Hg-OH_2$ bonds due to sd_z^2 hybridisation for d^{10}.

- Ligand field stabilisation energies affect the rate for transitions metals. Essentially ions which have large LFSE's will be less labile for both associative and dissociative activation. Hence d^3 (e.g. Cr^{3+}), d^8 (Ni^{2+}) and low spin d^4, d^5 and d^6 are expected to be inert, while d^0, d^{10}, d^1 and d^2 can be expected to be much more labile, and the rate should also follow the order $\underline{Mn^{2+} > Fe^{2+} > Co^{2+}. Cr^{2+}}$ $\underline{and\ Cu^{2+},}$ Jahn-Teller effect. Trivalent ions should have slower rates, as should second and third row ions.

- Al^{3+} is smaller than Cr^{3+} but the rate for Cr^{3+} is 3 orders of magnitude lower – effect of covalence and d electron configuration.

The many factors considered when assessing different rates are summarised below:

Charge – higher charge lowers the energy of d-orbitals, making them closer in energy to ligand orbitals. This leads to a better overlap, and a stronger bond (assuming they do not hydrolyse the water ligand).

Generally, as ΔH_a decreases, k will increase (common sense!). Similarly, increased ionic radius leads to increased rate (bigger target!).

An entropy change greater than 0 indicates a Dissociative-like mechanism (more disorder in the transition state). Smaller radius also favours the D mechanism (harder to attack by nucleophile of A mechanism).

CFSE – lower is better, since reaction involves loss of stabilising CFSE influence.

Considering now the change in electron configurations and orbital splitting during the reaction:

Factors to consider here:

- d^3 is inert, since to rearrange electrons, one must be promoted to an e_g orbital (antibonding – expends energy). Thus ΔHa will be high.
- CFSE = $6/5\Delta_o$. This is at a maximum, and this energy is lost on change of configuration, which is a loss of stabilisation.
- Cr^{3+} is small and charged, so the Cr-O bond is likely to be strong. One of these bonds is lost on reaction.
- Mechanism requires population of an antibonding orbital in the intermediate stage – this is energetically unfavourable.

All of these lead to a high **Ligand Field Activation Energy**, and thus it can be seen why Cr^{3+} is very inert to substitution.

For less charged metals, and for metals with lower CFSE, the exchange will occur more rapidly.

- Moving down a Group, the 4d and 5d orbitals are lower in energy, and make a closer energy match with better overlap to the ligands. This leads to a stronger bond, and so a higher ΔHa. Similarly, down the Group the orbital splitting is larger for $2^{nd}/3^{rd}$ row, which leads to a larger LFAE (bigger energy gap for promotion of any electrons into antibonding).

- Another factor to consider is an increased Volume of Activation. This is a factor when there are more d electrons (e.g. in Ni^{2+}), and leads to a greater entropy change, and drives the Dissociative mechanism of the reaction.

Predominant factor is electron configuration requirements, however.

### *Orbital Occupation Effects on Substitution Reactions of Octahedral Complexes*

The basic assumption is that there is a significant contribution to the activation energy in a substitution reaction is the change in d-orbital energy on going from the ground state of the complex to the transition state. Any loss in energy would contribute to the activation (and slow the rate). Using this approach the $[M(H_2O)_6]^{2+}$ ions show the following relative rates:

$$V^{2+} << Cr^{2+} > Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} < Cu^{2+} > Zn^{2+}$$
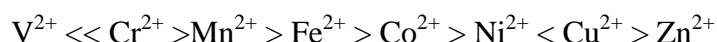
General Comments
- Series is generally in good agreement with experimental data.
- The d^3 ions are predicted to be substitutionally inert.
- Except for $Ni^{2+}(d^8)$, the high spin d^4-d^{10} M^{2+} ions are predicted to be labile by either C_{4v} or D_{3h} transition state pathways.
- Some deviation that need further explanation: Cr^{2+} (d^4), and Cu^{2+} (d^9) complexes are especially labile. This is due as mentioned earlier to the Jahn-Teller effect.
- Mn^{2+}, Fe^{2+}, and Co^{2+} are predicted to have equal labilities, but we observe experimentally that substitution rates decrease across the series. This is due to the increase in Zeff across the series and increase in E (M-L).

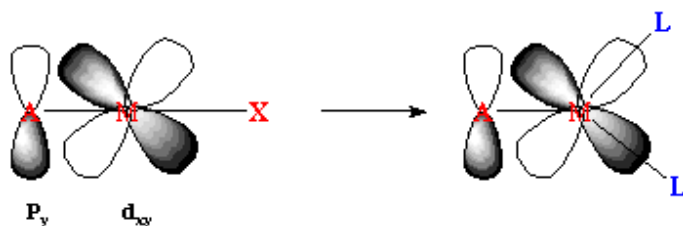### *Stereochemistry of Substitution of Octahedral Complexes*
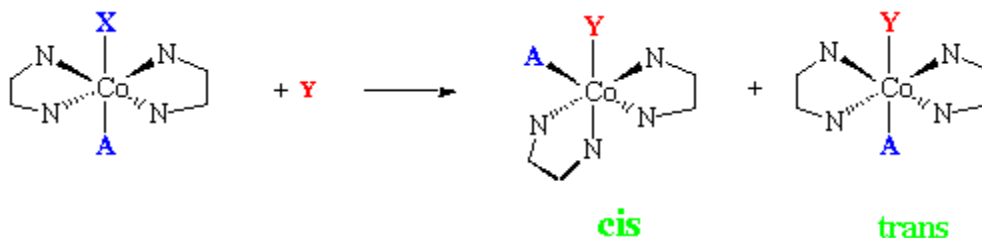
cis   trans

General Points about Stereochemistry
1. In general, trans-$[Co(en)_2ACl]^{2+}$ undergo stereochemical change on hydrolysis, whereas cis-$[Co(en)_2ACl]^{2+}$ react with retention of original chirality.
2. cis isomer generally react faster than trans isomers
3. Ligands A, that lead to stereochemical change in the trans series are those with p orbitals
4. If the reaction proceeds through a square pyramidal intermediate, retention of configuration will be observed.

5. Proceeding through a trigonal bipyramid, has 75% chance of leading to stereochemical change.

Points 3 and 5 above:

P_y d_{xy}

Stereochemistry of Substitution of Octahedral Complexes

Compound	D or I_d Mechanism			
	Tetragonal or Square Pyramid Intermediate		*Trigonal Bipyramid Intermediate*	
	cis product	trans product	cis product	trans product
trans-ML_4AX^{n+}	0	100	66.6	33.3
cis-ML_4AX^{n+}	100	0	83.3	16.6
trans-$M(LL)_2AX^{n+}$	0	100	66.6	33.3
cis-$M(L-L)_2AX^{n+}$	100	0	$\Lambda = 58.3; \Delta = 25.0$	16.7
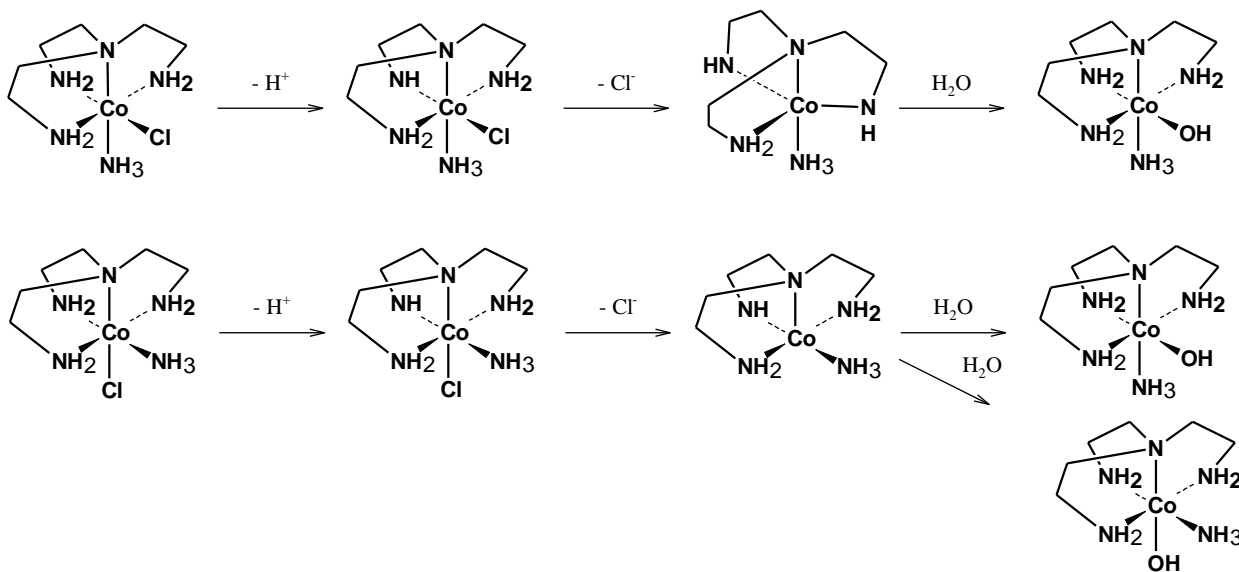
Reactions with $[Co(tren)(NH_3)Cl]^{2+}$ isomers show that the position trans to the leaving group is the most likely deprotonation site for a conjugate base mechanism. The reaction in fig is 10^4 times faster than that in fig. In addition most of the product in both reactions is best explained by a trigonal bipyramidal internmediate or transition statewith the deprotonated amine in the trigonal plane. The reaction in fig a. can form this state immediately; the reaction n requires rearrangement of an initial square pyramidal structure.
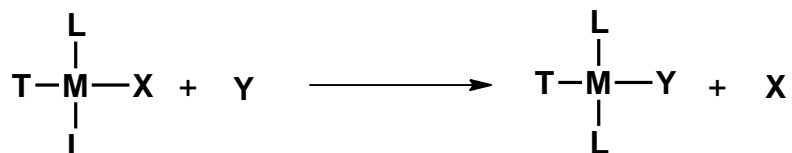
Kinetics of Substitution reactions of 4-coordinate square-planar metal complexes

Complexes with d^8 electronic configurations usually are four coordinate and have square planar geometries. These include complexes of Pt(II), Pd(II) and Ni(II) (also sometimes tetrahedral and often octahedral), Ir(I), Rh(I), Co(I) and Au(III).

Among d^8 metal ions most experimental work on square-planar complexes has involved Pt(II) since this metal gives reaction with convenient rates, and the compounds are highly stable to redox and geometry change, relatively easy to synthesize and undergo ligand exchange reactions at rates that are slow enough to allow easy monitoring. Reaction rate ratios for Pt(II), Pd(II) and Ni(II) is appr. $1:10^5:10^7$. Furthermore because isomerisation of less stable Pt(II) isomers to thermodynamically more stable ones is a slow process, scrambling of ligands is not generally a problem.

Rate Law

For the following reaction type:

$$\begin{array}{ccc}
\text{L} & & \text{L} \\
| & & | \\
\text{T}-\text{M}-\text{X} \;+\; \text{Y} \quad\longrightarrow\quad \text{T}-\text{M}-\text{Y} \;+\; \text{X} \\
| & & | \\
\text{L} & & \text{L}
\end{array}$$

Where Y is the entering nucleophilic ligand,

  X is the leaving ligand

  T is the trans to the leaving ligand

The observed for a large range of Pt complexes is of the form:

$$\text{Rate} = -\frac{d[MTL_2X]}{dt} = k_y[Y][MTL_2X] + k_s[MTL_2X]$$

$$= \frac{-d[MTL_2X]}{dt} = (k_s + K_y[Y])([MTL_2X])$$

Experiments are invariably carried out using excess of Y, and hence under pseudo first-order conditions. In such a case the experimental rate constant k is given by:

$$\text{Rate} = -\frac{d[MTL_2X]}{dt} = k[MTL_2X]$$

Hence the observed rate constant is related to the actual rate constants by the equation:

$$k = k_s + k_y[Y]$$

A plot of k versus [Y] will be linear with intercept k_s and slope k_y.

Types of substitution reactions

1. **Associative, A:** The M-Y bond is fully formed before M-X bond begins to break.
2. **Interchange Associative, I_a:** The M-X bond begins to break before the M-Y is fully formed, but bond making is more important than bond breaking.
3. **Disociative, D:** The M-X bond is fully broken formed before M-Y bond begins to form.
4. **Interchange Disociative, I_d:** The M-Y bond begins to form before the M-X bond is fully broken, but bond breaking is more important than bond making.

Nonzero values for both ky and ks indicate that MTL_2X is reacting and the implications of such a rate law for the mechanism of the reaction is that there must be two reaction pathways.

These two pathways (a and b) must be:

a) The ks term, first order w r t both complex and Y (k_y), Y involved in rate determining step indicates an associative pathway, A, similar to SN2 reaction of organic chemistry.
The term arise from the nucleophilic attack of MTL_2X by Y. As would be expected for a reaction in which bond making is important, rates of reaction depend markedly upon conc. of Y. Furthermore, the rates are significantly dependent on the nature of Y.

b) at first glance the k1 term, first order w r t complex (k_s), independent of Y and does not involve Y in rate determining step. this pathway is also associative and is solvent mediated. The solvent molecules will be nucleophiles and will therefore compete with Y for MTL_2X to form MTL_2S (sometimes called the solvent complex). Thus the two-term rate law could be written as:

$$\text{Rate} = -\frac{d[MTL_2X]}{dt} = k_1[S][MTL_2X] + k_2[MTL_2X][Y]$$

However because solvent is present in large excess, its concentration is essentially constant and therefore k1[S] = ks.
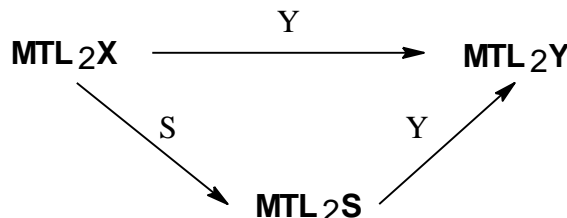

The ks term of the rate law shown in eqn. could also arise from dissociation (D) of X to give a three-coordinate complex which then reacts with Y.

In other words the form of the rate law does not help one distinguish between an A (or Ia) and D (or Id) mechanism for the ks pathway. The ambiguity in the interpretation of the ks term has caused much discussion and experimentation. It is found that reaction take place faster in more nucleophilic solvents, suggesting that solvent attack plays an important role.

Also dissociative reactions should be accelerated by thepresence of sterically demanding ligands; just the opposite is observed, in keeping with an A or Ia mechanism.

Further insight into the question of an associative verses a dissociative mechanism can be provided by thermodynamics data such as that shown in table for the substitution of bromide by iodide or thiourea in trans-[Pt(PEt₃)₂(R)Br].

X = I⁻ or $SC(NH_2)_2$; R = 2,4,6- $Me_3C_6H_2$
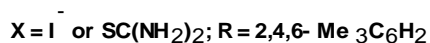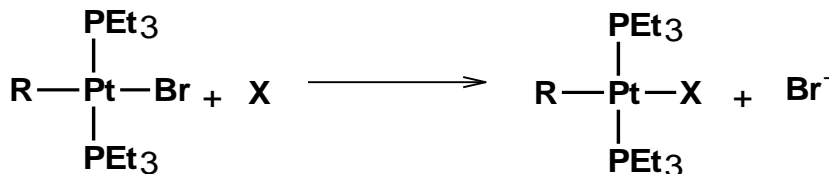
The reaction rate is primarily determined by the enthalpy of activation ($\Delta H^{\ddagger}$), which is usually the case in square planar nucleophilic substitution reactions. of greater importance, so for as a dissociative

verses an associative mechanism is concerned, are the entropies and volumes of activation, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$, respectively. Note that the values are negative for both the ks and ky steps. The observed decrease in entropy is what we would expect for a mechanism in which two particles come together to give an activated complex. The volume of activation is determined by doing the reaction under high pressure:

$$\Delta V^{\ddagger} = \frac{RT ln(\frac{k_2}{k_1})}{P_1 - P_2}$$

An activate complex with a smaller volume than the reacting species will give rise to a negative $\Delta V^{\ddagger}$ and is characteristic of association. For all of the reasons it is believed that square planar nucleophilic substitution reactions proceed by association rather than by dissociation.

For one metal complex with a range of nucleophiles k_s is the same. Often $k_s \ll k_y[Y]$ and it can be difficult to obtain accurate data.
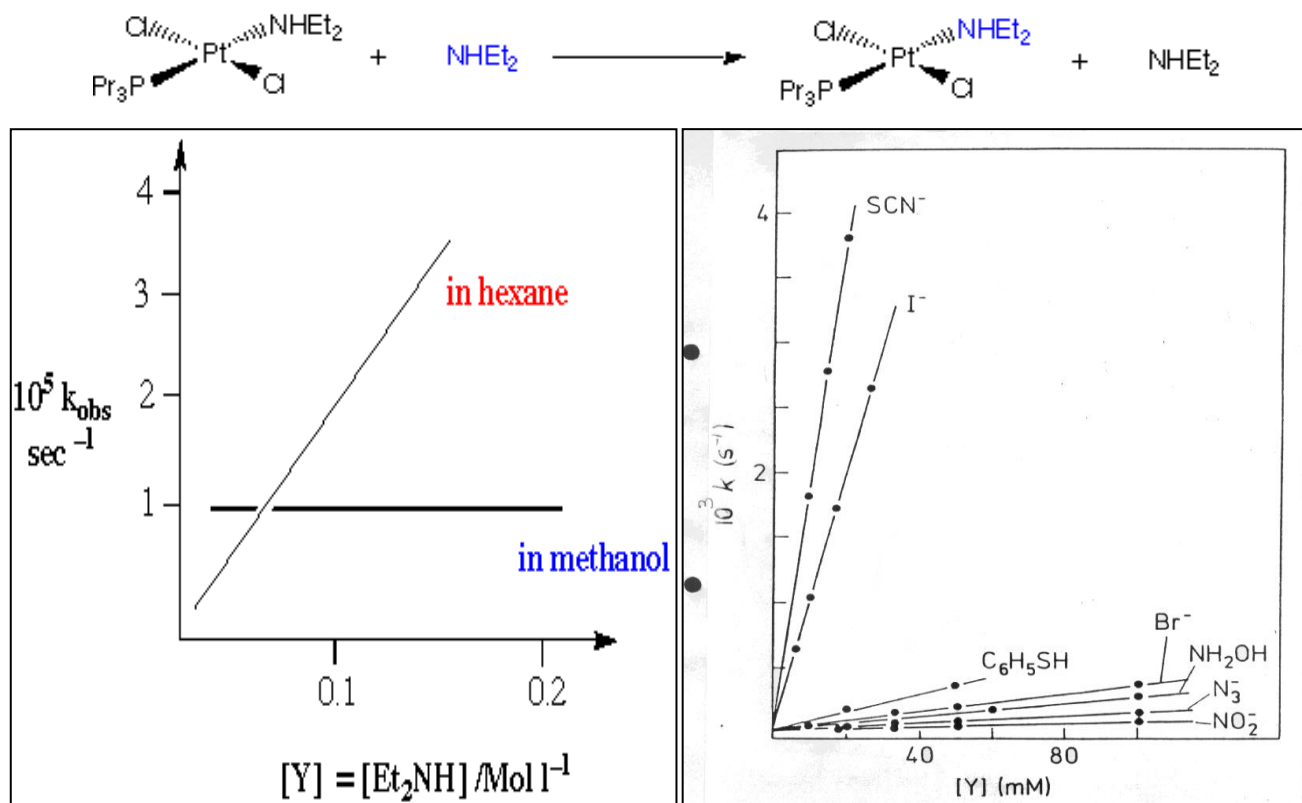

The graph is drawn for the reactions of *trans*-[Pt(pyridine)$_2$Cl$_2$] with a number of different nucleophiles in methanol.
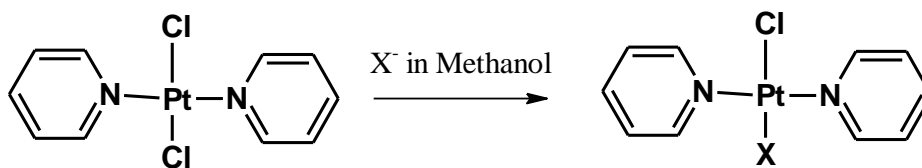
Note the vast range of different slopes and that all the lines have the same, non-zero, intercept.

Using this information it is possible to draw a reaction mechanism consistent with the rate law. Note: the mechanism (theory) must explain the rate law (experiment) and not vice versa. The mechanism is drawn for the example of $[Pt(NH_3)_3Cl]^+$ reacting with Y^- in H_2O as solvent, although other solvents can act as ligands in a similar fashion.
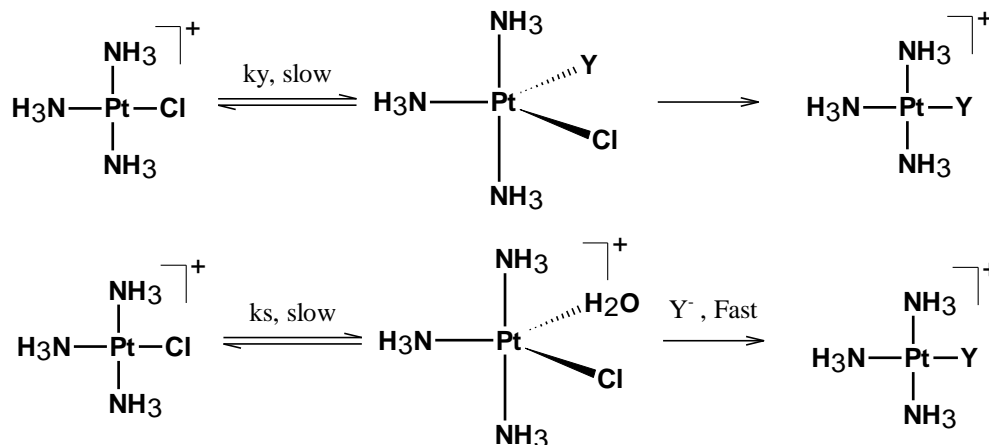
Note that in this mechanism both reaction pathways proceed via an associative process (A), involving a trigonal bipyramid transition state. Is there any chemical justification for this transition state?

(i) Many five coordinate transition metal complexes are known, e.g., $[Fe(CO)_5]$, $[CoL_2(CO)_3]^+$, $[Ni(CN)_5]^{3-}$

(ii) ML_3X complexes are sterically and electronically unsaturated and have space for Y to coordinate.

The evidence for an Associative mechanism

1. Rate law is consistent with associative mechanism
2. Influence of charge on metal

Complex	k(aquation) (X 10^5)	k (Cl⁻ exchange) (X 10^5)
$[PtCl_4]^{2-}$	3.9	<3
$[Pt(NH_3)Cl_3]^-$	5.6	<3
cis-$[Pt(NH_3)_2Cl_2]$	2.5	~3
trans-$[Pt(NH_3)_2Cl_2]$	9.8	78
$[Pt(NH_3)_3Cl]^+$	2.6	7

The data listed in the table is for the rates of reaction of some Pt complexes with water (aquation) and reaction with Cl-. This data indicates that there is relatively little effect of changing charge on metal, this is a characteristic of an associative (A) mechanism.

3. Steric hindrance -

For a series of $[Pt(PEt_3)_2RCl]$ complexes reacting with pyridine in ethanol solution, the table lists kinetic data which is consistent with an increase in the coordination number of the metal at the transition state.

R = C_6H_5 2-Me-C_6H_4 2,4,6-Me$_3$C$_6$H$_2$
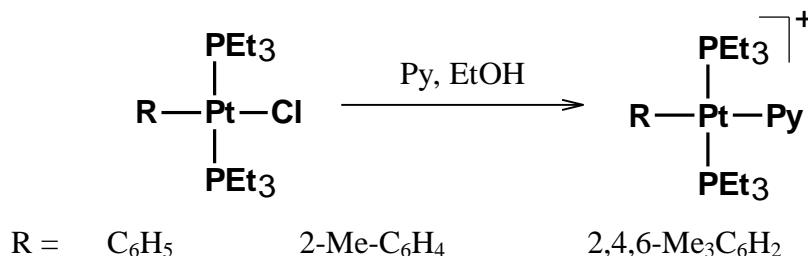
| trans | 100 000 | 200 | 1 |
| cis | 30 | 6 | 1 |

Factors affecting the rate of reaction /Factors Which Affect the Rate of Substitution

In the following sections, a number of parameters which influence the reactions of square planar complexes are investigated.
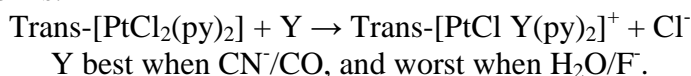
1. Role / Nature of the Entering Group
2. The Role / Nature of The Leaving Group
3. The Role / Nature of the Other Ligands in the Complex
4. Effect of the Metal Centre

Nature of the entering group – nucleophile

1. Rate is proportional to the nucleophilicity of entering group
2. Element specific
3. It is best to define the strength of Y by the term **NUCLEOPHILICITY** – the rate of attack on a complex by a given Lewis Base (relative to the rate of attack of a reference).
4. The nucleophilicity parameter is calculated as:

$$n_{Pt} = \log \frac{k_2(Y)}{k_2^0}, \; k_2^0 = methanol$$

Reference reaction is:
$$\text{Trans-}[PtCl_2(py)_2] + Y \rightarrow \text{Trans-}[PtCl\,Y(py)_2]^+ + Cl^-$$
Y best when CN^-/CO, and worst when H_2O/F^-.

The opposite is true for X. A good nucleophile is a bad leaving group (relevant for the D mechanism).

5. No correlation of n_{Pt} scale with other properties of the nucleophiles, such as basicity, redox potentials, or pH, e.g. strongly basic ligands such as OH- or OMe- do not react with Pt(II) substrates.
6. For the reactivity series I- > Br- > Cl- the most important factor seems to be the polarisability or "softness" resulting from the existence in low lying excited states.
$$PR_3 > AsR_3 > SbR_3 \gg NR_3$$
7. Notable exceptions to this series are NO_2^-, $SeCN^-$, which are "biphilic".
8. "Biphilic" ligands exhibit different reactivities depending on the charge on the complex.
   Biphilic Ligands:
9. Biphilic properties originate from π-acceptor properties from non-bonding electrons.
10. Availability of non-bonding electrons is dependent on ligand environment.

- A wide range of species containing an unshared electron pair (i.e., Lewis bases) can act as nucleophiles. Nucleophiles may be either neutral or negatively charged (NH_3, Cl^-, I^-, PR_3, H_2O, R^-)
- The concept of **Nucleophilicity** can be introduced. This is an attempt to provide a quantitative measure of the ability of a Lewis base to act as the entering group and to influence the reaction rate in a nucleophilic substitution reaction.
- Nucleophilicity is a concept that may apply at either a metal centre (inorganic) or at sp3 carbon (organic). However you should note that good organic nucleophiles MAY not be good inorganic nucleophiles. This can provide important mechanistic information.
- A scale of nucleophilicity is established by determining the relative rate of the reaction of a range of nucleophiles with a standard substrate. Organic chemists use MeBr or MeI as their standard

substrate. Inorganic chemists use the substitution reactions of trans-[Pt(pyridine)2Cl2] (shown in the graph earlier)

- If we measure k_y (rate for nucleophile Y) and k_n (rate for a standard nucleophile, methanol), then the ratio of the rates gives the Swain-Scott equation:

$$Log\frac{k_y}{k_n} = s\,X\,n$$

n = nucleophilicity, s = substrate parameter

- The list below gives values for the nucleophilicity (n) towards Pt(II) complexes of some come nucleophiles

MeOH	0.00	F-	2.7	Cl-	3.04
NH_3	3.07	NO_2	- 3.22	N_3	- 3.58
Br-	4.18	I-	5.46	Ph_3Sb	6.79
Ph_3As	6.89	CN-	7.14	Ph_3P	8.93

- Some general trends in nucleophilicity towards Pt(II) can be noted. Pt is a "soft acid" and so the fastest rates are observed with the more polarizable "soft bases" (I-, S and P ligands). The most important use of these trends in substitution power comes when we want to establish the best synthetic route to a particular compound.

$I^- > Br^- > Cl^- >> F^-$ $PR_3 > AsR_3 > SbR_3 >> NR_3$ Sulphur > Oxygen
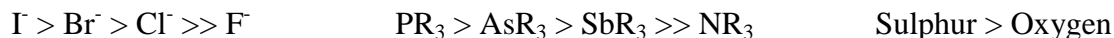
- Organic chemists are concerned with SN^2 reactions and find that nucleophilicity of a nucleophile with CH_3X as substrate can be related to basicity within certain groups of nucleophiles and bases. However, MeX and *trans*-[Pt(py)$_2$Cl$_2$] are very different substrates and there is little correlation between either:
  (a) Organic and inorganic (Pt) nucleophilicities, or
  (b) Inorganic nucleophilicity and basicity
- It is important to remember that nucleophilicity is a kinetic term, referring to the rate of the reaction with a particular nucleophile. In contrast, basicity is a thermodynamic term, referring to the reaction with H+. There is little or no correlation between these two terms. Nucleophilicity towards Pt is most heavily correlated with the polarizability of the entering ligand. Polarizable ligands (I-, SR-, PPh3, etc.) are more able to stabilise the transition state for substitution at Pt.

Influence of Trans ligands - <u>Trans Effect</u>

Based on empirical observations, but highly useful, Werner (1893) - described "*trans* elimination" and said that "Certain groups can more readily than others cause the elimination and substitution of other groups *trans* to them". Trans effect is defined as:

*"The trans effect is defined as the labilisation of ligands trans to certain other ligands"* or

"*The effect of a coordinated ligand upon the rate of substitution of ligands opposite to it."*

The *trans effect* has a very important synthetic use to predict the product of a reaction. The preparation of cis and trans isomers of aiamminedichloroplatinum(II). The cis isomer is exclusively prepared from [PtCl$_4$]$^{2-}$ and the trans derivative is from [Pt(NH$_3$)$_4$]$^{2+}$ precursors as shown in the equation.
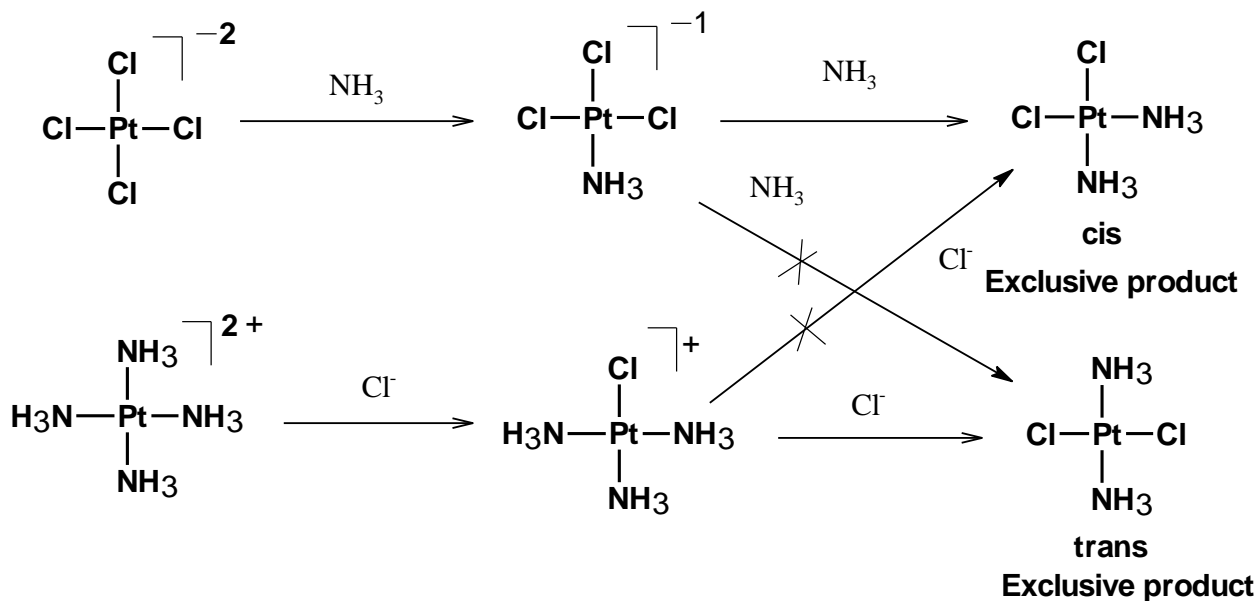
It is important to note that the *trans effect* is a **KINETIC** effect, relating to the rate of substitution of a ligand trans. In searching for a rationalisation of this effect we must look at the effect of these groups on the activation energy of the reaction.

Trans effect must be kinetically controlled since the thermodynamically most stable isomer is not always produced. This is obvious since it is possible to form two different isomers of a complex depending on the reaction sequence, and only one of the isomers can be the most stable in a thermodynamic sense. By carrying out a large number of reactions, it is possible to compare the trans-directing capabilities of a variety of ligands:
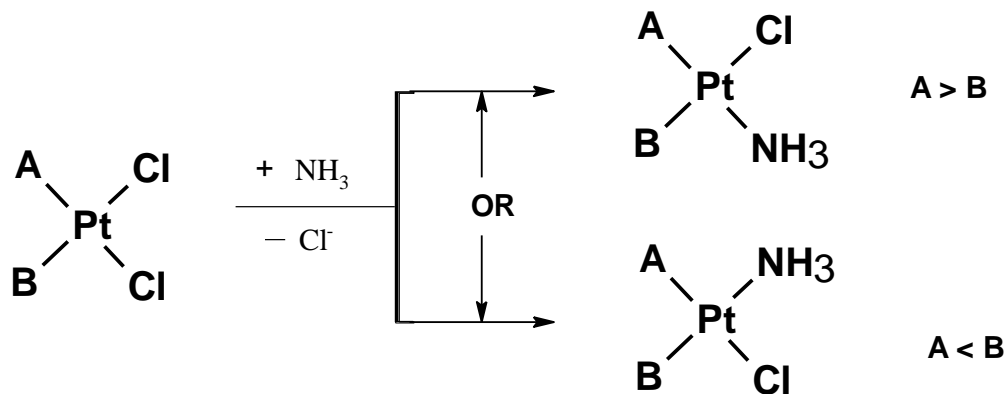
The same entering group NH3 is used for each reaction. A nd B can be selected from a wide range of ligands. The question for a given reaction becomes this: Which ligand A or B is most efficient at labilising a trans Cl- or equivalently at trans directing an incoming ligand? If the answer is A then A ranks higher in a trans directing series, which is another way of saying the reaction is faster when the chloro group trans to A is lost. The approximate ordering of ligands in a trans directing series is:

The ligands which shows the trans effect are known as "***trans directing ligands***". For Pt(II) complexes, the order of the ligands that show trans effect is generally arranged in the form of a series known as "***trans effect series***".

H_2O < OH- < (NH_3 ~ NR_3 ~ RNH_2) < Py < Cl- < Br- < ($SCN-$ ~ I- ~ NO_2^-) < HSO_3^- < (C_6H_5- ~ SR_2 ~ $SC(NH_2)_2$) < CH_3- < (PR_3 ~ AsR_3 ~ H^-) < (olefins ~ NO ~ CO ~ CN)

CN-, CO, and NO are powerful trans directors, while hydroxide and water are very poor.

Mechanism of nucleophilic substitution in square planar complexes

- A nucleophile Y attacking a square planar d^8 complex from either side of the plane. (In addition to being attracted to the somewhat electron deficient metal center, the ligand will experience repulsion from the filled d orbitals and form the bonding electrons).
- The ligand may coordinate to the metal through an empty p_z orbital to form a square pyramidal species. Electronic repulsions and steric factors, slow the attack somewhat.
- Once formed, the square pyramidal species will undergo a transformation to a trigonal bipyramidal structure. It will have 3 ligands (Y, T, and X) in its trigonal (equatorial) plane, and two ligands that were trans to each other in the original complex will occupy the axial positions.
- As X departs from the trigonal plane, the T-M-Y angle will open up and the geometry will pass through a square pyramid on its way to the square planar product.
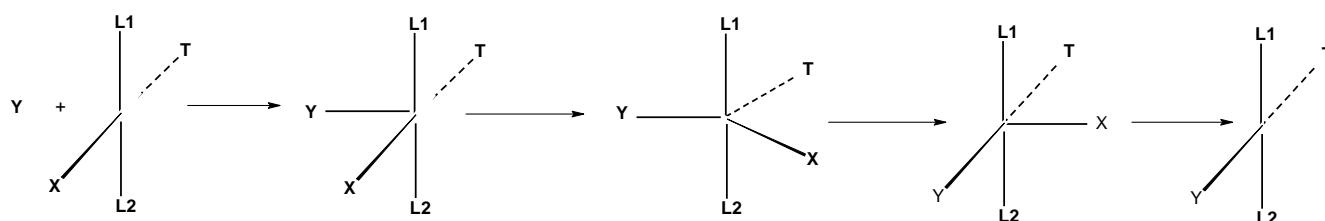

- The trigonal bipyramidal species that forms during the reaction and then rearranges to give products may exist either as an **activated complex** or as a true **intermediate**. The distinction between the two depends essentially on the lifetime of the species.
- The term activated complex refers to the configuration of reactants and products at a peak in the reaction profile energy curve that is at the transition state.
- The term intermediate implies that a species has a detectable lifetime and that it is at least somewhat more stable than any activated complexes that form along the reaction pathway.
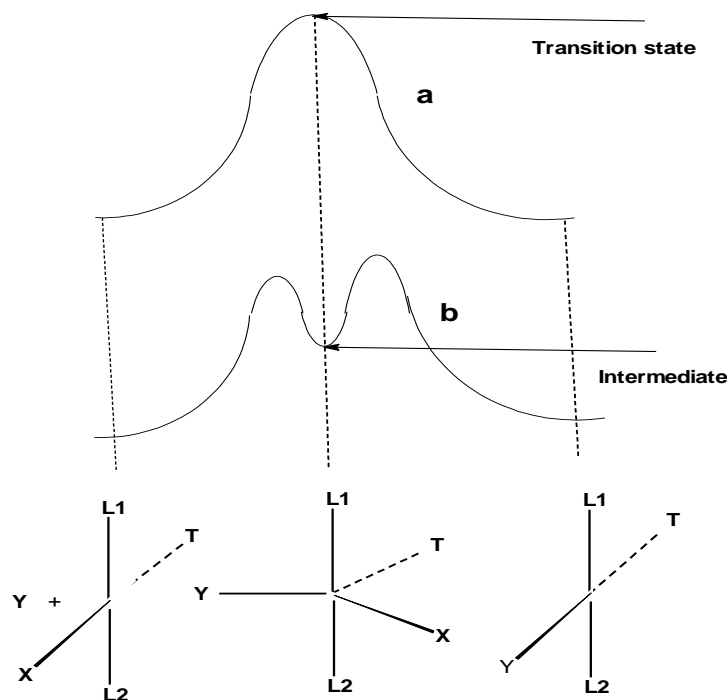
Origin of the trans effect

A number of theoretical models have been proposed to explain the trans effect. The two which have been most successful have been the electrostatic model of Langford and Gray and the molecular orbital model of Chatt and Orgel, relating to the σ and π bonding properties of ligands. It is this second model which we will discuss. This model divides ligands which show a high trans effect into two classes, good π-acceptors and good σ-donor ligands.

Some of the ligands which show a high *trans* effect are π-acceptor ligands, (e.g., C_2H_4, CN-, CO and PR_3). Consider the bonding interactions of a metal-PR_3 complex, as both the entering and leaving ligands are coordinated to the Pt(II) in the 5-coordinate transition state of the reaction.


Ligand to metal σ donation   **Metal to Ligand π back donation**
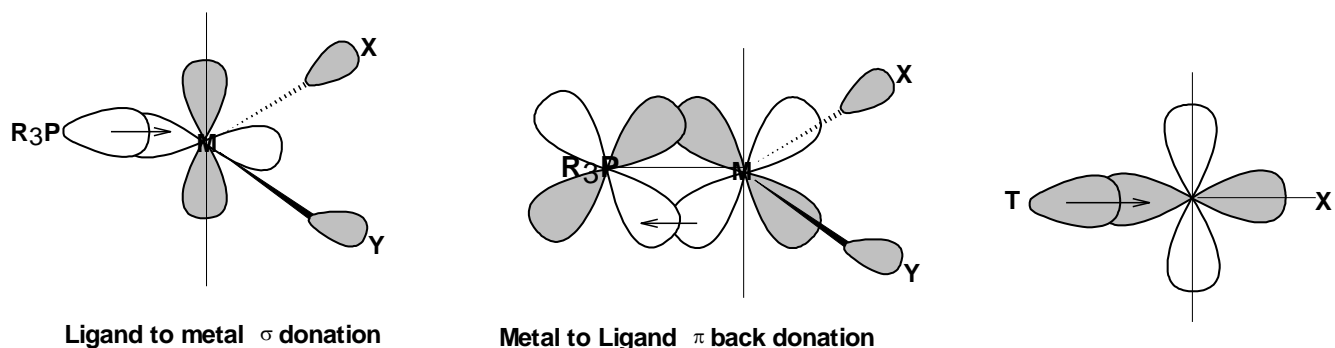
The simultaneous coordination of X and Y in the 5-coordinate transition state causes an increase in electron density at the metal; π-back donation to the *trans* ligand can reduce this electron density at the metal during the transition state. This lowers the activation energy by transition state stabilisation.

In contrast, some ligands which show a strong "*trans effect*" are good σ-bases (e.g., alkyl-, H-), so in the square planar **ground state** of the molecule they are donating electron density to the metal d orbital which is shared with the leaving group. This weakens the M-X bond in the ground state, as shown in the figure.

Trans effect and trans influence

The extent to which a ligand affects the bond trans to itself in a complex is termed as trans influence. I can be assessed by looking at the ground state properties such as bond lengths, coupling constants, and stretching frequencies. The effect of T on M-X bond in a square planar complex (its trans influence) can be viewed in terms of the metal orbitals which T and X have in common. The metal p_x orbital is directional and is shared by both ligands. If T forms a strong σ bond to M, the M-X bond is weakened due to the p_x orbital is not available to X. The net effect is to destabilise the substrate and thereby to reduce Ea. If we arrange X ligands in order of their ability to function as σ donors, we have an order which nearly parallels the "***trans effect series***":

OH- < NH$_3$ < Cl- < Br- < CO, CN-, CH$_3$- < I-, SCN- < PR$_3$ < H$^-$
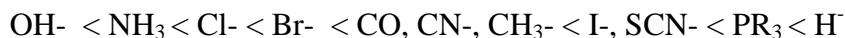
Two ligands in the above list CO, CN-,are not strong σ donors, but yet they strongly accelerate the substitution reaction. Exceptions such as these can be explained by considering how they might affect the energy of the transition state rather than in terms of their influence on the ground state. Both CO and CN- are good π accepting ligands, which suggests that they can effectively withdraw electron density that will accumulate on the ,metal as a result of adding a fifth ligand. The π accepting abilities of ligands decreases in the order shown:

OH- < NH$_3$ < Cl- < Br- < I- < SCN- < NO$_2^-$ < CN- < C$_2$H$_2$, CO

The high positions of CO, CN- and C2H2 in this series suggests that the enhanced reaction rates observed for these ligands stem from a capacity to lower the energy of the transition state via withdrawal of π electron density. ligands that are good π acceptors will also favour an equatorial position in the trigonal bipyramidal activated complex or intermediate that forms in the reaction. This is consistent with the overall scheme represented in fig. and provides an explanation for the labilisation of X as well. To the extent that T favors occupation of an equatorial position in the trigonal bipyramid, it will force X to be the ligand expelled in the formation of the square planar product.

The discussion above has considered a phenomenon by which the rates of substitution of Pt(II) complexes can be interpreted in terms of the properties of some of the ligands. This is a KINETIC effect, and is interpreted in terms of either stabilisation of the transition state or destabilisation of the ground state. Both of these result in a lowering of the activation barrier of the reaction.

The *trans* effect must not be confused with an apparently similar term, namely the "*trans* influence". This is a THERMODYNAMIC term, and relates only to the ground state of the molecule. Some ligands have marked influence on the geometry, structure, and other measurable factors of a molecule.
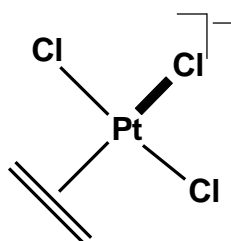
A complete structural *trans* influence order:

H- > PR3 > SCN- > I- , CH3- ~ olefin ~ CO ~ CN- > Br- > Cl- > NH3 > OH

As an example of how to measure *trans* influence, X-ray crystallography can be used to characterise the Pt-Cl containing species. The Pt-Cl bond strength increases (bond length decreases) in the order:
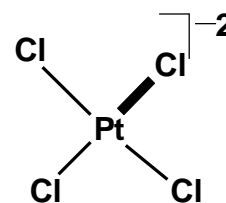
phosphine < olefin < chloride
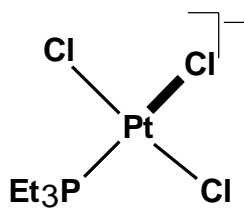
2.382 A   **2.327** A   **2.317** A

IR data for Pt-Cl stretching frequency in *cis*-[PtL$_2$Cl$_2$] complexes:

Consider the symmetric and asymmetric stretching frequencies of the Pt-Cl bonds in the cis-[PtL2Cl2] complexes listed.

Question: How many stretching frequencies would you see in the IR spectrum of the equivalent trans complexes?

|		
Pyridine	343(as),	329(sym)
PMe$_3$	303(as),	300(sym)
AsMe$_3$	314(sym),	294(as)
SbMe$_3$	308(sym),	298(as)
SEt$_2$	330,	318
SeEt$_2$	333,	317
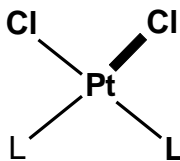
Pt-Cl frequency decreases (Pt-Cl bond weakens) along this series, as the *trans* ligand increases its *trans* influence,

$$N < S \sim Se < As \sim Te \sim Sb < P$$

The two *trans* series (trans influence and trans effect) are not the same. Some ligands (olefin, CN^- and CO) have high *trans* effect but low *trans* influence. The role of σ-donation is far more important in determining *trans* influence – a ground state property

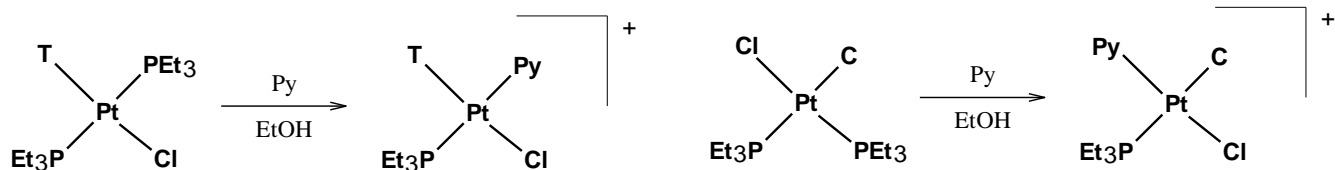**Groups cis to the leaving group - cis effect**

For the reaction:

$$[Pt(dien)X]^+ + py \rightarrow [Pt(dien)(py)]^{2+} + X^-$$
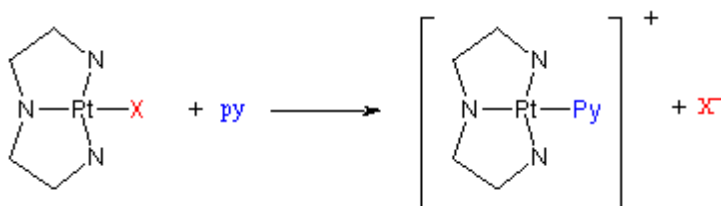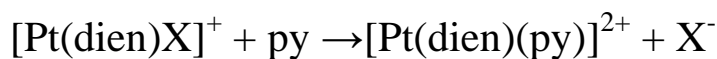
- H_2O at 25^oC the sequence of lability is: $NO_3 > H_2O > Cl > Br > I > N_3 > SCN > NO_2 > CN$ with a spread of over 10^6 in rate across series.
- Leaving group does not affect the nucleophilic discrimination factors only the intrinsic reactivity. The series tend to parallel the strength of the M-L bond.

The cis effect is a much less significant effect than the trans effect, and is observed for poor nucleophiles only. The same ligands which show a *trans* effect show much weaker *cis* effect. Thus, for the following reactions, in the first set of data the ligand which is being varied is trans to the leaving group, this is a trans effect series, and there is large range of reaction rate constants. The second set of data refers to a much weaker cis effect.

T=	H-	CH3 -	C6H5-	Cl	C =	CH3-	C6H5-	Cl
k(T)/k(Cl)	>10^4	1700	400	1	k(C)/k(Cl)	3.6	2.3	1.0

The origin of the *cis* effect is probably much the same as the *trans* effect, and has a origin in the molecular orbitals involved. The cis effect is weaker since *cis* ligands share the dx^2-y^2 orbital whilst *trans* ligands share two orbitals p_y and dx^2-y^2.

The Role or Nature of the leaving group

This is much more empirical than any of the factors discussed so far in this lecture. There is only one example worth discussing. A metal-halogen bond is generally more labile than a metal-

nitrogen bond. This is really a factor to use after all other factors have been exhausted to explain a particular reactivity. In reality there is only one example which you need to be aware of:
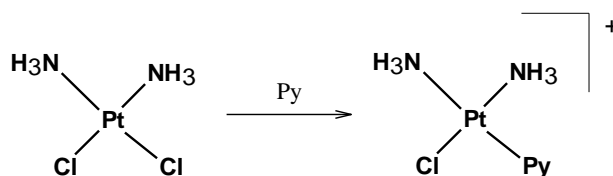
Identity of the Central metal

This order reflects the tendency of the metal to accommodate a five-coordinate geometry. There are more 5 and 6 coordinate complexes of Ni than of Pt, and this implies that the transition state for the associative substitution is more stable for Ni, giving an enhanced rate.

Reflects the tendency of the metal to accommodate a five-coordinate geometry.

There are more 5 and 6 coordinate complexes of Ni than of Pt. The associative transition state is more stable for Ni.

Rate = 33 0.58 6.7 x 10-6 M-1 sec-1

In order to understand the effect of changing the metal from a 3d to a 5d metal we can calculate Crystal Field Stabilisation Energies for 4 and 5 coordination, assuming that magnitude of Dq or Δ is invariant of geometry.

The CFSE values are -2.42 Dq for D4h starting material, -1.84 Dq for C4v square pyramid, and -1.44 Dq for D3h trigonal bipyramid.

The activation energy thus contains a contribution due to the d orbital energy change between ground and activated states. Dq is larger for 4d and 5d transition metals, so the Crystal Field contribution to the activation energy will increase.
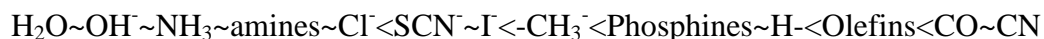
Energy (Dq)

The Nature of other Ligands in the Complex

The Trans Ligands

Definition: The trans effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it.

For square planar complexes, this is a kinetic effect.
- T is a spectator ligand trans to the Leaving Group. If T is a π-donor it will push electrons in to the metal, and weaken the M-X bond opposite it.
- π-acceptors instead stabilise the transition state by reducing the electron density in antibonding orbitals.
- For example, in the substitution reactions of Pt(II) square planar complexes, labilising effect is in the order:
  $H_2O \sim OH^- \sim NH_3 \sim amines \sim Cl^- < SCN^- \sim I^- < -CH_3^- < Phosphines \sim H- < Olefins < CO \sim CN$
- Note that the "labilising effect" is used to emphasise the fact that this is a kinetic phenomenon.
- This labilisation may arise because of destabilisation (a thermodynamic term) of the ground state and/or a stabilisation of the transition state.
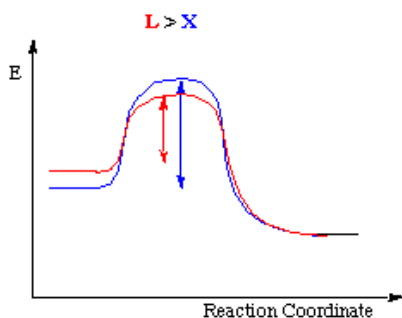
- The trans influence is purely a thermodynamic phenomenon. That is, ligands can influence the ground state properties of groups to which they are trans. Such properties include:
  (i)   Metal-Ligand bond lengths
  (ii)   Vibration frequency or force constants
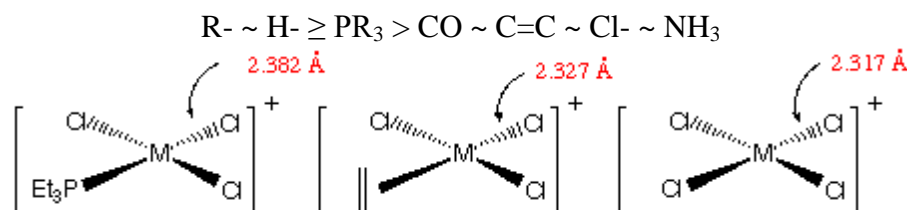 (iii) NMR coupling constants

The trans influence series based on structural data, has been given as:

$$R\text{-} \sim H\text{-} \geq PR_3 > CO \sim C{=}C \sim Cl\text{-} \sim NH_3$$

The cis ligands

- In cases where a relatively poor nucleophile act as the entering group,

$$C = CH_3^- > Ph^- > Cl^-$$

$$\frac{k_y(C)}{k_y(Cl^-)} \;=\; 3.6 \quad 2.3 \quad 1.0$$
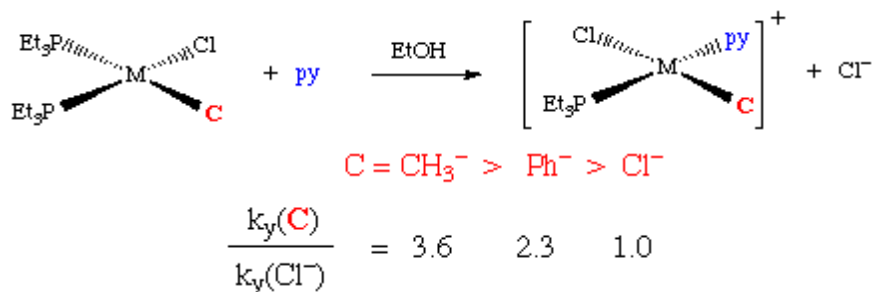
- Note: Compare with the trans series below, it acts in the same way.

4. Effect of the Metal Centre

The order of reactivity of a series of isovalent ions is:

$$Ni(II) > Pd(II) \gg Pt(II)$$
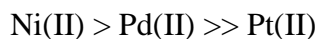
➢ This order of reactivity is the same order as the tendency to form 5-coordinate complexes.
➢ The more readily the formation of a 5-coordinate intermediate complex is, the greater the stabilisation of the transition state and so the greater the bimolecular rate enhancement.

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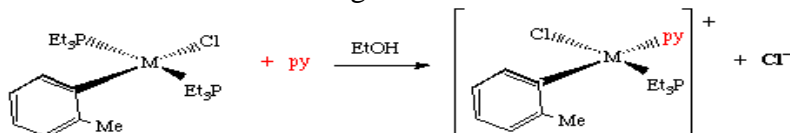
Electron Transfer Reactions

Oxidation and reduction reaction reactions of transition metal complexes, like all redox reactions involve the transfer of an electron from one species to another - in this case from one complex to another.

- Reducing agent or Reductant (R) is a substance which undergo oxidation,
- Oxidizing agent or Oxidant (O) is a substance which undergo reduction
- **The oxidized and reduced species are often metal ions surrounded by ligands or solvating molecules such as metal complex molecules or ions.**
- Oxidation-reduction (Redox) reactions of transition metal complexes, involve the transfer of one or more electrons from one species (R) to another (O) in this case, from one complex to another. Therefore they are known as **electron transfer reactions** in coordination chemistry.
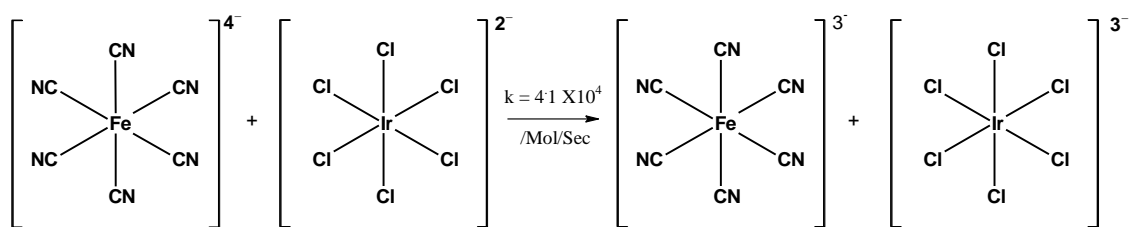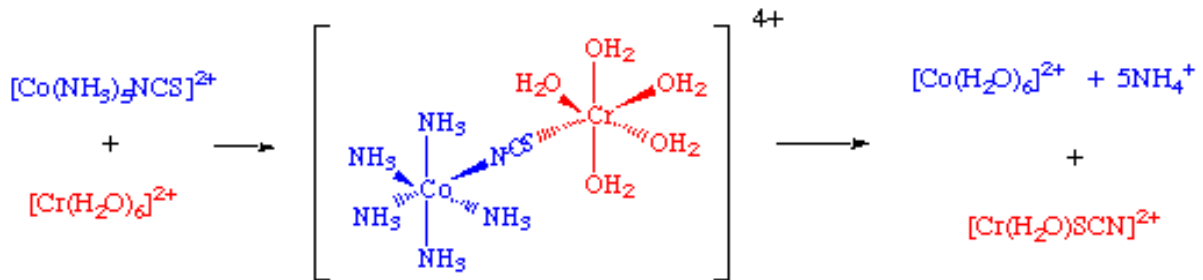- Henry Taube divided redox mechanisms or Electron transfer reactions into two broad mechanisms:
  1. **Outer sphere electron transfer reactions and**
  2. **Inner sphere electron transfer reactions**
- The exchange of electron may occur between two separate coordination spheres of two complex molecules in a nonbonding or **outer sphere reaction**.
- When the ligands of both reactants are tightly held and there is no change in the coordination sphere on reaction, the reaction proceeds by outer-sphere electron transfer.
- The two complex molecules may be connected by a common ligand through which the electron is transferred is called a bridging or **inner-sphere reaction**.

1. **Outer sphere Electron transfer reactions**: In principle outer sphere mechanism involves electron transfer from reductant complex (undergo oxidation) to oxidant complex (undergo reduction) with the coordination shells or spheres of each staying intact. That is one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant. Such a mechanism is established when rapid electron transfer occurs between two substitution-inert complexes. The exchange of an electron may occur between two separate coordination spheres in a non-bridging or outer sphere reaction. *In this type of reactions, bonds are neither made nor broken.* Ex.

1. **Inner sphere Electron transfer reactions**: An inner sphere mechanism is one in which the reactant and oxidant share a ligand in their inner or primary coordination spheres the electron being transferred across a bridging group. The two molecules may be connected by a common ligand through which the electron is transferred in which case the reaction is called a bridging or inner sphere reaction. *In this type of reactions, old bonds are broken new bonds are made.* Ex.

$$[Co(NH_3)_5NCS]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow \left[\begin{array}{c} [\text{Cr complex with } OH_2, NCS \text{ bridge to Co with } NH_3] \end{array} \right]^{4+} \longrightarrow [Co(H_2O)_6]^{2+} + 5NH_4^+ + [Cr(H_2O)SCN]^{2+}$$

The rates of electron transfer reactions have been studied well by Taube's research group. The rates of electron transfer reactions have been studied by many different methods.

- Chemical analysis of the products
- Stopped flow spectrophotometry and
- The use of radioactive and stable isotope tracers.

The rate of reaction for electron transfer depends on many factors, including,

- The rate of substitution in the coordination sphere of the reactants,

- The match of energy levels of the two reactants,

- Salvation of the two reactants, and

- The nature of the ligands.

Outer Sphere Electron-Transfer

When the ligands of both reactants are tightly held and there is no change in the coordination sphere on reaction, the reaction proceeds by outer-sphere electron transfer.

$$[ML_n]^{x+} + [ML_n]^{y+} \rightleftharpoons [ML_n]^{y+} + [ML_n]^{x+}$$
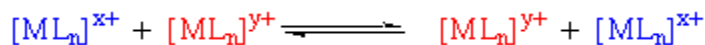
In outer sphere reactions,

- The mechanism which involves electron transfer from reductant (R) complex to oxidant (O) complex with the coordination spheres of each staying intact. That is the reaction of one reactant becomes involved in the outer or second coordination sphere of the other reactant and an electron flows from the reductant to oxidant.
- Such a mechanism is established when rapid electron transfer occurs between two substitution-inert complexes.
- In this type of mechanism the bonds are neither broken nor made. The rate of electron transfer reaction is faster than the ligand exchange. In outer sphere reactions the ligands in the coordination sphere do not change, the primary change on electron transfer is a change in M-L bond lengths or distance.
- A higher oxidation state on the metal leads to shorter σ bonds, with the extent of change depending on the electronic structure.
- The changes in bond distances are larger when e_g electrons involved, because the e_g orbitals are anti-bonding, removal of electrons from these orbitals results in a more stable compound and shorter bond distances.
- A larger ligand field stabilization energy makes oxidation easier. Comparing water and ammonia as ligands we can see that the stronger field of ammonia makes oxidation of Co(II)

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relatively easy. $[Co(NH_3)_6]^{3+}$ is a very strong oxidizing agent. The aqueous Co(III) ion, on the other hand, has a large enough potential to oxidize water.

- The ligands in the coordination sphere do not change
- The primary change on electron transfer is a change in bond distance
- A higher oxidation state on the metal leads to shorter σ bonds, with the extent of change depending on the electronic structure.
- The changes in the bond distance are larger when e_g electrons are involved, as in the change from high spin Co(II) ($t_{2g}^5 e_g^2$) to low-spin Co(III) (t_{2g}^6). Because e_g orbitals are antibonding removal of electrons from these orbitals result in a more stable compound and shorter bond distances.
- A larger LFSE makes oxidation easier.

Mechanism
- Electron transfer from the reductant to the oxidant, with the coordination shells or spheres of each staying intact. (One reactant becomes involved with outer sphere or second coordination sphere of the other reactant).
- Such reactions are observed in electron-transfer reactions of substitutionally inert complexes.
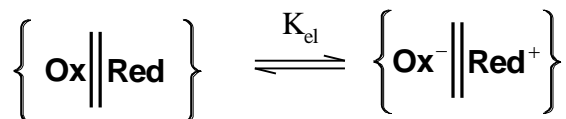
Elementary Steps in the Outer Sphere Mechanism
- Formation of a precursor (cage) complex:

$$ \textbf{Ox} \ + \ \textbf{Red} \ \xrightleftharpoons{K_A} \ \left\{ \textbf{Ox} \middle\| \textbf{Red} \right\} $$
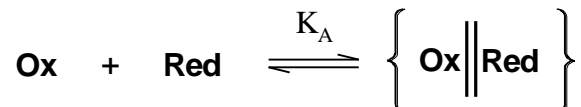
- Chemical activation of the precursor, reorganisation of the solvent molecules and changes in metal-ligand bond lengths must occur before electron transfer can take place.

$$ \left\{ \textbf{Ox} \middle\| \textbf{Red} \right\} \ \rightleftharpoons \ \left\{ \textbf{Ox} \middle\| \textbf{Red} \right\}^* $$
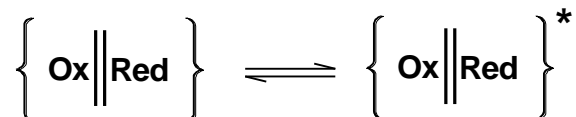
- Electron transfer and relaxation of the successor complex: This step is always considered to be fast, the rate is generally determined by k_{el}.

$$ \left\{ \textbf{Ox} \middle\| \textbf{Red} \right\} \ \xrightleftharpoons{K_{el}} \ \left\{ \textbf{Ox}^- \middle\| \textbf{Red}^+ \right\} $$

- Dissociation to the separated products

$$ \left\{ \textbf{Ox} \middle\| \textbf{Red} \right\} \ \longrightarrow \ \textbf{Ox}^- \ + \ \textbf{Red}^+ $$

$$ k_{obs} = K_A \, k_{el} $$
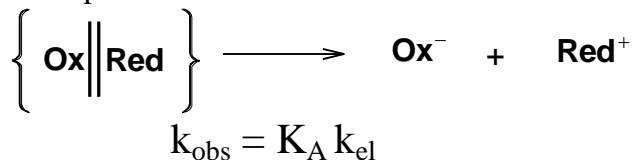
Important factors are:
- Solvent reorganisation
- Electronic structure
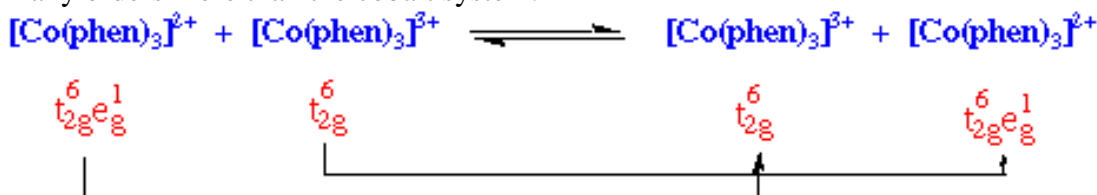- M-L reorganisation small

Franck-Condon Factors

Electron-transfer processes must satisfy the Frank-Condon restrictions, i.e. the act of electron transfer is much shorter than atomic motion. The consequences are that no angular momentum can be transferred to or from the transition state during electron transfer, there is also restrictions in changes in spin.
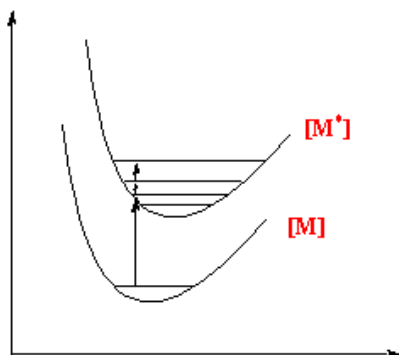
Electron-transfer timescale ~ 10^{-15} sec
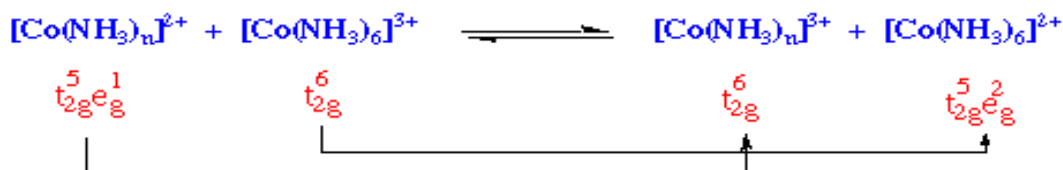Nuclear motion ~10^{-13} sec

Example 1:

It should be noted that all self-exchange reactions between Co(III)/Co(II) couple are slow. The nature of the ligand bound has been a significant influence on the reaction rate. in particular ligands with π-systems provide easy passage of electrons. For $[Co(phen)_3]^{3+}/[Co(phen)_3]^{2+}$ exchange k is 40 M-1s-1, many orders more than the cobalt system.

$$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \rightleftharpoons [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$$

$$t_{2g}^6 e_g^1 \qquad t_{2g}^6 \qquad t_{2g}^6 \qquad t_{2g}^6 e_g^1$$

Has an outer sphere electron transfer rate of 1.1 M^{-1} sec^{-1}, simply requires the transfer of electron from e_g orbital of one Co to the other.

Example 2:

The importance of bond distortion magnitudes is revealed in the self-exchange reaction of hexamminecobalt complexes:
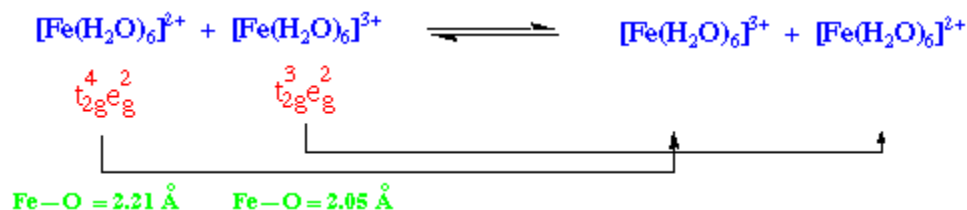

$$[Co(NH_3)_n]^{2+} + [Co(NH_3)_6]^{3+} \rightleftharpoons [Co(NH_3)_n]^{3+} + [Co(NH_3)_6]^{2+}$$

$$t_{2g}^5 e_g^1 \qquad t_{2g}^6 \qquad t_{2g}^6 \qquad t_{2g}^5 e_g^2$$

This reaction is very slow k = 10^{-9} M^{-1} sec^{-1} requires a change of spin multiplicity as well. The second order rate constant for this slow reaction is 10-6 $M^{-1}s^{-1}$. The Co-N bond length in Co(III) is 1.936(15) A while in Co(II) it is 2.114(9)A, a difference of 0.178 A. Considerable elongation of the Co(III)-N bond and compression of the Co(II)-N bond is necessary before elelctron transfer can occur.

Example 3:

In contrast, the self-exchange rate constant for the $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{2+}$ couple is $8.2X10^2$ $M^{-1}s^{-1}$ and the Ru-N bond length difference is 0.04(6)A. This much faster rate for the Ru exchange is consistent with a small bond length adjustment prior to electron transfer. The cobalt and ruthenium systems are not entirely analogous, however since cobalt goes from a low spin d6 complex to a high spin d7 complex while ruthenium remains low spin both the oxidised and reduced forms. It has been argued that the cobalt reaction is anomalously slow because it is spin forbidden.

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Example 4:

In addition the oxidant and reductant must structurally reorganise themselves before electron transfer so that the energies of their transition states are equal. For example:

$$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$$

$$t_{2g}^4 e_g^2 \qquad t_{2g}^3 e_g^2$$

Fe—O = 2.21 Å   Fe—O = 2.05 Å

If electron transfer took place at their equilibrium positions, then we would have compressed Fe(II) ion and a stretched Fe(III) ion. These are in vibrationally excited states and would release energy, contravening thermodynamics. Thus the reagents must match their energies before electron transfer can occur.
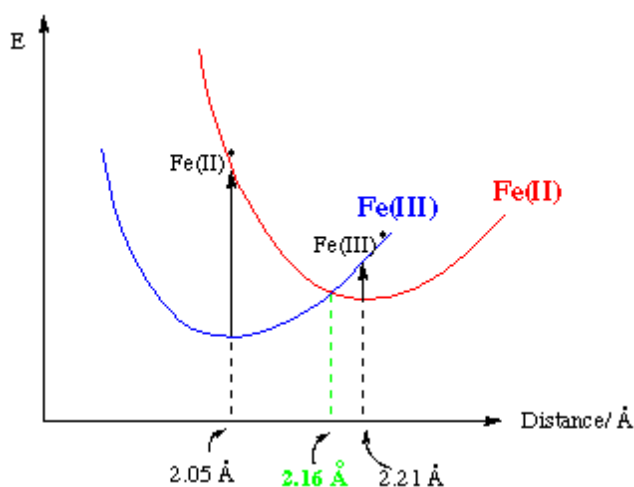
Theory: $E_{act} \sim 25.0$ kJ mol^{-1}
Expt: $E_{act} \sim 44.1$ kJ mol^{-1}

Activation, electron transfer reaction between solvated Fe(III) and Fe*(II) has been studied with radioactive isotopes of iron.

In this reaction an elelctron is transferred from a t2g orbital of Fe(II) to a t2g orbital of Fe(III). The bond lengths in Fe(II) and Fe(III) complexes are unequal which tells us that the energies of the orbitals are not equivalent. If the electron transfer could take place without an input of energy, we would obtain as products the Fe(II) complex with bond lengths typical of Fe(III) and the Fe(III) complex with bond lengths typical of Fe(II), both could then relax with the release of energy. This would clearly violate the first law of thermodynamics. In fact there must be an input of energy in order for electron transfer to take place. The actual process occurs with shortening of bonds in the Fe(II) complex and lengthening of the bonds in the Fe(III) complex until the participating orbitals are of the same energy. Vibrational stretching and compression along the metal-ligand bonds allow the required configuration to be achieved.

➢ The energy of activation ΔG*, for this reaction is 33 kJ/mol.
Q. Why it is not zero since reactants and products are same?
In order for electron transfer to occur the energies of the participating electronic orbitals must be the same, as required by the **Frank Condon principle**.

The energy of activation may be expressed as the sum of the three terms, in which

- $\Delta G_t^{\ddagger}$ is the energy required to bring the oxidant and reductant into a configuration in which they are separated by the required distance (for charged reactants this includes work to overcome coulombic repulsion),
- $\Delta G_i^{\ddagger}$ is the energy required for bond compression and stretching to achieve orbitals of equal energy, and
- $\Delta G_0^{\ddagger}$ is the energy needed for solvent reorganisation outside of the first coordination sphere.

$$\Delta G^{\ddagger} = \Delta G_t^{\ddagger} + \Delta G_i^{\ddagger} + \Delta G_0^{\ddagger}$$
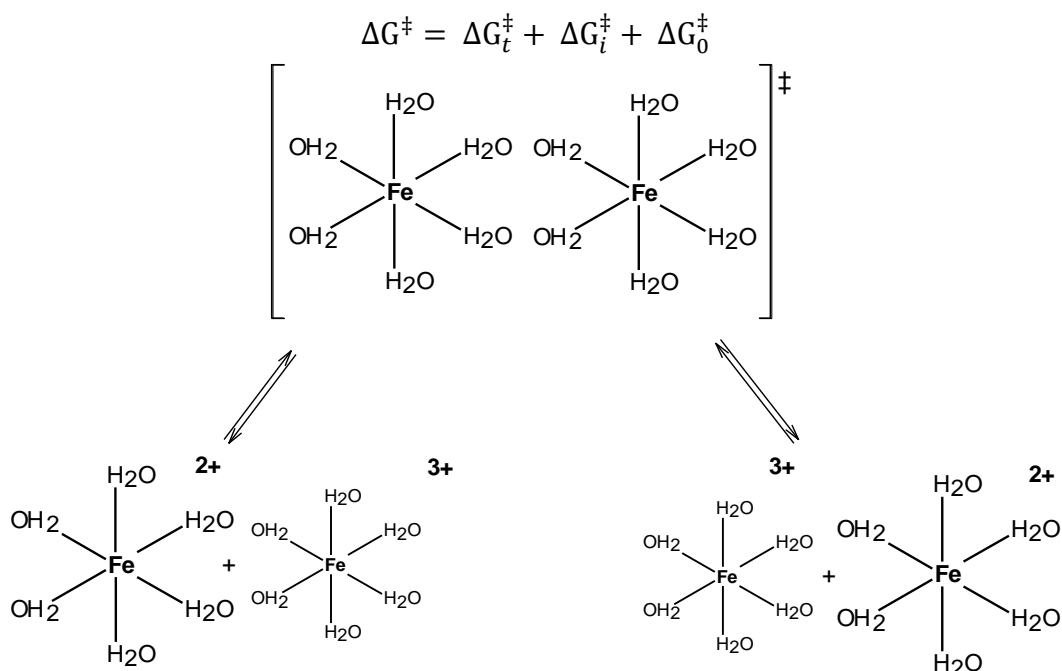
Fig. Extension and compression of the Fe-O bonds in $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$ to form an activated complex in which all metal-ligand distances are identical, a prerequisite for electron transfer between the two complexes.

Potential energy diagrams further clarify the connection between molecular motion and electron transfer. the potential energy of all reactant and associated solvent nuclei before electron can be approximated as a harmonic potential well. The potential energy of all product and solvent nuclei after electron transfer can be described similarly. The reactants and products of above eqn. have the same energy, as shown in fig. At the intersection of the potential energy surfaces I the requirement of equal orbital energies is met. For electron transfer to occur at I however the coupling of vibrational and electronic motion must take place. The extent of this interaction is related to ΔE shown in the fig. If the coupling interaction is strong which the condition is when bond distortions are small, electron transfer is favourable. if the interaction is weak associated with large bond distortions $\Delta G_i^{\ddagger}$ will be large and the reaction will be slow. These considerations are equally applicable to heteronuclear reactions as shown in fig.

$$[Fe(OH_2)_6]^{2+} + [Fe(OH_2)_6]^{3+}$$
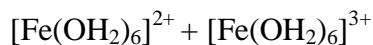
Fe(II) shortens, Fe(III) lengthens – minimises energy.

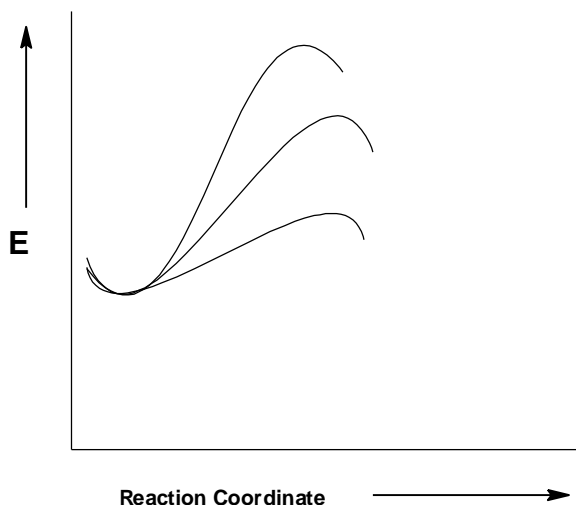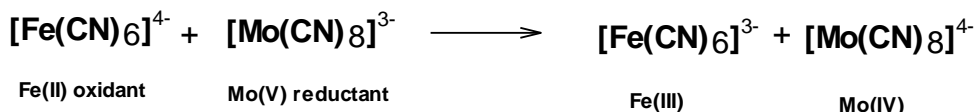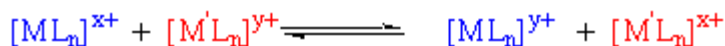A high ΔH_a indicates sharp potential curves as bonds distort, therefore a large ΔG_a.

Generalised Rules for Chemical Activation

- ➢ The factors mentioned above can be combined with basic MO theory to give a basis for predicting trends in electron transfer rates using electron structure arguments.
- ➢ You could expect more facile electron transfer when both donor and acceptor MO's are * type.

Reasons are:
- ➢ Changing M-L distance is usually less for a change in d* than d* orbital
- ➢ Donor-acceptor overlap is better for ** transfer than ** transfer, since *orbitals point to faces of Oh rather than the corners (*)

Cross Reactions and the *Marcus Equation*

$$[ML_n]^{x+} + [M'L_n]^{y+} \rightleftharpoons [ML_n]^{y+} + [M'L_n]^{x+}$$

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$$

Fe(II) oxidant   Mo(V) reductant   Fe(III)   Mo(IV)

E

Reaction Coordinate ⟶

In general the rates of outer sphere electron transfers involving a change in free energy are given by the Marcus Equation used to calculate the rate constants.

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

Where k_{11} is the rate constant for the self exchange process involving the hexacyanoferrate complexes.

$$[Fe(CN)_6]^{4-} + [Fe^*(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Fe^*(CN)_6]^{4-} \quad k_{11} = 7.4 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$$

Where k_{22} is the rate constant for the self exchange process involving the octacyanomolebdenum complexes.

$$[Fe(CN)_6]^{4-} + [Fe^*(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Fe^*(CN)_6]^{4-} \quad k_{11} = 7.4 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$$

K_{12} is the equilibrium constant for the overall cross reaction.

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \rightleftharpoons [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-} \quad k_{12} = 1.0 \times 10^4 \text{ M}^{-}1\text{s}^{-}1$$

Fe(II) oxidant   Mo(V) reductant   Fe(III)   Mo(IV)

The parameter f $_{12}$ is usually close to 1.

$$Log f_{12} = \frac{(Log K_{12})^2}{4} \left(Log \frac{k_{11}k_{22}}{Z^2}\right.$$

This last term contains Z, which is the collision frequency of two uncharged particles in solution and is taken as 10^{11} M^{-1}s^{-1}. The factor f_{12} has been described as a correction for the difference in free energies of the two reactants and)is often close to unity. In this case it is 0.85. When all of the appropriate values are substituted into eqn. k12, is calculated to be 4×10^4 M-1s-1, which compares quite well with the experimental value of 3.0×10^4 M^{-1}s^{-1}. k12 values for many outer sphere cross reactions are given in the table. Confidence in the Marcus equation is high enough that, if it leads to a calculated rate constant that is in strong disagreement with an experimental value, a mechanism other than outer sphere should be considered.

The Marcus equation connects thermodynamics and kinetics, as shown by the dependence of k_{12} on K_{12}: as K_{12} increases, the reaction rate increases. Thus outer sphere reactions which are thermodynamically more favourable tend to proceed faster than those which are less favourable. These observations may be surprising to you since most elementary treatments of reaction dynamics keep thermodynamics (how far) and kinetics (how fast) separate. Here we see that how fast a reaction occurs can depend to some degree on how far it goes, or the driving force, ΔG. The simplified Marcus equation we have presented here, however, breaks down when K12 becomes large. The complete theory reveals that rate increases rapidly with increases spontaneously, reaching a maximum when the change in free energy is equal to the sum of reorganisation energies, and then decreases as the driving force increases further.

The barrier to electron transfer consists of two parts, the "intrinsic" contribution and the thermodynamic part ($\Delta G_{12}°$). The free energy of activation for electron transfer (ΔG_{12}^{++}) is given by:

$$\Delta G_{12}^{\ddagger} = \frac{\Delta G_1^{\ddagger} + \Delta G_2^{\ddagger}}{2} + \frac{\Delta G_{12}^0}{2}$$

Summary

➢ Simple electron transfer. No sharing of ligands.
➢ Occurs when redox is faster than ligand substitution.
➢ The key to the mechanism is the matching of the energies of the reactants.

To Enhance Outer-Sphere Electron Transfer Rates

➢ Minimal solvent reorganisation (large ligands)
➢ Small changes in M-L bond lengths (π^* -> π^*)
➢ Good orbital overlap (π-> π^*, π-acceptor ligands)

• Ideally, the electron transfer should be between the same energies of reactants, so that electrons do not have to move (Frank-Condon Principle).

• This means BOND LENGTHS adjust to match (ΔG_{in}). There is also a solvent rearrangement factor, ΔG_{out}.

The degree of bond lengthening is governed by **several factors**.

1. *Nature of Metal Centre* –
    • The larger 4d/5d orbitals allow for greater bond length adjustments due to reduced e-e repulsions and larger orbital splittings.
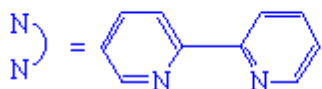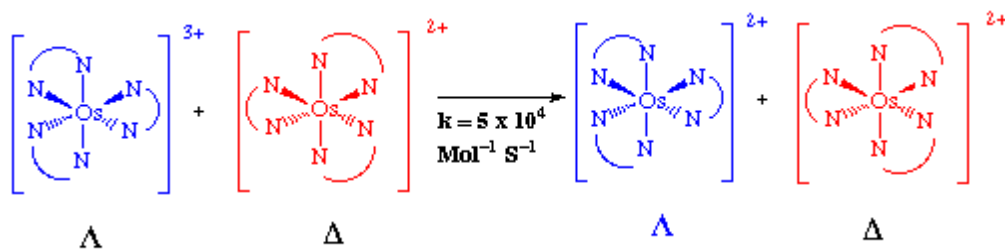
- Electron Configuration is often an important factor, since placing electrons into antibonding orbitals during oxidation increases bond lengths greatly. Also change from low to high spin expends energy. Both of these increase ΔG_{in}.
- Large metals (2nd / 3rd row) tend to be low spin, so do not vary bond lengths as significantly.
- This is because the low spin configuration means that antibonding orbitals are not occupied, and these would reduce bond lengths far more than non-bonding orbitals would.

2. *Nature of Ligand* –

- Also an important factor. For example, the pyridine ligand, possessing a π- delocalised MO, can extend this over the metal t_{2g} orbitals, which greatly decreases the reorganisation energy, so there is a faster transfer.
- Strong field ligands may also split the crystal field of the metal greatly, making them adopt a low spin configuration. This reduces Δr as mentioned above.

- Comparing water and ammonia as ligands we can see the stronger field of ammonia makes oxidation of Co(II) relatively easy.
 Ex. Rate constants for Outer Sphere Electron-Transfer:

Oxidant↓	**Reductant** → $[Cr(bipy)_3]^{2+}$	$[Ru(NH_3)_6]^{2+}$
$[Co(NH_3)_5(NH_3)]^{3+}$	6.9×10^2	1.1×10^{-2}
$[Co(NH_3)_5(F)]^{2+}$	1.8×10^3	--
$[Co(NH_3)_5(OH)]^{2+}$	3×10^4	4×10^{-2}
$[Co(NH_3)_5(NO_3)]^{2+}$	--	3.4×10^1
$[Co(H_2O)_5(H_2O)]^{3+}$	5×10^4	3.0
$[Co(NH_3)_5(Cl)]^{2+}$	8×10^5	2.6×10^2
$[Co(NH_3)_5(Br)]^{2+}$	5×10^6	1.6×10^3
$[Co(NH_3)_5(I)]^{2+}$	--	6.7×10^3

The rates show very large differences. The rates depend on the ability of the electrons to tunnel through the ligands. This is a quantum mechanical property whereby electrons can pass through potential barriers that are too high to permit ordinary transfer. Ligands with π or p electrons or orbitals that can be used in bonding provide good pathways for tunnelling, those like NH_3, with no extra lone pair and no low-lying anti-bonding orbitals, do not.

Ex. $[Co(NH_3)_6]^{3+}$ is a very weak oxidising agent. The aqueous Co(III) ion on the other hand, has a large enough potential to oxidise water:

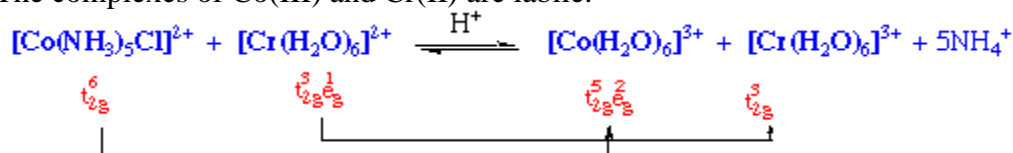$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{3+}$$

$$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$$
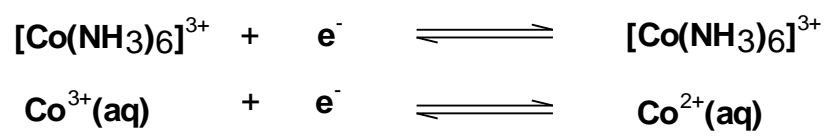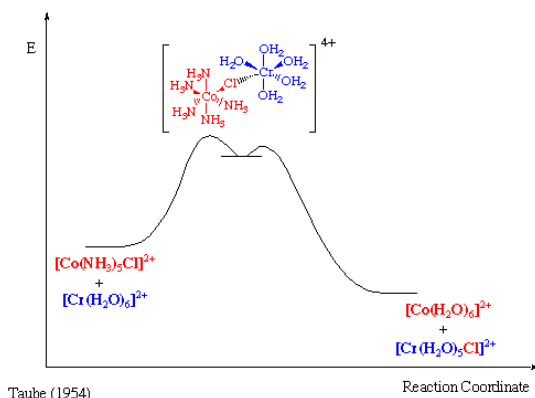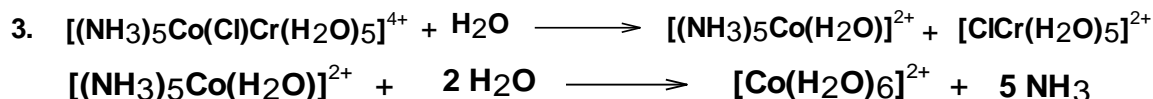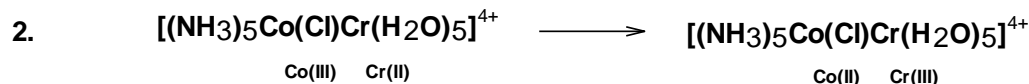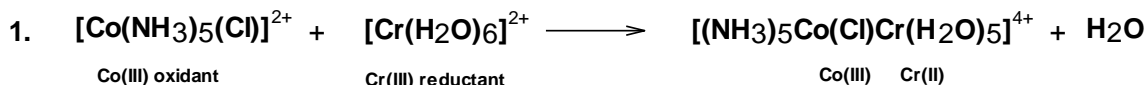
Inner Sphere Electron Transfer

Inner sphere reactions are more complicated than outer sphere reactions because in addition to electron transfer, bonds are broken and bonds are made. A ligand which bridges two metals is intimately involved in the electron transfer.

The classic example of this type of mechanism was provided by Taube and co-workers. Their system involved the reduction of Co(III) in $[Co(NH_3)_5Cl]^{2+}$ by chromium(II) in $[Cr(H_2O)_6]^{2+}$ and was specifically chosen because ,

i.   Both Co(III) and Cr(II) form inert complexes and
ii.   The complexes of Co(III) and Cr(II) are labile.

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \xrightleftharpoons{H^+} [Co(H_2O)_6]^{3+} + [Cr(H_2O)_6]^{3+} + 5NH_4^+$$

$$t_{2g}^6 \qquad t_{2g}^3 e_g^1 \qquad\qquad t_{2g}^5 e_g^2 \qquad t_{2g}^3$$

- Under these circumstances the Cl atom, while remaining finally attached to the inert Co(III) ion, can displace a water molecule from the labile Cr(II) complex to form a bridged intermediate;
- Reduction of hexaamminecobalt(3+) by hexaaquochromium(2+) occurs slowly (k = 10-3 M-1sec-1) by an outer sphere mechanism.
- However, if one ammonia ligand on Co(III) is substituted by Cl⁻, reaction now occurs with a substantially greater rate (k = 6 x 10^5 M^{-1} sec^{-1}).
- The reductant and the oxidant share a ligand in their primary coordination sphere, the electron being transferred across a bridging group.

1. $[Co(NH_3)_5(Cl)]^{2+}$ + $[Cr(H_2O)_6]^{2+}$ ⟶ $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}$ + H_2O
    Co(III) oxidant   Cr(III) reductant   Co(III)   Cr(II)

2. $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}$ ⟶ $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}$
    Co(III)   Cr(II)   Co(II)   Cr(III)

3. $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}$ + H_2O ⟶ $[(NH_3)_5Co(H_2O)]^{2+}$ + $[ClCr(H_2O)_5]^{2+}$

    $[(NH_3)_5Co(H_2O)]^{2+}$ + $2H_2O$ ⟶ $[Co(H_2O)_6]^{2+}$ + $5NH_3$

Taube (1954)

The redox reaction now takes place within this di-nuclear complex with formation of reduced Co(II) and oxidised Cr(III). The latter species forms an inert chloroaqua complex, but the Co(II) is labile so the intermediate dissociates with the chlorine atom remaining with chromium.

The five coordinate Co(II) species presumably immediately picks up a water molecule to fill its sixth coordination position and then hydrolyses rapidly to $[Cr(H_2O)_6]^{2+}$. Formally such an inner sphere reaction consists of the transfer of a chlorine atom from cobalt to Cr, decreasing the oxidation state of the former but increasing that of the later. in addition to the self-consistency of the above model (inert and labile species) and the observed formation of a chlorochromium complex, further evidence for this mechanism has been obtained by running the reaction in the presence of free radioisotopes of chlorine ion in the solution. Very little of this labelled chloride is ever found in the product, indicating that the chloride transfer has indeed been through the bridge rather than indirectly through free chloride.

**Rate constants for the reaction of $[Co(NH_3)_5X]^{2+}$ with Cr^{2+}:**

X	k_r $M^{-1}s^{-1}$
NH_3	8.9×10^{-5}
H_2O	0.5
OH^-	1.5×10^6
F^-	2.5×10^5
Cl^-	6×10^5
Br^-	1.4×10^6
I^-	3×10^6
N_3^-	3×10^5

The importance of the nature of the bridging ligand in an inner sphere reaction is shown in table. The reduction of $[Co(NH_3)_5Cl]^{2+}$ is about 10^{10} faster than the reduction of $[Co(NH_3)_5X]^{2+}$. The bound ammonia ligand has no nonbonding pairs of electrons to donate to a second metal. Thus the reduction of the hexamine complex cannot proceed by an inner sphere mechanism. If ligands are not available which can bridge two metals, an inner sphere mechanism can always be ruled out. A second important feature of an inner sphere reaction is that its rate can be no faster than the rate of exchange of the ligand in the absence of a redox reaction, since exchange of the ligand is an intomate part of the process. As was noted earlier electron transfer reactions must be outer sphere if they proceed faster than ligand exchange.
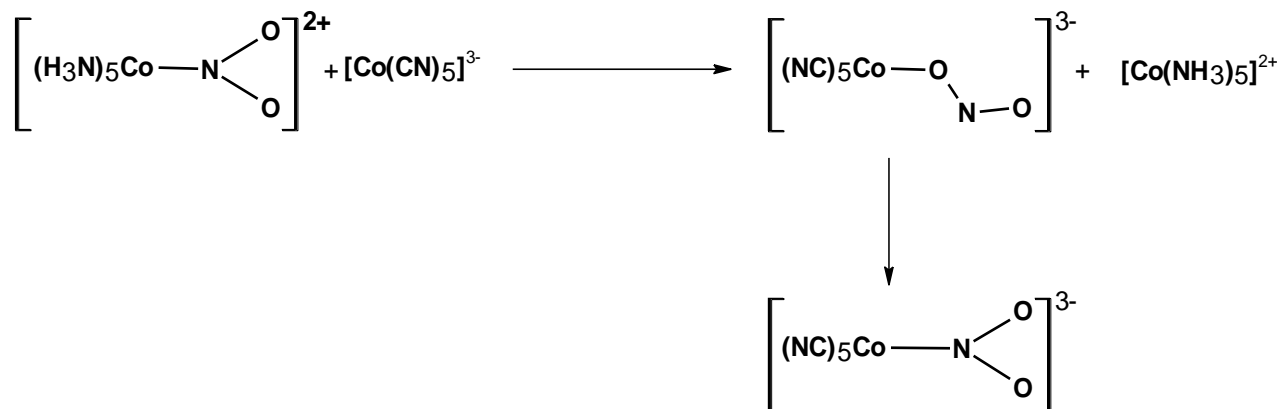
It is often difficult to distinguish between outer and inner sphere mechanisms. The rate law is of little help since both kinds of electron transfer reactions usually are second order (first order w r t each reactant):

<p align="center">Rate = k [oxidant][reductant]</p>

Furthermore although the chloro ligand is transferred from oxidant to reductant, it is not always the case that the bridging ligand is transferred in an inner sphere reaction. after electron transfer takes place in the dinuclear complex, the subsequent dissociation may leave the ligand that functioned as a bridge attached to the metal with which it began. If the bridging ligand stabilised its original complex more than the newly formed complex, failure of its transfer would be no surprise. For ex.

$$[Co(CN)_5]^{3-} + [Fe(CN)_6]^{3-} \longrightarrow [(CN)_5Co\text{-}NC\text{-}Fe(CN)_5]^{6-}$$

<p align="center">Crystaline Salt</p>
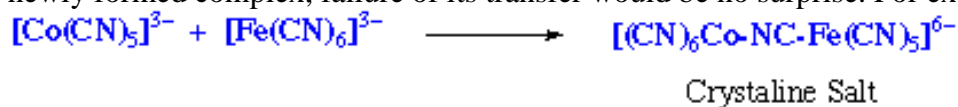
- Presumably the C-bound cyano group stabilises the d^6 (Fe^{2+}) configuration of $[Fe(CN)_6]^{4-}$ more than the N-bound cyano group would stabilise a d^6 (Co^{3+}) configuration in $[Co(CN)_5(NC)]^{4-}$.
- If the bridging ligand contain only one atom (ex. Cl-), both metal atoms of the complex must be bound to it. However, if the bridging ligand conatains more than one atom (ex. SCN-), the two metal atoms may or may not be found to the same bridging-ligand atom.
- The two conditions are called **adjacent** and **remote** attack, respectively. A remote attack may lead to both linkage isomers:
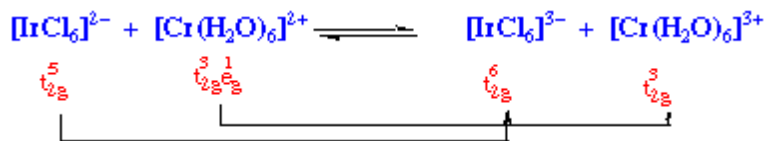
$$[(H_3N)_5Co-N\diagdown^O_O]^{2+} + [Co(CN)_5]^{3-} \longrightarrow [(NC)_5Co-O\diagdown_{N-O}]^{3-} + [Co(NH_3)_5]^{2+}$$

$$\downarrow$$

$$[(NC)_5Co-N\diagdown^O_O]^{3-}$$

In the above instance the kinetically favoured nitrito complex isomerises to the thermodynamically favoured nitrito complex in seconds.

Prerequisites for Inner Sphere Mechanism

➢ One reactant (usually the oxidant) possesses at least one ligand capable of binding simultaneously to two metal ions.
➢ The other reactant is substitutionally labile; i.e. one ligand must be replaced by the bridging ligand.

Examples

$$[IrCl_6]^{2-} + [Cr(H_2O)_6]^{2+} \rightleftharpoons [IrCl_6]^{3-} + [Cr(H_2O)_6]^{3+}$$
$$t_{2g}^5 \qquad t_{2g}^3 e_g^1 \qquad t_{2g}^6 \qquad t_{2g}^3$$

• Ligand transfer is not a requirement for inner sphere mechanism.

The Elementary Steps and Rate Expression for the Inner Sphere Mechanism

2. **Formation of a precursor complex:** A substitution reaction that leaves the oxidant and reductant linked by the bridging ligand.

$$Ox\text{---}X + Red\,(H_2O) \rightleftharpoons Ox\text{---}X\text{---}Red + H_2O$$
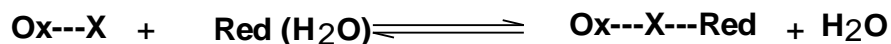
3. **Activation of the precursor, and electron transfer:** The actual transfer of electron (frequently accompanied by transfer theligand)

$$Ox\text{---}X\text{---}Red \rightleftharpoons {}^-Ox\text{---}X\text{---}Red^+$$
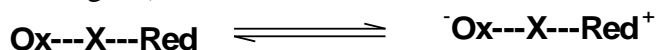
4. **Dissociation to the separated products:** Sepeartion of products

$$^-Ox\text{---}X\text{---}Red^+ + H_2O \rightleftharpoons Ox(H_2O)^- + Red(X)^+$$
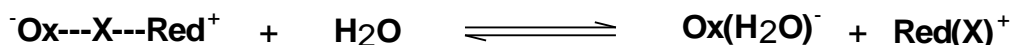
The overall reaction can be given by:

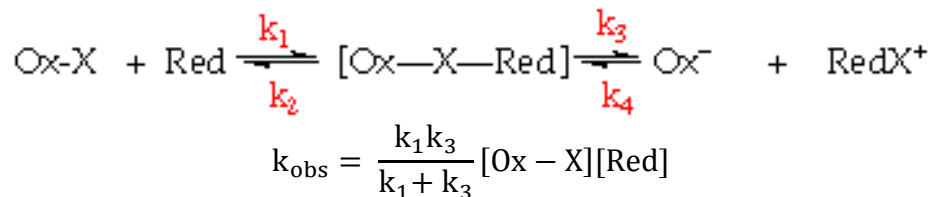$$\text{Ox-X} + \text{Red} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [\text{Ox—X—Red}] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{Ox}^- + \text{RedX}^+$$

$$k_{obs} = \frac{k_1 k_3}{k_1 + k_3} [\text{Ox} - \text{X}][\text{Red}]$$

k_1 is rate limiting, formation of the precursor complex (usually substitution of the bridging ligand for H_2O on the Red complex).

k_3 is rate determining, electron transfer within the complex, or fission of the successor complex. Both extremes give 2nd order kinetics

1. $[Co(NH_3)_5(Cl)]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow [(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+} + H_2O$

     Co(III) oxidant   Cr(III) reductant   Co(III)   Cr(II)

2. $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+} \longrightarrow [(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+}$

          Co(III)   Cr(II)   Co(II)   Cr(III)

3. $[(NH_3)_5Co(Cl)Cr(H_2O)_5]^{4+} + H_2O \longrightarrow [(NH_3)_5Co(H_2O)]^{2+} + [ClCr(H_2O)_5]^{2+}$
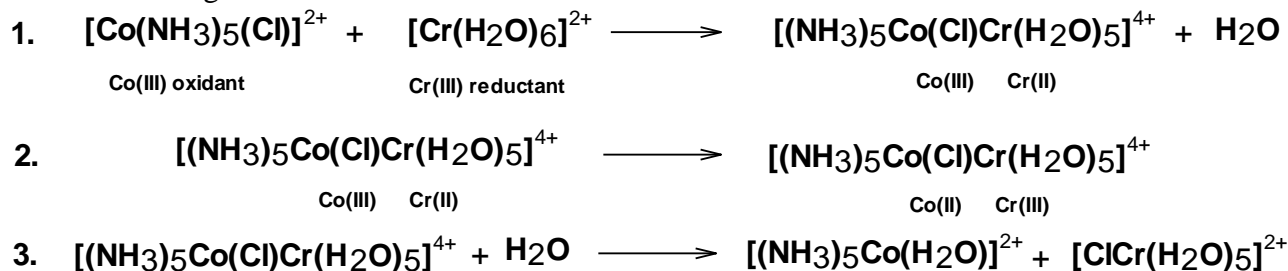
In this case these are followed by a reaction made possible by the labile nature of Co(II):

$$[(NH_3)_5Co(H_2O)]^{2+} + 2 H_2O \longrightarrow [Co(H_2O)_6]^{2+} + 5 NH_3$$
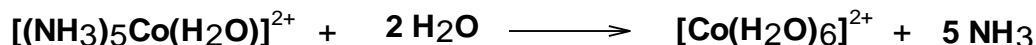
The transfer of chloride to the chromium in these reactions is easy to follow experimentally because Cr(III) is substitutionally inert and the products can be separated by ion exchange techniques and their composition can be determined. When this is done, all the Cr(III) appears as $CrCl^{2+}$.

The $[Cr(H_2O)_6]^{2+}$-$[Cr(H_2O)_5Cl]^{2+}$ exchange reaction (which results in no net change) has also been studied using radioactive ^{51}Cr as a tracer. All the chloride in the product came from the reactant, with none entering from excess Cl⁻ in the solution. The reaction could also be determined by following the amount of radioactivity found in the $CrCl^{2+}$ at different times during the reaction.

In many cases the choice between inner and outer sphere mechanisms is difficult. In the Table, the outer sphere mechanism is required by the reducing agent. $[Ru(NH_3)_6]^{2+}$ is an inert species and does not allow formation of bridging species fast enough for the rate constants observed. Although $[Cr(bipy)_3]^{2+}$ is labile, the parallels in the rate constants of the two species strongly suggest that its redox reactions are also outer-sphere. In other cases, the oxidant may dictate an outer sphere mechanism.

In table $[Co(NH_3)_6]^{2+}$ and $[Co(en)_3]^{3+}$ have outer sphere mechanisms because their ligands have no lone pairs with which to form bonds to the reductant. The other reactions are less certain, although Cr^{2+} (aq) are usually assumed to react by inner sphere mechanisms in all cases in which bridging is possible.

Rate constants for aquated reductants:

	Cr^{2+}	Eu^{2+}	V^{2+}
$[Co(en)_3]^{3+}$	~2X10^{-5}	~5X10^{-3}	~2X10^{-4}
$[Co(NH_3)_6]^{2+}$	8.9X10^{-5}	2X10^{-2}	3.7X10^{-2}
$[Co(H_2O)_5(H_2O)]^{3+}$	5X10^{-1}	1.5X10^{-1}	5X10^{-1}
$[Co(NH_3)_5(NO_3)]^{2+}$	9X10^{1}	1.5X10^{-1}	5X10^{-1}

$[Co(NH_3)_5(NH_3)]^{3+}$	~$9X10^1$	~$1X10^2$	
$[Co(NH_3)_5(Cl)]^{2+}$	$6X10^5$	$3.9X10^2$	5
$[Co(NH_3)_5(Br)]^{2+}$	$1.4X10^6$	$2.5X10^2$	$2.5X10^1$
$[Co(NH_3)_5(I)]^{2+}$	$3X10^6$	$1.2X10^2$	$1.2X10^2$

V^{2+} (aq) reactions appear to be similar to those of Cr^{2+} (aq) although the range of rate constants is similar than that for Cr^{2+}. This seems to indicate that the ligands are less important and makes an outer sphere mechanism more likely. This is reinforced by comparison of the rate constants for the reactions of $[Cr(bipy)_3]^{2+}$ and V^{2+} with the same oxidants. V^{2+} may have different mechanisms for different oxidants, just as Cr^{2+} does.

Eu^{2+} (aq) is an unusual case. The rate constants do not parallel those of either the more common inner or outer sphere reactants or the halide data are in reverse order from any others. The explanation offered for these rate constants is that the thermodynamic stability of the EuX^+ species helps drive the reaction faster for F^-, with slower rates and stabilities as we go down the series. Because of the smaller range of rate constants, Eu^{2+} reactions are usually classed as outer sphere reactions.

When $[Co(CN)_5]^{3-}$ reacts with Co(III) oxidants ($[[Co(NH_3)_5(X)]^{2+}]$) that have potentially bridging ligands, the product is $[Co(CN)_5X]^{2+}$, evidence for an inner sphere mechanism. Rate constants for a number of these reactions are given in the table.

The reaction with $[Co(NH_3)_6]^{3+}$ must be outer sphere, but has a rate constant similar to the others. The reaction with thiocyanate or nitrite as bridging groups also shows interesting behaviour. With N-bonded $[(NH_3)_5Co(NCS)]^{2+}$, it reacts by bonding to the free N end of the ligand and then rearranges rapidly to the more stable S-bonded form. In a similar fashion, a transient O-bonded intermediate is detected in reactions of $[Co(NH_3)_5(NO_2)]^{2+}$ with $[Co(CN)_5]^{3-}$.

Rate constants for reactions with $[Co(CN)_5]^{3-}$

Oxidant↓	k (M-1 s-1)
$[Co(NH_3)_5(F)]^{2+}$	$1.8X10^3$
$[Co(NH_3)_5(OH)]^{2+}$	$9.3 X 10^4$
$[Co(NH_3)_5(NH_3)]^{3+}$	$8 X 10^4$
$[(NH3)5CoNCS]^{2+}$	$1.1X10^6$
$[Co(H_2O)_5(N_3)]^{3+}$	$1.6X 10^6$
$[Co(NH_3)_5(Cl)]^{2+}$	$5X 10^7$

Other reactions that follow an inner sphere mechanism have been studied to determine which ligands bridge best. The overall rate of reaction usually depends on the first two steps (substitutuion and transfer of electron), and in some cases it is possible to draw conclusions about the rates of the individual steps. For ex. ligands that are reducible provide better pathways, and their complexes are more quickly reduced. Benzoic acid is difficult to reduce, but 4-carboxy-N-methylpyridine is relatively easy to reduce. The rate constants for the reaction of the corresponding pentamine Co(III) complexes of these two ligands with Cr(II) differ by a factor of 10, although both have similar structures and transition states. For both ligands the mechanism is inner sphere, with transfer of the ligand to Cr, indicating that coordinateion to the Cr(II) is through the carbonyl oxygen. The substitution reaction should have similar rates so the difference on overall rates is a result of the transfer electrons through the ligand. The data in the table show these effects and extend the data to glyoxylate and glycolate, which are still more easily reduced. The transfer of an electron through such ligands is very fast when compared with similar reactions with ligands that are not reducible.

Ligands reducibility and electron transfer
Rate constants for the reaction:

$$[Co(NH_3)_5(L)]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow Co^{2+} + 5\,NH_3 + [Cr(H_2O)_5(L)]^{2+} + H_2O$$

L	$k_2(M^{-1}s^{-1})$	comments
C_6H_5COO	0.15	Benzoate is difficult to reduce
CH_3COO	0.34	Acetic acid is difficult to reduce
$CH_3NC_5H_4COO$	1.30	N-methyl-4carboxypyridine is more reducible
$CH=OCOO$	3.1	Glyoxilate is easy to reduce
$CH_2(OH)COO$	7×10^3	Glycolate is very easy to reduce

Remote attack on ligands with two potentially bonding groups is also found. Isonicotinamide bonded through the pyridine nitrogen can react with Cr2+ through the carbonyl oxygen on the other end of the molecule, transferring the ligand to the chromium and an electron through the ligand from the chromium to the other metal.

The rate constants for the different metals are shown in table. The rate constants for the Cobalt pentamine and the chromium penta-aqua complexes are much closer than usual. The rate for Co compounds with other bridging ligands is frequently as much as 10^5 larger than the rate for corresponding Cr compounds, primarily because of the greater oxidising power of Co(III). With isonicotinamide compounds the rate seems to depend more on the rate of electron transfer from Cr^{2+} to the bridging ligand, and the readily reducible isonicotinamide makes the two reactions more nerly equal in rate. The much faster rate found for the ruthenium pentamine has been explained as the result of the transfer of an electron through the π system of the ligand into the t_{2g} levels of the Ru(III) (low-spin Ru(III) has a vacancy in the t_{2g} level). A similar electron transfer to Co(III) or Cr(III) places the incoming electron in the eg levels, which have σ symmetry.

Rate constants for reduction of isonicotinamide (4-pyridine carboxylic acid amide) complexes by $[Cr(H_2O)_6]^{2+}$

Oxidant	$k_2 \ (M^{-1}s^{-1})$
$[NH_2C=OC_5H_4N)Cr(H_2O)_5]^{3+}$	1.8
$[NH_2C=OC_5H_4N)Co(NH_3)_5]^{3+}$	17.6
$[NH_2C=OC_5H_4N)Ru(NH_3)_5]^{3+}$	5×10^5

Important Factors which Affect the Rate of Inner Sphere Reactions

1. Formation of the Precursor Complex

This step is closely related to the rates of substitution in Octahedral Complexes.

> ➤ Octahedral d^3 are relatively inert
> ➤ High spin d^4 and d^5 are labile

Thus the rates of electron transfer involving $[V(H_2O)_6]^{2+}$ (d^3) are comparable to the rate of water substitution.

2. Electronic Structure of Oxidant and Reductant

- Many electron transfer reactions are greatly enhanced when they proceed via an inner sphere mechanism.

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- This can be explained by consideration of the symmetries of the reductant orbital from which the electron is lost and the oxidant orbital into which the electron moves.

EXAMPLE

The σ* → σ* electron transfer is the most accelerated, and is the route that requires most chemical activation, i.e. bond rearrangement in the transition state. These requirements seem to be largely overcome by forming 3-centre bonds in the transition state.

3. Nature of the Bridging Ligand

- Inner sphere electron transfer reactions are very sensitive to the nature of the bridging ligand.
- The bridging group has two roles:
    1. To bring the metal centres together (Thermodynamic contribution), important factor here is the stability of the intermediate, and M-L bond strengths.
    2. The kinetic contribution is the transfer the electron, important factor is the matching of the donor and acceptor MO's.
- Bridging ligands can be organic or inorganic.
- However the major difficulty is deciding whether the e-transfer is either outer or inner sphere. A useful test has been developed, consider the reaction;

$$[Co(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} \rightleftharpoons [Co(H_2O)_6X]^{3+} + [Cr(H_2O)_6]^{3+}$$

$$X = N_3^- \text{ or } NCS^-$$

The azide ion can better form an intermediate, than thiocyanate.

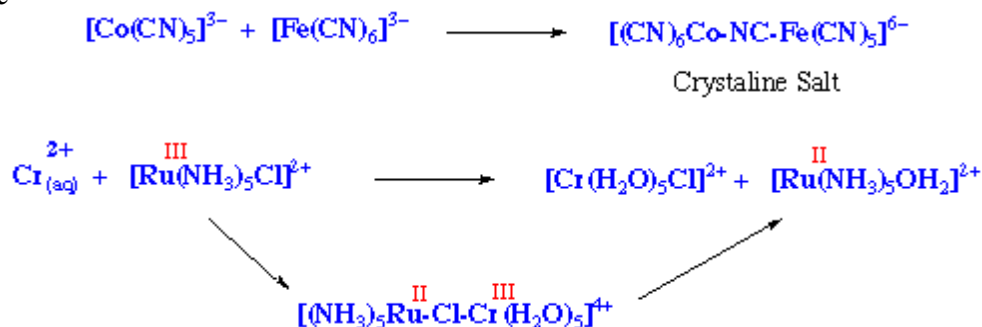$$M^-(ox)\text{--}N=N^+\text{--}N^- \quad \text{or} \quad M^-(ox)\text{--}N=C=S$$

Studies of inner sphere reactions involving organic bridging ligands, show that reduction rates can be controlled by steric effects, electronic structure of the bridge, the point on attack on the bridge, and its reducibility.

4. Fission of the Successor Complex

Occasionally, the rate determining step can be the fission of the binuclear complex, after etransfer has occurred.

For example

$$[Co(CN)_5]^{3-} + [Fe(CN)_6]^{3-} \longrightarrow [(CN)_5Co\text{-}NC\text{-}Fe(CN)_5]^{6-}$$

Crystaline Salt

$$Cr^{2+}_{(aq)} + [Ru^{III}(NH_3)_5Cl]^{2+} \longrightarrow [Cr(H_2O)_5Cl]^{2+} + [Ru^{II}(NH_3)_5OH_2]^{2+}$$

$$[(NH_3)_5Ru^{II}\text{-}Cl\text{-}Cr^{III}(H_2O)_5]^{4+}$$

The reason of the stability of the binuclear complex in this case is that both Cr(III) (d^3) and Ru(II) (d^6) are substitutionally inert.

Differentiation between Outer Sphere and Inner Sphere Electron Transfer reactions
1. Outer sphere mechanism is open to all redox active systems, while inner sphere mechanism requires substitutionally labile reactants and products.
2. Evidence from ligand transfer, labelling, etc..
3. ΔV
5. Marcus Relationship (outer sphere reactions)
6. N_3^- vs. NCS- ratio (Outer Sphere) ~ 1 ratio (Inner Sphere) >> 1

Relative Rates of Reduction of N3- and NCS- Complexes

| Oxidant	Reductant	$k(N_3^-)/k(NCS^-)$	Reaction Type
$[Co(NH_3)_5X]^{2+}$	Cr^{2+}	10^4	Inner Sphere
$[Co(NH_3)_5x]^{2+}$	V^{2+}	27	Not Determined
$[Co(NH_3)_5x]^{2+}$	Fe^{2+}	$>3 \times 10^3$	Inner Sphere
$[Co(NH_3)_5x]^{2+}$	$[Cr(bipy)_3]^{2+}$	4	Outer Sphere
$[Co(H_2o)_5x]^{2+}$	Cr^{2+}	4×10^4	Inner Sphere

Mixed valence complexes:

Theoretical treatments of electron transfer between two transition metals ions in solution are complicated by contributions arising from solvent reorganisation and by transfer pathway uncertainties. If, however the reducing and oxidising agents are separated by a bridge within a single bimetallic complex, there will be no solvent molecules between the metal ion and the pathway will be defined.

Furthermore, electron transfer over various distances can be studied by varying the length of the bridge and this can provide some insight into important biological processes. One could envision some systems in which the two metal ions are so far removed from one another that electron transfer does not take place nor can it be induced:

$$M^{2+} \text{ ---------------------- } M^{3+}$$
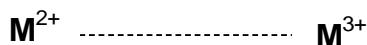
In other systems the two metal ions may be so strongly coupled that properties of the separate +2 and +3 ions are lost and the entire unit is best represented as two + 2 ½ ions.

$$M^{21/2+} \text{ ---------------------- } M^{21/2+}$$
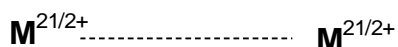
Of greater interest is systems in which modest coupling exists between metal centers, for in these it is possible to photolytically induce electron transfer. The potential energy diagram in fig. shows by means of a vertical arrows the photochemical energy necessary for an electron to pass from the potential energy surface of $M^{2+}.....M^{3+}$. This means that intervalence transitions are observed in the electronic spectra (often in the near IR region). Of these complexes, but are not found in the spectra for monometallic complexes of either M^{2+} or M^{3+}. Of course the electron could also pass thermally form one surface to the other, as for outer ssphere electron transfer, through equilization of orbital energies by vibrational elongation and contraction of metal-ligand bonds. A comparison of optical and thermal electron transfer is shown in fig. In the optical process depicted in the top part of the fig., we see that transfer occurs prior to bond length adjustment, but in the thermal process, bond length changes takes place as required by the Frank-Condon principle prior to electron transfer.
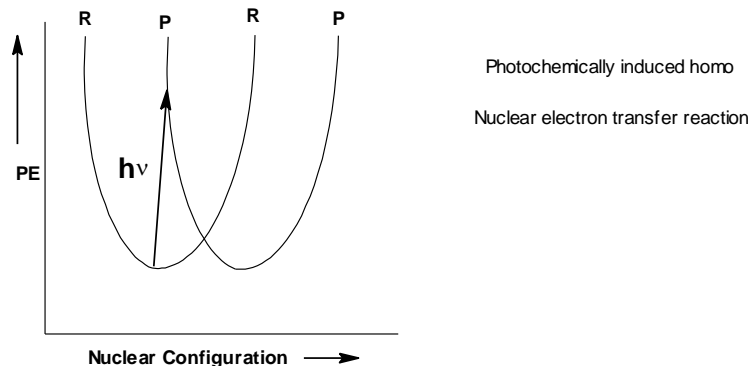
Excited state outer sphere electron transfer reactions

The redox properties of transition metal complexes may change dramatically if it has absorbed energy and exists in an excited state. One of the most famous and widely studied complexes in this area is tris(2,2'-bipyridine)ruthenium(II) cation, $[Ru(bpy)_3]^{2+}$. When this cation absorbs light at 452 nm, the excited state species that initially forms, $[**Ru(bpy)_3]^{2+,}$ relaxes to a relatively long-lived one, $[*Ru(bpy)_3]^{2+}$. The electronic transition involved in the absorption is an example of a metal to ligand charge transfer in which a d electron of Ru is promoted to a π antibonding orbitals of one of the bipyridine ligands. thus the excited state complex. $[*Ru^{II}(bpy)_3]^{2+}$ may be formulated as $[Ru^{III}(bpy)_2(bpy^-)]^{2+}$. The availability of an electron in a ligand antibonding orbital makes this excited state cation a much better reducing agent than the ground state cation.

Furthermore the hole created at the Ru center enhances its electron-seeking power and as a result, the excited cation is also a much better oxidising agent than it was in its ground state. a comparison of the redox properties of the ground state with those of the excited state is shown in fig.
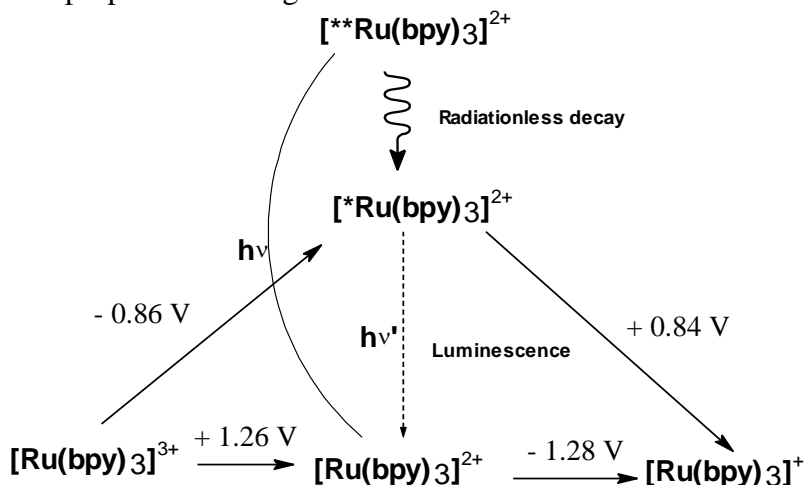

Fig. Absorption of blue light by $[Ru(bpy)_3]^{2+}$ gives $[**Ru(bpy)_3]^{2+}$ which relaxes to $[*Ru(bpy)_3]^{2+}$ without light emission. $[*Ru(bpy)_3]^{2+}$ may emit orange red light (luminescence) or undergo oxidation or reduction. Standard reduction potentials associated with individual processes are shown in the diagram.

Here we see that $[*Ru(bpy)_3]^{2+}$ is a better oxidising agent than $[Ru(bpy)_3]^{2+}$ by 2.12 V (0.84 V + 1.28 V) and a better reducing agent by 2.12 V (0.86 V + 1.26 V). These are large voltages from which one can easily see the potential for a wide range of redox chemistry.

Interest in $[Ru(bpy)_3]^{2+}$ skyrocketed after Creutz and Sutin suggested that it had possibilities for the photochemical cleavage of water.

$$H_2O(l) \xrightarrow[\Delta G^0 = 238 \text{ kJ/mol}]{h\nu} H_2(g) + 1/2\ O_2(g)$$
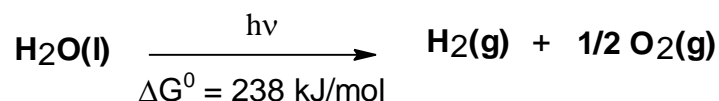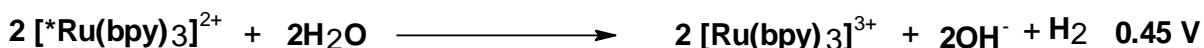
The suggestion led to the speculation that solar energy could be used to make hydrogen gas which could then be used as fuel. At pH 7 and 105 Pa, potentials for the reduction and oxidation of water are as follows:
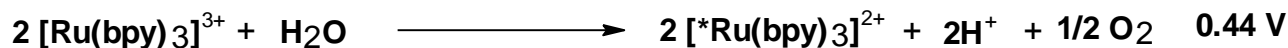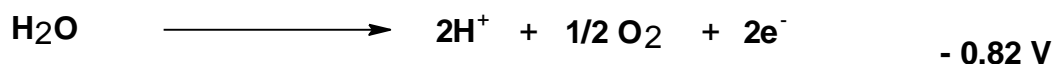
$$2e^- + 2H_2O \longrightarrow 2OH^- + H_2 \qquad - 0.41\ V$$

$$2H_2O \longrightarrow 2H^+ + 1/2\ O_2 + 2e^- \qquad - 0.82\ V$$
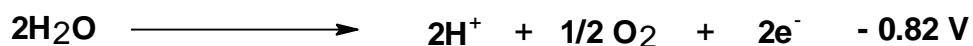
Water does not absorb visible light, but one could envision a sequence of reactions that utilise $[Ru(bpy)_3]^{2+}$ as a photosensitiser for the decomposition. The first step would be absorption of solar energy by $[Ru(bpy)_3]^{2+}$.

$$[Ru(bpy)_3]^{2+} \xrightarrow{\ h\nu\ } [{}^*Ru(bpy)_3]^{2+}$$
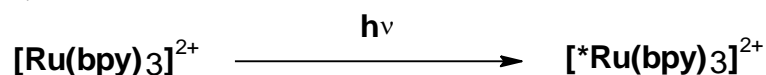
The excited state cation has the potential to reduce water.

$$2\ [{}^*Ru(bpy)_3]^{2+} \longrightarrow 2\ [Ru(bpy)_3]^{3+} + 2e^- \qquad 0.86\ V$$

$$2e^- + 2H_2O \longrightarrow 2OH^- + H_2 \qquad - 0.41\ V$$

$$2\ [{}^*Ru(bpy)_3]^{2+} + 2H_2O \longrightarrow 2\ [Ru(bpy)_3]^{3+} + 2OH^- + H_2 \quad 0.45\ V$$

The $[Ru(bpy)_3]^{3+}$ generated in the above reaction could then oxidise water.

$$2\ [Ru(bpy)_3]^{3+} + 2e^- \longrightarrow 2\ [{}^*Ru(bpy)_3]^{2+} + 2OH^- + H_2 \qquad 1.26\ V$$

$$H_2O \longrightarrow 2H^+ + 1/2\ O_2 + 2e^- \qquad - 0.82\ V$$

$$2\ [Ru(bpy)_3]^{3+} + H_2O \longrightarrow 2\ [{}^*Ru(bpy)_3]^{2+} + 2H^+ + 1/2\ O_2 \quad 0.44\ V$$

If we sum equations obtain eqn.1. The absence of a Ru complex in the overall equation reveals its catalytic nature. A scheme for photochemical reduction of H_2O to H_2 using methylviogen, MV^{2+} as the quenching agent is shown in fig.
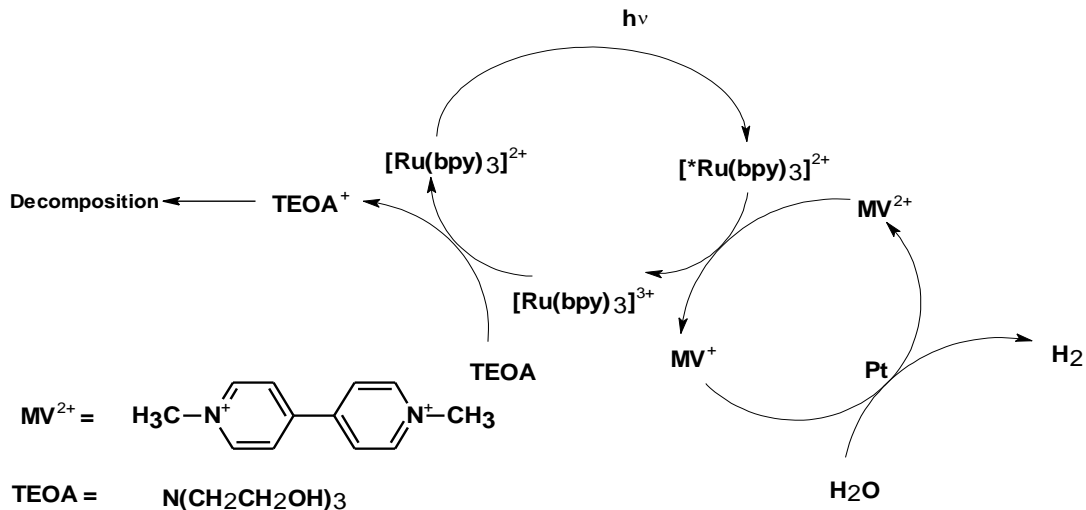
Two Electron Transfer Reactions

Many p-Block and transition metals has stable oxidation states separated by two, and do not usually form stable in complexes with odd numbers of electrons;

e.g Sn(II)/Sn(IV);   Tl(I)/Tl(III);   P(III)/P(V);   Pt(II)/Pt(IV)

One of the best understood two-electron transfer reaction, in T.M. chemistry is the Pt(II)-catalysed exchange of free Cl^- for chloride bound to Pt(IV).
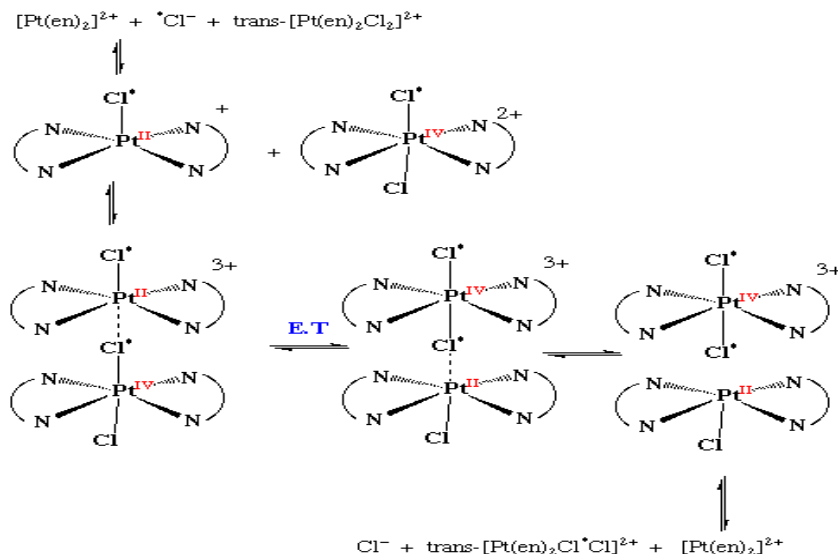
$$[Pt(en)_2]^{2+}$$
$$trans-[Pt(en)_2Cl_2]^{2+} + *Cl^- \quad \rightarrow \quad trans-[Pt(en)_2(*Cl)(Cl)]^{2+} + Cl^-$$
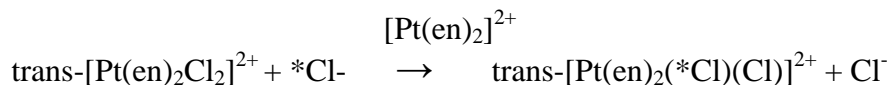
The rate law:

$$k_f = k[Pt(II)][Pt(IV)][Cl^-]$$

The mechanism seems to involve rapid addition of free chloride to the Pt(II) complex to form a five coordinate, which then forms an inner sphere complex with Pt(IV).

The Pt centres are then in very similar environments and two-electron transfer takes place. (c.f. Frank Condon restrictions)
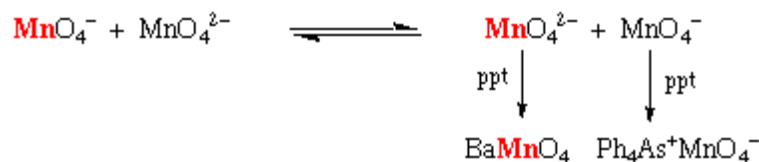
Mechanism:

Exchange of *Cl⁻ was found to occur at the same rate as change in optical rotation in the reaction of trans-$[Pt(l\text{-pn})_2Cl_2]^{2+}$ with $[Pt(en)_2]^{2+}$

Inner sphere reactions also use the tunnelling phenomenon, but in this case a single ligand is the conduit.
Inner sphere electron-transfer will lead to change in the total optical rotation, thus if equal concentrations of reagents are used:
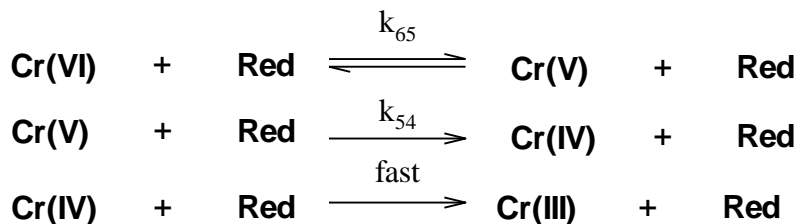
Rate of Racemisation ≡ Rate of Electron Transfer

$$MnO_4^- + MnO_4^{2-} \rightleftharpoons MnO_4^{2-} + MnO_4^-$$
$$ppt \downarrow \qquad \qquad ppt \downarrow$$
$$BaMnO_4 \qquad Ph_4As^+MnO_4^-$$

Complementary and Non-Complementary Reactions

All the electron transfer reaction discussed previously are described as complementary.

➤ The oxidant and reductant change their oxidation state by an equal number of units. This termed a Complementary Reaction.
➤ The oxidant and the reductant change their oxidation states by a different number of units. This is termed a Non-Complementary Reaction
• Most non-complementary reactions precede via elementary steps each involving one electron transfers. The most commonly observed kinetic scheme is, for example in chromate ion oxidations ($HCr(VI)O_4^-$):

$$Cr(VI) + Red \xrightleftharpoons{k_{65}} Cr(V) + Red$$

$$Cr(V) + Red \xrightarrow[\text{fast}]{k_{54}} Cr(IV) + Red$$

$$Cr(IV) + Red \longrightarrow Cr(III) + Red$$

Applying steady-state approximation to Cr(V) then the following rate law can be derived:

$$\frac{-d[HCrO_4]^-}{dt} = \frac{k_{65}k_{54}[Cr(VI)][Red]^2}{k_{54}[Red] + k_{54}[Ox]}$$