In general, chemical reactions move from one energy minimum (the reactants) through a higher energy structure (the transition state) to another energy minimum (the products). In simple cases, the energies and bond distances can be shown as a three-dimensional surface, with two different bond distances along the base-plane axes and free energy as the vertical dimension. The reaction MX + Y ⟶ MY + X begins at a point representing the Short M—X distance of the bond to be broken and the longer distance between the two reactants MX and Y. As the M—X bond breaks and the M—Y bond forms, the reaction point moves to represent the short M—Y bond distance and the logner distance between the two products MY and X. The free energy surface usually has a saddle shape, much like a mountain pass between two valleys. For more complex reactions, such a visual representation is difficult or impossible, but the path between the reactants and the products is always the lowest energy pathway and must be the same regardless of the direction of the reaction. This is the **principle of microscopic reversibility,** frequently described by the mountain pass analogy; the lowest pass going in one direction must also be the lowest pass going in the opposite direction.

If the reaction is such that the conversion from reactants to products takes place with no hesitation at the transition point as in figure (a), the structure at that state is called the **transition state.** If there is a structure that lasts a bit longer as in figure (b), and particularly if it is detectable by some experimental means, it is called an **intermediate.** Frequently, the kinetic equations include intermediates, even if they remain undetected. Their presence allows treatment by a **steady-state approximation,** in which the concentration of the intermediate is assumed to be small and essentially unchanging during much of the reaction.

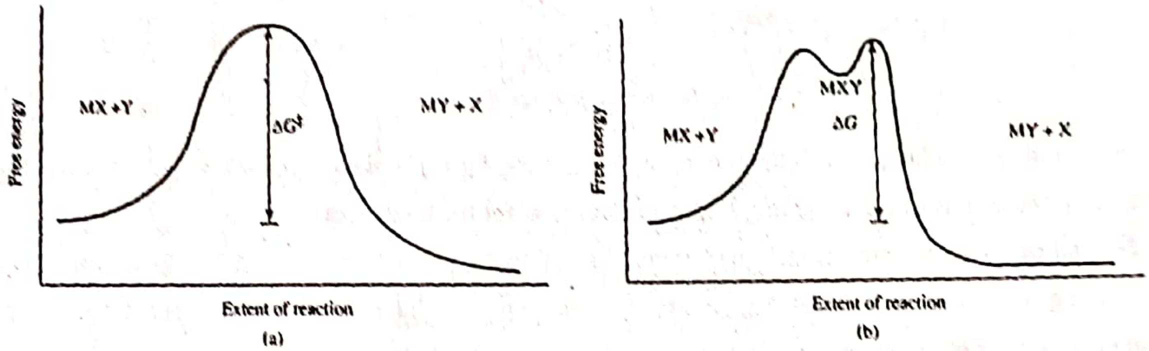


FIGURE Energy Profiles and Intermediate Formation. (a) No intermediate. The activation energy is the energy difference between the reactants and the transition state. (b) An intermediate is present at the small minimum at the top of the curve. The activation energy is measured at the maximum point of the curve.

A number of different parameters can be obtained from kinetics experiments. First, the order of the reaction, indicated by the power of the reactant concentration in the differential equation that describes it, can be determined, together with the **rate constant** that describes the speed of the reaction. By studying a reaction at differetn temperatures, the **free energy of activation** and the **enthalpy** (or **heat**) and **entropy of activation** can be found. These allow further interpretation of the mechanism and the energy surface.

The ability of a complex to engage in reactions that result in replacing one or more ligands in its coordination sphere (by other ligands in solution, for instance) is called its lability. Those complexes for which such substitution reactions are rapid are called **labile,** whereas those for which such substitution reaction proceed slowly (or not at all) are called **inert.** We note that these terms are kinetic terms, because they reflect rates of reaction. These terms should not be confused with the thermodynamic terms **stable** and **unstable,** which refer to the tendency of species to exist (as governed by the equilibrium constant K or β) under equilibrium conditions. A simple example of this distinction is provided by the $[Co(NH_3)_6]^{3+}$ ion, which will persist for months in an acid medium because of its kinetic inertness (slow reactivity) despite the fact that it is thermodynamically unstable, as shown by the large equilibrium constant (K ~ 10^{25}) for reaction (i).

$[Co(NH_3)_6]^{3+}$

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \longrightarrow [Co(H_2O)_6]^{3+} + 6NH_4^+ \qquad \text{...(i)}$$

In contrast, the overall formation constant ($\beta_4 = 10^{22}$) for reaction (ii) indicates that the thermodynamic stability of $[Ni(CN)_4]^{2-}$ is high.

$$Ni^{2+} + 4CN^- \longrightarrow [Ni(CN)_4]^{2-} \qquad \text{...(ii)}$$

Nevertheless, the rate of exchange of CN^- ligands with excess CN^- in solution is immeasurably fast by ordinary techniques. The complex $[Ni(CN)_4]^{2-}$ is both thermodynamically stable and kinetically labile; the terms are not contradictory. In other words, it is not required taht there be any relationship between thermodynamic stability and kinetic lability.

Two extreme mechanistic possibilities may be considered for any ligand substitution process or for any single step in a series of substitution reactions. First, there is the dissociative (D) mechanism in which the ligand to be replaced dissociates from the metal center and the vacancy in the coordination sphere is taken by the new ligand. This mechanism is shown in Reaction (iii):

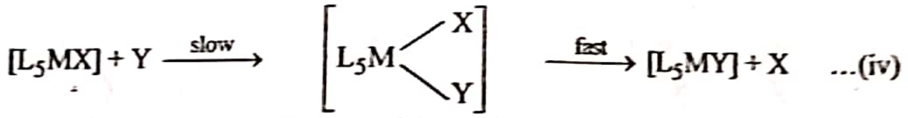
dissociative mechanism

$$[L_5MX] \xrightarrow{\text{slow}} X + \underset{\text{Five-coordinate intermediate}}{[L_5M]} \xrightarrow[\text{fast}]{+Y} [L_5MY] \quad ...(iii)$$

r.d.s = $[L_5MX]$

where L represeents a nonlabile ligand, X is the leaving legand, and Y is the entering ligand. The important feature of such a mechanism is that the first step (dissociation of the leaving group) is rate determining. Once formed by cleavage of the bond to the leaving group, X, the five-coordinate intermediate will react with the new ligand, Y, almost immediately. This mechanism for ligand substitution is comparable to the S_N1 mechanism in organic systems, because the formation of the intermediate with reduced coordination number is unimolecular, as well as rate determining.

The other extreme possibility for ligand substitution is the addition-elimination mechanism, or the associative (A) mechanism. In this case the new ligand, Y, directly attacks the original complex to form a seven-coordinate intermediate in the rate-determining step, as shown in Reaction (iv).



$$[L_5MX] + Y \xrightarrow{\text{slow}} \left[L_5M\langle^{X}_{Y}\right] \xrightarrow{\text{fast}} [L_5MY] + X \quad ...(iv)$$

Seven-coordinate complex

r.d.s = $[L_5MX][Y]$

After rate-determining association between the entering ligand Y and the metal complex, the leaving group X is lost in a fast step. The rate-determining step is bimolecular for the mechanism.

Instead of a five-or-seven-coordinate intermediate, a transition state may be reached in which some degree of bond breaking accompanies a given degree of bond making. The interchange of the ligands X and Y could be accomplished mostly by breaking the bond to the leaving group (interchange-dissociative, I_d) or by making the bond to the entering group (interchange-associative, I_a), but in each case both ligands are bound to the metal to one extent or another. Figure (v) presents reaction profiles for each of the four mechanistic cases just mentioned.

(1) **Solvent Inervention :** Many reaction of complexes have been studies in solvents that are themselves ligands. Water, for instance, is a respectable ligand, and is present in aqueous solution in high and effectively constant concentration (~55.5 *M*). The substitution of X by Y might take place by the sequence of Reactions.

$$[L_5MX] + H_2O \longrightarrow [L_5MH_2O] + X \quad \text{(Slow)} \quad ...(v)$$

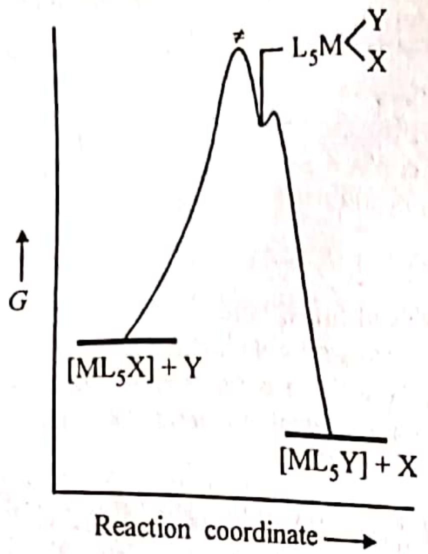
$$[L_5MH_2O] + Y \longrightarrow [L_5MY] + H_2O \quad \text{(Fast)} \quad ...(vi)$$

A simple first order rate law would be observed, and yet either Reaction (v) and (vi) could proceed by an A (or I_a) or a D (or I_d) mechanism.

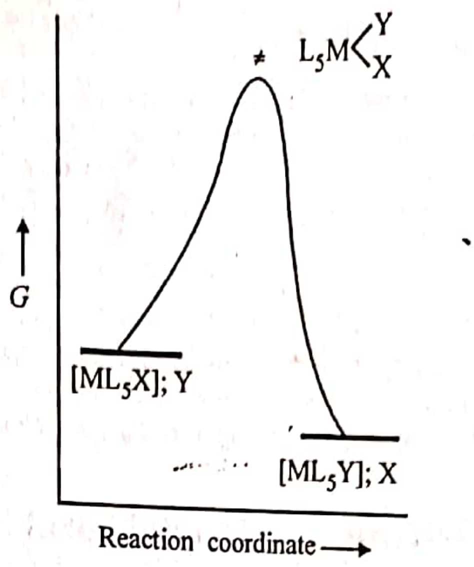
Intervention of the solvent in Reaction (v) obscures the molecularity of the rate-determining step; the reaction will necessarily be observed to be first order because of the high and constant concentration of the entering ligand, H_2O.

(2) **Ion-pair Formation :** When the reacting complex and the entering ligand are both ions, especially when both have high charges, ion pairs (or outer sphere complexes) will form, as in Reaction (vii).

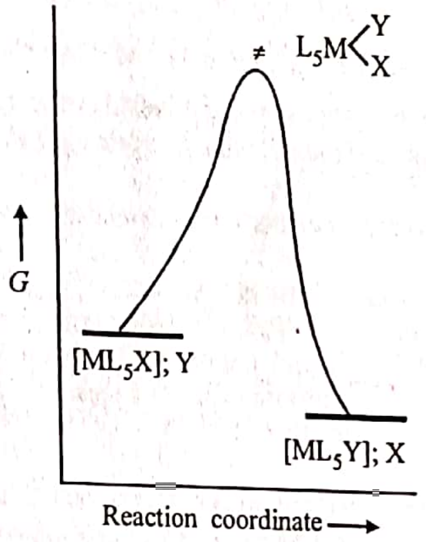
$$[L_5MX]^{n+} + Y^{m-} = \{[L_5MX]Y\}^{n-m} \quad \text{...(vii)}$$



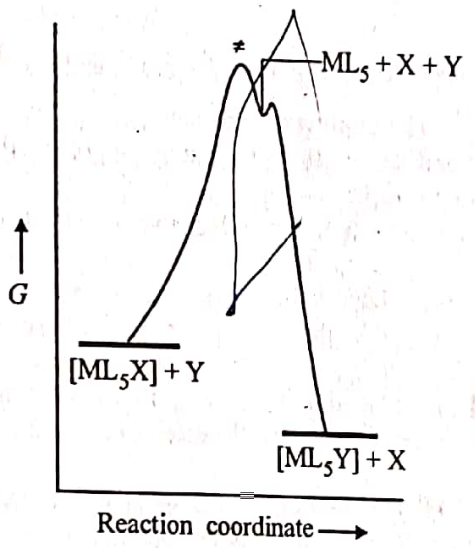
(*a*)



(*b*)



(*c*)



(*d*)

In the product of Reaction (vii), the entering ligand Y has been stabilized at the outer edge of the coordination sphere of the complex $[L_5MX]^{n+}$ primarily by electrostatics. In cases where charges on ions are not involved, an entering group Y may be bound at the periphery of the metal complex through, for instance, hydrogen bonding. Outer-sphere on ion-pair equilibrium constants K_{os} are generally in the range 0.05-40, depending on the charges on the ions and on their effective radii. Where ion pairs (or neutral outer-sphere complexes) are featured as intermediates in the reaction path that leads to ligand substitution, then observed rate laws will be second order, whether or not the mechanism at the rate-determining step involves associative or dissociative activation.

(3) Conjugate-base Formation : When experimental rate laws contain $[OH^-]$, there is the question whether OH^- actually attacks the metal in a true associative fashion, or whether it appears in the rate law through operation of the mechanism shown in equation (viii) and (ix).

$$[Co(NH_3)_5Cl]^{2+} + OH^- = [Co(NH_3)_4(NH_2)Cl]^+ + H_2O \quad \text{(Fast) ....(viii)}$$

$$[Co(NH_3)_4(NH_2)Cl]^+ \xrightarrow[\text{then } H^+]{+Y^-} [Co(NH_3)_5Y]^{2+} + Cl^- \quad \text{(Slow) ...(ix)}$$

In this conjugate-base CB) mechanism, the hydroxide first deprotonates a ligand (usually NH_3) forming the conjugate base, here leading to the NH_2^- ligand. It is then the conjugate base of the original metal complex that reacts with the incoming ligand.

Mechanism in Octahedral Complexes

The mechanism of a reaction is the sequence of elementary steps by which the reaction takes place.

Substitution reactions in inorganic chemistry have been divided into three classes based on the relative importance of bond making and bond breaking in the rate-determining step:

(1) *Associative, A.* The M—Y bond is fully formed before M—X begins to break.
(2) *Dissociative, D.* The M—X bond is fully broken before the M—Y bond begins to form.
(3) *Interchange mechanism, I.* This mechanism takes place in one step. The leaving and entering groups exchagne in a single step by forming an activated complex but not a true intermediate.

$$ML_nX + Y \longrightarrow X\cdots ML_n\cdots Y \longrightarrow ML_nY + X$$

(a) *Interchange associative, I_a.* The M—X bond begins to break before the M—Y bond is fully formed but bond making is more important than bond breaking and no detectable intermediates appear.
(b) *Interchange dissociative, 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 and no detectable in termediate appear.

M—Y

Gate ** Kinetics of Octahedral Substitution (Water Exchange)

Although it is probable that if the reaction rates were known for all possible octahedral complexes a continuous series could be formed. Metal ions are classified in four categories based on the rate of exchange of coordinated water.

Class (I) : The exchange of water is extremely fast. First-order exchange rate constants are on the order of $10^8\ s^{-1}$. The complexes are bound by essentially electrostatic forces and include the complexes of the alkali metals and larger alkaline earth metals. (Ca^{2+}, Ba^{2+}, Sr^{2+}), Group 12 elements (except Zn^{2+}) and Cr^{2+} and Cu^{2+} from first transition series.
These are deffusion controlled reaction. The metal ions are characterised by low charge and large size.

Except V^{2+}
1st transition
Lanthanides
tripositive

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 from first transition series** [excepting V^{2+}, which is slower and Cr^{2+} and Cu^{2+} which are in Class (I)], **Mg^{2+}, and tripositive lanthanides.** These ions form complexes in which the bonding is somewhat stronger than in those of Class I ions, but LFSEs are relatively small. Values for ions in this category ragne from about 10 to $30 \times 10^{-28}\ C^2\ m^{-1}$.

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 group are most of the tripositive transiton metal ions, stabilized to some extent by LFSE, Be^{2+}, Al^{3+}, V^{2+} and Ga^{3+} ions.** The Z^2/r ratios are greater than about $30 \times 10^{-28}\ C^2\ m^{-1}$.

$Z^2/r > 30 \times 10^{-28}$

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^{3+} (low spin d^5), Pt^{2+} (low spin d^8).** Best estimates for Co^{3+}, which oxidizes water and is therefore unstable in aqueous solution, also place it in this class.

Thermodynamic Stability

When a metal ion in aqueous solution interacts with a neutral and monodentate ligand, the following equilibrium is established.

$$[M(H_2O)_x]^{n+} + L \rightleftharpoons [M(H_2O)_{x-1}L]^{n+} + H_2O$$

where x = no. of water molecules in the aqueous complex
n = oxidation no. of the metal ion.

When L is an anionic monodentate ligand, the following eq^m will established.

$$[M(H_2O)_x]^{n+} + L^- \rightleftharpoons [M(H_2O)_{x-1}L]^{(n-1)+} + H_2O$$

The above equilibrium reaction can be written in a simplified and generalised form without refering to the no. of coordinated water molecules and charge on the central metal ion.

$$M + L \rightleftharpoons ML$$

The eq^m constant for this equation is given by

$$K_f = \frac{[ML]}{[M]\,[L]}$$

K_f is called the formation constant or stability constant of the complex.

Note that the concn of water is constant in dilute solutions of the metal complex and it is incorporated into

K_f·

If the large amount of the complex is formed, then the eq^m concentrations [ML] is larger than the product of [M] and [L]. Then K_f is greater than 1.0. Such a situation would arise when the ligand L binds to the metal more tightly than H_2O. Thus a large value of K_f indicates that L is a stronger ligand than H_2O. Similarly when K_f is less than 1.0, the L is a weaker ligand than H_2O. The magnitude of the formation constant is the measure of stability of a coordination complex in a thermodynamic sense. The formation constant is a measure of the thermodynamic stability of a metal complex.

Thermodynamic and Kinetic Stability

The ability of a complex to engage in reactions that result in replacing one or more ligands in its coordination sphere (by other ligands in solution) is called its lability. Those complexes for which such substitution reactions are rapid are called labile, i.e., the complexes in which the ligands are rapidly replaced by others are called labile complexes. The labile complexes are those that have half lives for a reaction under a minute. Special techniques are required for collecting data during such reactions. The techniques are nmr, stopped flow or relaxation methods, pressure pumps etc.

$t_{1/2} = 1\,min$
⇓
Labile

The inability or less ability of a complex to engage in reactions that result in replacing one or more ligands in its coordination sphere by other ligands is called inertness of the complex. The complexes for which substitution reactions proceed slowly (or not at all) are called inert complexes. Inert complexes are those whose substitution reactions have half lives longer than a minute.

$t_{1/2} > 1\,min$
inert

The terms (labile and inert) are kinetic terms because they reflect rates of reaction and mechanisms of reactions such as substitution, electron transfer or group transfer reactions, isomerisation or racemisation.

These terms (labile and inert) should not be confused with the thermodynamic terms stable and unstable, which refer to the tendency of species to exist (as governed by eq^m constants K or β) under equilibrium conditions.

The compound may be unstable with respect to a particular condition or reactant such as heat, light, acid or base but not to another.

Consider the following cyano complexes : $[Ni(CN)_4]^{2-}$, $[Mn(CN)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$. All of these complexes are extremely thermodynamic stable. If the rate of exchange of radio carbon labeled cyanide is measured, we find that despite the thermodynamic stability. $[Ni(CN)_4]^{2-}$ exchanges cyanide ligands very rapidly (is labile), $[Mn(CN)_6]^{3-}$ is moderately labile and $[Cr(CN)_6]^{3-}$ is inert.

$$[Ni(CN)_4]^{2-} + 4{*}CN^- \longrightarrow [Ni({*}CN)_4]^{2-} + 4CN^- \qquad t_{1/2} = 30\ S$$

$$[Mn(CN)_6]^{3-} + 6{*}CN^- \longrightarrow [Mn({*}CN)_6]^{3-} + 6CN^- \qquad t_{1/2} = 1\ h$$

$$[Cr(CN)_6]^{3-} + 6{*}CN^- \longrightarrow [Cr({*}CN)_6]^{3-} + 6CN^- \qquad t_{1/2} = 24\ days$$

$[Co(NH_3)_6]^{3+}$
⇓
unstable
⇓
but stable in acidic medium

$[Ni(CN)_4]^{2-}$ is thermodynamically stable but kinetically labile. ✓

$[Cr(CN)_6]^{3-}$ is thermodynamically stable but kinetically inert. ✓

$[Fe(H_2O)_5F]^{2+}$ is very stable (has a large eq^m constatant for formation) but it is labile. ✓

but remain in persistent for months

$[Co(NH_3)_6]^{3+}$ is thermodynamically unstable in acid and can decompose to the eq^m mixture to the right.

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \rightleftharpoons [Co(H_2O)_6]^{3+} + 6NH_4^+$$

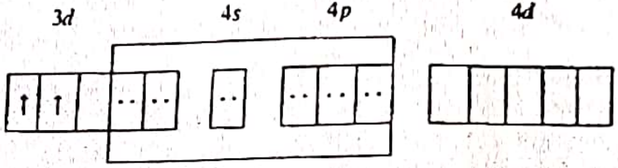
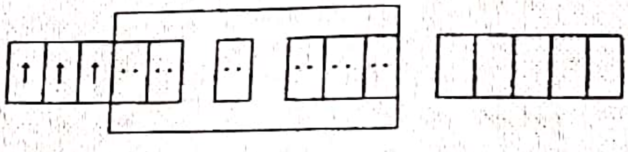
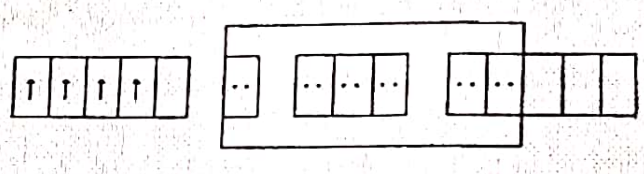
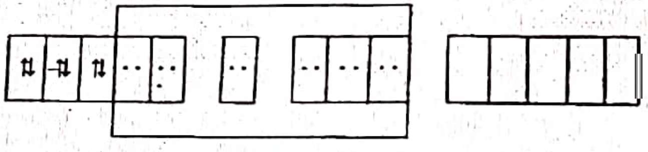
but it reacts very slowly (has a very high activation energy) and is therefore inert.

The above examples indicate that there is no relationship between thermodynamic terms (stable and unstable) and kinetic terms (labile and inert).

Labile and Inert Complexes on the Basis of VBT

Certain aspects of the valence-bond theory can be used to correlate the lability of complex ions with their electronic configurations. Experimental observations on the lability and magnetic properties of some complex species are shown in the following table. As before, the magnetic data give an indication of the type of hybrid orbital used by the metal atom for bonding. From hybrid designations it is apparent that the labile complexes possess vacant, low-lying, unhybridized metal orbitals which can act as a point of attack by an incoming ligand. The inert complexes have electron density in the unhybridized metal orbitals, suggesting that they are not as readily available for bond formation to a ligand. This argument is essentially the same as that used to explain the difference in the relative ease of hydrolysis of CCl_4 and $SiCl_4$.

TABLE **The lability, magnetic properties, and metal hybridization for some complex ions**

Compound	Class	Number of unpaired electrons	d^2sp^3 hybridzation
$V(NH_3)_6^{3+}$	labile	2	
$Cr(CN)_6^{3-}$	inert	3	
$MnCl_6^{3-}$	labile	4	
$Co(CN)_6^{3-}$	inert	0	

3 d orbital must be vacant for labilization

Labile and Inert Complexes according to CFT

The octahedral complexes react by SN^1 (dissociation) or SN^2 (association) mechanism and the symmetry is lowered and there may or may not be loss in CFSE in going from octahedral to 5-coordinated square pyramidal or 7-coordinated pentagonal bipyramidal intermediates. Higher the loss in CFSE, lower will be lability of the octahedral complex and such complexes are inert. If there is no loss or little loss in CFSE, the complexes are generally labile.

The loss in CFSE in going from octahedral to five coordinated square pyramidal or seven coordinated pentagonal bipyramidal is given the negative sign and for no loss in CFSE, change in CFSE is zero or positive. But this is difficult to assign the CFSE (or LFSE) of the activated complex without exact knowledge of its structure. In the absence of such knowledge, approximation can be made on the basis of likely structures. **Bosolo** and **Pearson** have presented values for strong and weak fields for square pyramidal (C.N. = 5) and pentagonal bipyramidal (C.N. = 7) intermediates. Change in LFSE upon changing a six coordinate complex to a five coordinate (square pyramidal) or a seven coordinate (pentagonal bipyramidal) species given by Bosolo and Pearson ar given in the following table.

Higher loss in LFSE in oc → TBP lower labile = -ve sign of str.

System	High Spin C.N. = 5	High Spin C.N. = 7	Low Spin C.N. = 5	Low Spin C.N. = 7
d^0	0	0	0	0
d^1	+0.57	+1.28	+0.57	+1.28
d^2	+1.14	+2.56	+1.14	+2.56
d^3	−2.00	−4.26	−2.00	−4.26
d^4	+3.14	−1.07	−1.43	−2.98
d^5	0	0	−0.86	−1.70
d^6	+0.57	+1.28	−4.00	−8.52
d^7	+1.14	+2.56	+1.14	−5.34
d^8	−2.00	−4.26	−2.00	−4.26
d^9	+3.14	−1.07	+3.14	−1.07
d^{10}	0	0	0	0

The units of LFSE are in Dq or Δ/10.

Negative quantities refer to loss of LFSE and destabilisation of the complex.

In general for tripositive metal ions, lability for low spin complexes is expected to increase in the order of 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).

On the basis of the above table the following predications are made.

1. Both high spin and low spin octahedral complexes of $d^0, d^1, d^2, d^7, d^{10}, d^7, d^9$, high spin d^4, d^5 and d^6 are generally labile.
2. Both high spin and low spin d^3, d^8, low spin d^5, d^6 and d^4 are generally inert.
3. The ion with maximum loss of CFSE will form the most inert (i.e., least labile) complex. Thus the order of inertness of low spin complexes formed by d^3, d^4, d^5 and d^6 ions is:

Order of Inertness	d^6	>	d^3	>	d^4	>	d^5
Loss of CFSE for SN^1 mechanism	−4.0		−2.0		−1.43		−0.86
Loss of CFSE for SN^2 mechanism	−8.52		−4.26		−2.98		−1.70

$d^6 > d^3 > d^4 > d^5$

Consequently the order of lability is

$$d^6 < d^3 < d^4 < d^5$$

down the gr

lability decrease

Inertness is quite common among the complexes of the second and third *d* series, which reflects the high loss of LFSE and strength of metal-ligand bonding.

It is generally observed that lability decreases for on analogous series of compounds in descending order within a group. The lability of complexes of isoelectronic ions with in the same group such as those of Ni(II) and Pt(II) decreases on moving down the group. Both ions possess an empty nonbonding a_{24} (p_z) orbital available for occupancy by a fifth group. Loss of LFSE for the heavier Pt(II) is greater than for Ni(II). Thus Ni(II) complex is more labile than Pt(II).

Geometry of the Complex

In general 4-coordinated complexes (both tetrahedral and square planar) react more rapidly than analogous 6-coordinated complexes, e.g., the very stable $[Ni(CN)_4]^{2-}$ undergoes rapid exchange with $^{14}CN^-$.

$$[Ni(CN)_4]^{2-} + 4\,^{14}CN^- \rightleftharpoons [Ni(^{14}CN)_4]^{2-} + 4CN^-$$

While 6-coordinated complexes like $[Mn(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ which have almost about the same stability as $[Ni(CN)_4]^{2-}$ undergoes slow exchange. The greater rapidity of reactions of 4-coordinated complexes may be due to the fact that there is enough room round the central metal ion for the entry of fifth group into the coordination sphere to form an activated complex. The presence of this additional group helps in the release of one of the original four ligands already present in the 4-coordinated complexes.

Comparision of dipositive with tripositive species is difficult because the reaction rate is affected by the charge on the central metal ion with higher charge strengthing the metal-ligand bonding and reducing lability. For example Ru(III) complex is less labile than Ru(II) just as Fe(III) is less labile than Fe(II). However V(III) is more labile than V(II). When isoelectronic pairs such as $V^{2+}|Cr^{3+}$ or $Mn^{2+}|Fe^{3+}$ are considered, evaluation of charge effect is more straight forward. (Higher the charge lower will be the lability).

V^{3+} more labile than V^{2+}

Cr^{3+}/V^{2+}

Mn^{2+}/Fe^{3}

For Non-Transition Metal

Central ion with high oxidation state have slower ligand exchange (i.e., less labile). Order of lability is:

$$\text{e.g., } [\overset{+3}{\text{Al}}F_6]^{3-} > [\overset{+4}{\text{Si}}F_6]^{2-} > [\overset{+5}{\text{P}}F_6]^{-} > \overset{+6}{\text{S}}F_6$$

higher ox. state of Metal
⇓
Complex less labile

$$[Na(H_2O)_n]^{+} > [Mg(H_2O)_n]^{2+} > [Al(H_2O)_n]^{3+}$$

smaller ions have slower exchange rates.

smaller ion [small radius
⇓
less labile

$$\underset{112\text{ pm}}{[Sr(H_2O)_6]^{2+}} > \underset{99\text{ pm}}{[Ca(H_2O)_6]^{2+}} > \underset{66\text{ pm}}{[Mg(H_2O)_6]^{2+}}$$

$[Cu(H_2O)_6]^{2+}$ reacts most readily. This may be due to the fact that the two water molecules above and below the square plane of the tetragonally distorted shape of $[Cu(H_2O)_6]^{2+}$ are exchanged.

The remaining four water molecules lying in the square plane react slowly. The two water molecules above and below the square plane react rapidly because the metal to ligand bond length is larger on z-axis.

Kinetic Consequences of Reaction Pathways

Dissociation (*D*)

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:

$$ML_4X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

The stationary-state (or steady-state) hypothesis assumes a very small concentration of the intermediate, ML_5, and requires that the rates of formation and reaction of the intermediate must be equal. This in turn requires that the rate of change of $[ML_5]$ be zero during much of the reaction. Expressed as a rate equation.

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

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,

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

2nd order

leads to the rate law:

$$\frac{d[ML_5Y]}{dt} = \frac{k_2k_1[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

Interchange (I)

In an interchange (I) reaction, a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combination. 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.

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5X \cdot Y$$

$$ML_5X \cdot Y \xrightarrow{k_2} ML_5Y + X$$

When $k_2 << k_{-1}$, 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 $k_1 = k_1 / k_{-1}$.

Applying the stationary-state hypothesis:

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

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 concentrations of ML_5X and Y, which we will call $[M]_0$ and $[Y]_0$:

$$[M]_0 = [ML_5X] + [ML_5X \cdot Y]$$

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

$$[Y]_0 \cong [Y]$$

From the stationary-state equation,

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

The final rate equation then becomes

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5X \cdot Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + (k_2/K_{-1})} \cong \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}$$

where k_2/k_{-1} is ver small and can be omitted because $k_2 << k_{-1}$ is required for the first step to be an equilibrium.

k_1 can be measured experimentally in some cases and estimated theoretically in others form calculation of the electrostatic energy of the interaction, with fair agreement in cases 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.

As can be seen from these equation, both *D* and *I* mechanism 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 equation have the similar forms shown here.)

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

At low [Y], the denominator simplifies to [X] for the dissociative and to 1 for the interchange equation. Both then are second order (first order in M and Y, rate = $k[M]_0[Y]_0$ or $k[M]_0[Y]_0/[X]$), with the rate of the dissociative reaction slowing as more free X is formed.

At high [Y], a common condition in kinetic experiments, the second term in the denominator is larger, $[X] + k'[Y] = k'[Y]$ and $1 + k'[Y]0$ and [Y] cancels, making the reaction first order in complex and zero order in Y (rate = $(k/k')[M]_0$).

Association (*A*)

In an associative 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:

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5XY$$

$$ML_5XY \xrightarrow{k_2} ML_5Y + X$$

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

$$\frac{d[ML_5Y]}{dt} = \frac{k_2k_1[ML_5X][Y]}{k_{-1}+k_2} = k[ML_5X][Y]$$

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

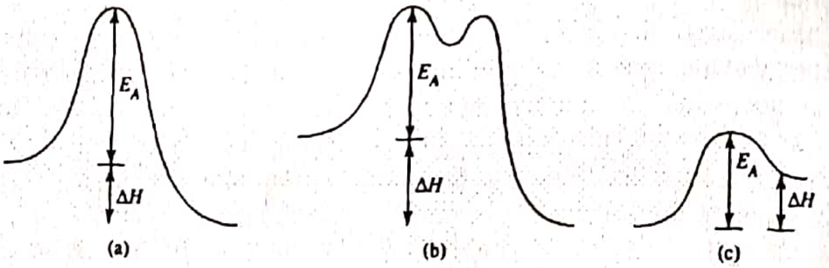
As with the dissociative mechanism, there are very few clear examples of associative mechanisms in which the intermediate is detectable. Most reactions fit better between the two extremes, following associative or dissociative interchange mechanism.

Experimental Evidence in Octahedral Substitution

Dissociation

Most substitution reaction of octahedral complexes are believed to be dissociative, with the complex losing one ligand to become as 5-coordinate square pyramid in the transition state and the incoming ligand filling the vacant site to form the new octahedral product. Theoretical justification for the inert and labile classifications comes from ligand field theory, with calculation of the change in LFSE between the octahedral reactant and the presumed 5-coordinate transition state, either square pyramidal or trigonal-bipyramidal in shape. Table gives the **ligand field activation energy** (LFAE), calculated as the difference between the LFSE of the square pyramidal transition state and the LFSE of the octahedral reactant. LFAEs calculated for trigonal-bipyramidal transition states are generally the same or larger than those for square-pyramidal transition states. These calculations provide estimates of the energy necessary to form the transition state. When combined with the general change in enthalpies of formation, the activation energies of the square-pyramidal transition state match the experimental facts (d^3 and d^8 complexes are intert in both the strong- and weak-field cases, and d^6 strong-field complexes are inert). Examination of these numbers shows that the activation energies of the square-pyramidal transition state match the experimental facts (d^3, low-spin d^4 through d^6, and d^8 are inert). Therefore, the calculation of LFAE supports a square-pyramidal geometry (and a dissociative mechanism) for the transition state. However, all these numbers assume an idealized geometry not likely to be found in practice, and the LFAE is only one factor that must be considered in any reaction.

FIGURE Activation Energies and Reaction Enthalpies. (a), (b), Large E_a, slow reaction. (c) Small E_a, fast reaction. (a), (b), $\Delta H < 0$, large equilibrium constant; (c) $\Delta H > 0$, small equilibrium constant. In (b), the intermediate is potentially detectable.



Even the thermodynamically favorable reactions, a large activation energy means that the reaction will be slow. For thermodynamically unfavorable reactions, even a fast reaction (with small activation energ) would be unlikely to occur. The rate of reaction depends on the activation energy, as in the Arrhenius equation,

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln \; k = \ln \; A - \frac{E_a}{RT}$$

Some of the possible energy relationships for reactions are shown in above figure. In (a) and (b), the reaction is exothermic ($\Delta H < 0$), and the equilibrium constant is large. In (a), the reaction is spontaneous ($\Delta H < 0$), but E_a is large, so few molecules have enough energy to get over the barrier and the reaction is slow. In (b), the reaction is spontaneous, with an intermediate at the dip near the top of the activation energy curve. Intermediates of this sort are frequently described, but can be detected and identified in only a few cases. In (c), the reaction can go quickly because of the low activation energy, but has a small equilibrium constant because the overall enthalpy change is positive.

Other metal ion factors that affect reaction rates of octahedral complexes include the following (relative rates for ligand exchange are indicated by the inequalities):

1. *Oxidation state of the central ion.* Central ions with higher oxidation states have slower ligand exchange rates.

$$\underset{3+}{[AlF_6]^{3-}} > \underset{4+}{[SiF_6]^{2-}} > \underset{5+}{[PF_6]^{-}} > \underset{6+}{SF_6}$$

$$\underset{1+}{[Na(H_2O)_n]^{+}} > \underset{2+}{[Mg(H_2O)_n]^{2+}} > \underset{3+}{[Al(H_2O)_6]^{3+}}$$

2. *Ionic radius*. Smaller ions have slower exchange rates.

$$\underset{112\text{ pm}}{[Sr(H_2O)_6]^{2+}} > \underset{99\text{ pm}}{[Ca(H_2O)_6]^{2+}} > \underset{66\text{ pm}}{[Mg(H_2O)_6]^{2+}}$$

Both effects can be attributed to a higher electrostatic attraction between the central atom and the attached ligands. A strong attraction between the two will slow the reaction, because reaction is presumed to require dissociation of a ligand from the complex.

The evidence for dissociative mechanism can be grouped as follows:

1. The rate of reaction changes only slightly with changes in the incoming ligand. In many cases; **aquation** (substition by water) and **anation** (substitution by an anion) rates are comparable. If dissociation is the rate-determining reaction, the entering group should have no effect at all on the reaction rate.
2. Decreasing negative charge or increasing positive charge on the reactant complex decreases the rate of substitution. Larger electrostatic attraction between the positive metal ion and the negative ligand should slow the dissociation.
3. Steric crowding on the reactant complex increases the rate of ligand dissociation. When ligands on the reactant are crowded, loss of one of the ligands is made easier. On the other hand, if the reaction has an *A* or I_a mechanism, steric crowding interferes with the incoming ligand and slows the reaction.
4. The rate of reaction correlates with the metal-liagnd bond strength of the leaving group, in a linear free energy relationship.
5. Activation energies and entropies are consistent with dissociation, although interpretation of these parameters is difficult. Another activation parameter now being measured by experiments at increased pressure is the volume of activation, the change in volume on forming the activated complex. Dissociative mechanism generally result in positive values for ΔV_{act} because one species splits into two, and associative mechanism result in negative ΔV_{act} values because two species combine into one, with a presumed volume smaller than the total for the reactants. However, caution is needed in interpreting volume effects because solvation effects, particularly for highly charged ions, may be larger than the difference expected for the reaction otherwise.

Linear Free Energy Relationships

Many kinetic effects can be related to thermodynamic effects by a linear free energy relationship (LFER). Such effects are seen when, for example, the bond strength of a metal-ligand bond (a thermodynamic function) plays a major role in determining the dissociation rate of that ligand (a kinetic function). When this is true, a plot of the logarithm of the rate constants (kinetic) for different leaving ligands versus the logarithm of the equilibrium constants (thermodynamic) for the same ligands in similar compounds is linear. The justification for this coorelation is found in the Arrhenius equation for temperature dependence of rate constants and the equation for temperature dependence of equilibrium constants. In logarithmic form, they are

$$\underset{\text{kinetic}}{\ln k = \ln A - \frac{E_a}{RT}} \quad \text{and} \quad \underset{\text{thermodynamic}}{\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}}$$

If the pre-exponential factor, A, and the entropy, ΔS°, are nearly constant and the activation energy, E_a, depends on the enthalpy of reaction, ΔH°, there will be a linear correlation between $\ln k$ and $\ln K$. A straight line on such a log-log plot is indirect evidence for a strong influence of the thermodynamic parameter, ΔH°, on the activation energy of the reaction. In molecular bonding terms, a stronger bond between the metal and the leaving group results in a larger activation energy, a logical connection for a dissociative mechanism.

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$

From this evidence, Langford argued that the X^- group is essentially completely dissociated and acts as a solvated anion in the transition state of acid hydrolysis and that water is at most weakly bound in the transition state.

Associative Mechanisms.

Associative reactions are also possible in octahedral substitution, but are much less common. In the case of water substitution by several different anions in $[Cr(NH_3)_5(H_2O)]^{3+}$, the rate constants are quite similar (within a factor of 6), indicatve of an I_d mechanism.On the other hand, the same ligands reacting with $[Cr(H_2O)_6]^{3+}$ mechanism show a large variation in rates, indicative of an I_a mechanism.

Reactions of Ru(III) Compounds frequently have associative mechanism and those of Ru(II) compunds have dissociative mechanisms. The entropies of activation for substitution reactions of $[Ru(III)(EDTA)H_2O)]^-$ are negatve indicating association as part of the transtition state.They also show a very large of rate constants depending on the incoming ligand, as required for I_a mechanism, but those of Ru(II) are nearly the same for different ligands, as required for an I_d mechanism. The reasons for this difference are not certain.

The Conjugate Base Mechanism

The cases in which second-order kinetics seemed to require an associative mechanism have subsequently been found to have a **conjugate base mechanism** (called S_N1CB, for substittion, nucleophilic, unimolecular, conjugate base). These reactions depend on amine, ammine, 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.

$$[Co(NH_3)_5X]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)X]^+ + H_2O \text{ (equilibrium)} \qquad (1)$$

$$[Co(NH_3)_4(NH_2)X]^+ \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^- \qquad \text{(slow)} \qquad (2)$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH)]^{2+} \qquad \text{(fast)} \qquad (3)$$

Overall,

$$[Co(NH_3)_5X]^{2+} + OH^- \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$$

rate = $K\,[Co(NH_3)_4(NH_2)X]^+$

In the third step, addition of a ligand other than water is also possible; in basic solution, the rate constant is k_{Kb} and the equilibrium constant for the overall reaction is K.

Additional evidence for the conjugate base mechanism has been provided by several realted studies:

1. RNH_2 compound (R = alkyl) react faster than NH_3 compounds, possibly because steric crowding favors the 5-coordinate intermediate formed in Step 2.
2. When substituted amines are used, and there are no protons on the nitrogen available for ionization, the reaction is very slow or nonexistent.

Anation Reactions

An important reaction of the aqua ions is the addition of an anion,

$$[M(H_2O)_6]^{n+} + X^- \longrightarrow [M(H_2O)_5X]^{(n-1)+} + H_2O \qquad \text{...(x)}$$

Such reactions are especially germane to the synthesis of new complexes starting with the simple aqua ions. Anation reactions may also be considered to include reactions in which coordinate water in the substituted complexes $[ML_5H_2O]^{n+}$ is replaced by an incoming anion. In either case, two remarkably general observations have been made concerning the rates at which water ligands are replaced by anions.

The most reasonable explantion for these observations is that the overall process invovles the following three steps:

$$[M(H_2O)_6]^{n+} + X^- \xrightarrow{K_{OS}} \{[M(H_2O)_6]X\}^{(n+1)+} \qquad \text{...(xi)}$$

$$\{[M(H_2O)_6]X\}^{(n-1)+} \xrightarrow{k_0} \{[M(H_2O)_5]X\}^{(n-1)+} + H_2O \qquad \text{...(xii)}$$

$$\{[M(H_2O)_5]X\}^{(n-1)+} \xrightarrow[\text{fast}]{\text{very}} [M(H_2O)_5X]^{(n-1)+} \qquad \text{...(xiii)}$$

In the first step an outer-sphere complex (here an ion pair) is formed with an equilibrium constan K_{OS} (Reaction {xi}). A coordinated water molecule is then lost (Reaction {xii}). with rate constant k_0, a rate constant that should be close to that for water exchange in the parent aqua ion. In the third step, which is very fast, and may not be distinct from the second step, the entering ligand X^- slips into the coordination spot vacated by the water ligand. The most appropriate rate law for the overall sequence of above reactions is given by equation (xiv).

$$\text{rate} = k_{obs}[M(H_2O)_6^{n+}]\,[X^-] \qquad \text{...(xiv)}$$

Aquation Reactions

Complexes that are present in aqueous solution are susceptible to aquation or hydrolysis reactions in which a ligand is replaced by water. Even where other enctiring ligands Y are part of an overall reaction, it appears that there are few reactions in which the leaving ligand X is not first replaced by water. Thus solvent intervention is a key feature in substitutions of X by Y, and aquation of the ligand X in $[ML_5X]$ is a reaction of fundamental importance.

Our discussion will emphasize aquation of the ligand X in amine complexes of Co^{III}, as seen in Reaction (xv), **where A represents an amine-type ligand such as NH_3.**

$$[CoA_5X]^{n+} + H_2O \longrightarrow [CoA_5OH_2]^{(n+1)+} + X^- \quad \ldots(xv)$$

The rate law observed for such aquation reaction is a two-term rate law, shown in equation (xvi).

$$\text{rate} = k_a[CoA_5X^{n+}] + k_b[CoA_5X^{n+}][OH^-] \quad \ldots(xvi)$$

The first term, involving the acid hydrolysis rate constant k_a, predominates at low pH, where (OH^-) is low. The second term, involving the base hydrolysis rate constant, k_b, predominates at high pH. The two-term rate law is an indication that two paths for aquation are possible, an acid hydrolysis and a base hydrolysis reaction path. At intermediate values of pH, both paths will be available. In general, k_b is approximately 10^4 times k_a, and it is often true that complexes that are inert under acidic conditions become labile in the presence of bases. The ammines of Co^{III}, for instance, are so labile towards substitution in aqueous base that they generally decompose in that medium through rapid, successive substitutions leading to hydroxides and hydrous metal oxides.

Acid Hydrolysis

The ligand undergoing substitution is replaced in the first coordination sphere by the entering ligand, water. Since the entering ligand is present in high and effectively constant concentration, the rate law does not contain (H_2O), and tells us nothing about the order of the reaction with respect to water. The rate law is, in fact, simply a first order rate law,

$$\text{rate} = k_a[CoA_5X^{n+}] \quad \ldots(xvii)$$

Most acid hydrolysis reactions of octahedral complexes appear to proceed through dissociative process (D or I_d). Some of the evidence that supports this conclusion comes from the study of (1) leaving group effects, (2) steric effects, and (3) charge effects.

Leaving Group Effect

Rate constants k_a for the Reactions

$$[CoA_5X]^{2+} + H_2O \longrightarrow [CoA_5OH_2]^{3+} + X^-$$

and equilibrium constants K_a for the Reactions

$$[CoA_5OH_2]^{3+} + X^- = [CoA_5X]^{2+} + H_2O$$

are given below:

X^-	$k_a\ (s^{-1})$	$K_a\ (M^{-1})$
NCS^-	5.0×10^{-10}	470
F^-	8.6×10^{-8}	20
$H_2PO_4^-$	2.6×10^{-7}	7.4
Cl^-	1.7×10^{-6}	1.25
Br^-	6.3×10^{-6}	0.37
I^-	8.3×10^{-6}	0.16
NO_3^-	2.7×10^{-5}	0.077

Sterif Effect

The ligand A—A in reaction are bidentate diamines that have been substituted in the carbon chains to provide increase crowding in the coordination sphere of the cobalt reaction. The complexes having the larger ligands (A—A) react more quickly. Dissociative activation is indicated. No five-coordinate intermediate has been detected, so an I_d mechanism is assigned.

Charge effects also indicate dissociative activation for substitution reactions of octahedral complexes of cobalt. Compare, for instance,

$$[Co(NH_3)_5Cl]^{2+} \qquad (k_a = 6.7 \times 10^{-6}\ s^{-1})$$

with

$$trans-[Co(NH_3)_4Cl_2]^{+} \qquad (k_a = 1.8 \times 10^{-3}\ s^{-1})$$

Where the charge on the cobalt reactant is higher, the rate of separation of the anion Cl^- is slower.

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Base Hydrolysis

Aquation reactions of octahedral complexes of Co^{III} that take place in basic solution display the rate law shown in equation (xviii).

$$rate = k_b[CoA_5X^{n+}][OH^-] \qquad \text{...(xviii)}$$

This is simply the second-order term in the general rate law. The second-order rate term in equaio (xvi) predominates in basic solution, so that one observes simple second-order kinetics.

Base hydrolysis of Co^{III} complexes is generally much faster than acid hydrolysis because $k_a < k_b$. This, in itself, provides evidence against a simple A mechanism. Therefore, this reaction favors the CB mechanism, because there is no reason to expect OH^- to be uniquely capable of attack on the metal.

Reactions Rates Influenced by Acid and Base

Substitution reactions taking place in water solution can often be accelerated by the presence of an acid or base. If the coordinated leaving group (X) has lone pairs which can interact with H^+ or metal ions such or Ag^+ or Hg^{2+}, the M—X bond may be weakened and loss of X facilitated. This effect is seen in the aquation of $[Cr(H_2O)_5F]^{2+}$.

$$[Cr(H_2O)_5F]^{2+} + H^+ \rightleftharpoons [Cr(H_2O)_5{-}F{-}H]^{3+}$$
$$[Cr(H_2O)_5\cdots F\cdots H]^{3+} + H_2O \longrightarrow [Cr(H_2O)_6]^{3+} + HF$$

Available lone pairs of the bound fluorine group are attached to the hydrogen ion, leading to the formation of a weak acid. The rate constant for the overall reaction is $6.2 \times 10^{-10}\ s^{-1}$ in neutral solution but $1.4 \times 10^{-8}\ s^{-1}$ in acid solution. When ammonia, which possesses no free lone pairs when it is bound to a metal, is the leaving group, no acceleration is observed.

Hydroxide ion also may have an appreciable effect on the rate of hydrolysis of octahedral complexes. The rate constant for hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in basic solution is a million times that found for acidic solutions. Furthermore, the reaction is found to be second order and dependent on the hydroxide ion concentration:

$$rate = k[Co(NH_3)_5Cl]^{2+}[OH^-]$$

Although an associative mechanism is consistent with these results, the prevailing opinion is that the reaction takes place via proton abstraction:

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$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^{+} + H_2O$$
$$[Co(NH_3)_4(NH_2)Cl]^{+} \xrightarrow{r.d.s.} [Co(NH_3)_4(NH_2)]^{2+} + Cl^- \qquad \text{...(A)}$$
$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{fast} [Co(NH_3)_5(OH)]^{2+}$$

According to this viewpoint, the hydroxide ion rapidly sets up an equilibrium with the amidocobalt complex. The rate-determining step is the dissociation of this complex [equation (A)], but since its concentration depends on the hydroxide ion concentration through equilibrium, the reaction rate is proportional to the hydroxide ion concentration.

This mechanism is first order nucleophilic substitution, conjugate base ($S_{N1}CB$) mechanism.

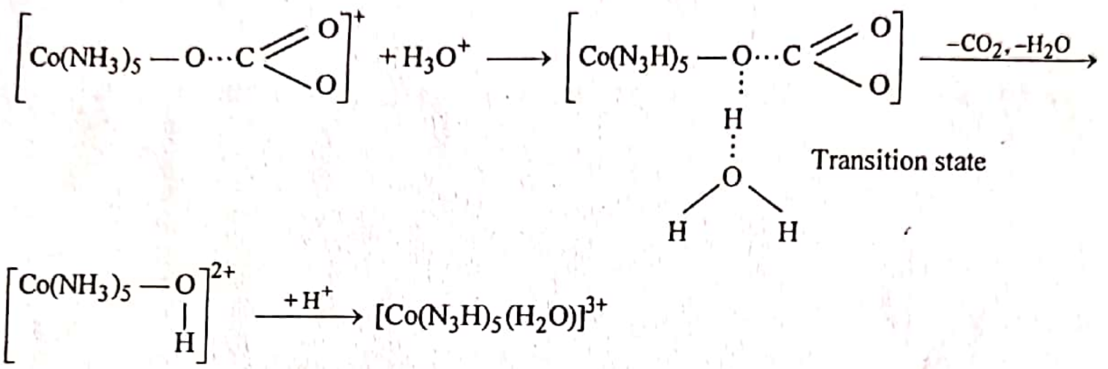
Attack on Ligands

There are some reactions where ligand exchange does not involve the breaking of metal-ligand bonds; instead, bonds within the ligands themselves are broken and reformed. One well-known case is the aquation of a carbonate complex.

$$[Co(NH_3)_5OCO_2]^+ + 2H_3{}^*O^+ \longrightarrow [Co(NH_3)_5(H_2O)]^{3+} + 2H_2\overset{*}{O} + CO_2 \qquad \text{...(xix)}$$

When isotopically labeled water ($H_2{}^*O$) is used, it is found that no *O gets into the coordination sphere of the cobalt during aquation.

The most likely path for this aquation involves proton attack on the oxygen atom bonded to cobalt. This attack is followed by elimination of CO_2 and protonation of the hydroxo complex, as in Reaction. (xx).



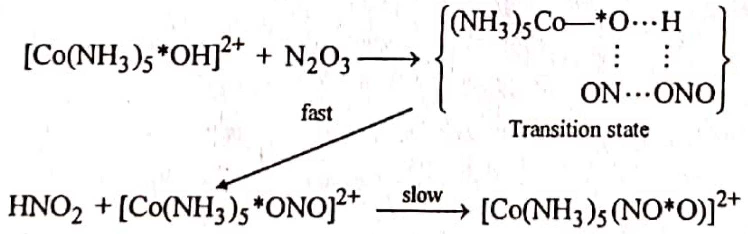
...(xx)

As another example, consider the reaction of nitrite with the pentaamminеaquacobalt(III) ion, as in reaction (xxi).

$$[Co(NH_3)_5({}^*OH_2)]^{3+} + NO_2^- \longrightarrow [Co(NH_3)_5(N{}^*OO)]^{2+} + H_2O \qquad \text{...(xxi)}$$

Isotopic labeling studies show that the oxygen of the aqua ligand is one of the oxygen atoms that is found in the nitro ligand. This remarkable result can be explained by the sequence of reaction (xxii) to (xiv).

$$2\,NO_2^- + 2H^+ = N_2O_3 + H_2O \qquad \text{...(xxii)}$$



$$[Co(NH_3)_5{}^*OH]^{2+} + N_2O_3 \longrightarrow \left\{\begin{matrix} (NH_3)_5Co\text{—}{}^*O\cdots H \\ \vdots \quad \vdots \\ ON\cdots ONO \end{matrix}\right\} \qquad \text{...(xxiii)}$$

Transition state

fast

$$HNO_2 + [Co(NH_3)_5{}^*ONO]^{2+} \xrightarrow{\text{slow}} [Co(NH_3)_5(NO{}^*O)]^{2+} \qquad \text{...(xxiv)}$$

In the transition state, it is an O—H bond that is broken, not a Co—O bond. The oxygen of the aqua ligand is, therefore, retained in the nitro ligand.

UNIT-X Ligand Substitution Reactions in Square Planar Complexes

Trans effect

Consider the formation of diamminedichloroplatinum (II) from

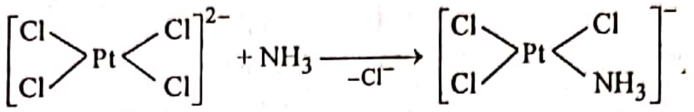
(i) displacement of Cl^- ions from $[PtCl_4]^{2-}$ by NH_3.

(ii) displacement of NH_3 from $[Pt(NH_3)_4]^{2+}$ by Cl^- ions

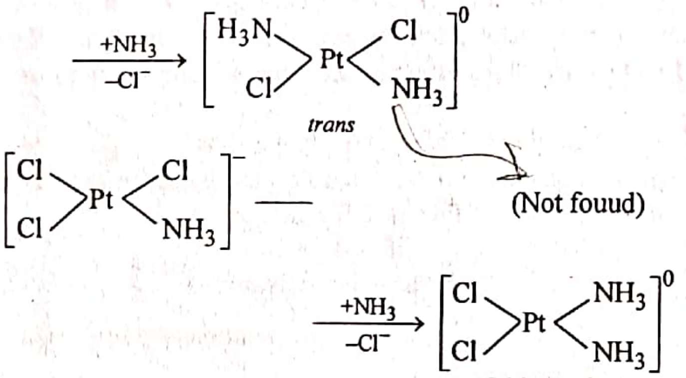
(i) Displacement of Cl^- ions from $[PtCl_4]^{2-}$ by NH_3

The reaction of formation of diamminechloroplatinum (II) takes place in two steps.

Step I : This step inudves a simple displacement of one Cl^- ion by NH_3 because all the four ligands in $[PtCl_4]^{2-}$ are identical. Only one compound is formed.



Step II : In this step two products are formed but experimetns have shown that displacement of that Cl^- ion takes place which is *cis* to NH_3.



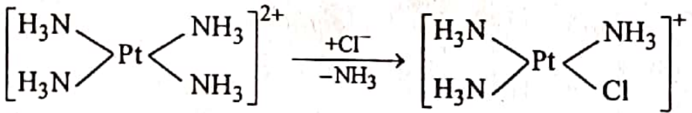
(Not fouud)

(Major Product)

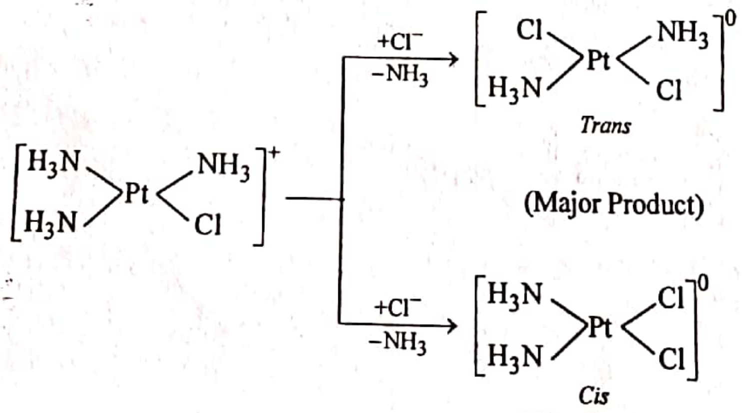
(ii) Displacement of NH_3 from $[Pt(NH_3)_4]^{2+}$ by Cl^- ions

The reactions of formation of diammidedichloroplatinum (II) from $[Pt(NH_3)_4]^{2+}$ by the displacement of NH_3 by Cl^- ions takes place in two steps.

Step I : In this step simple displacement of NH_3 from $[Pt(NH_3)_4]^{2+}$ by Cl^- ion occurs, because all the four ligands are identical.



Step II : In this step two products can be formed but only one product is formed exclusively. The exclusive product is that which is formed by the displacement of NH_3 trans to Cl^- in $[Pt(NH_3)_3Cl]^+$.



(Major Product)

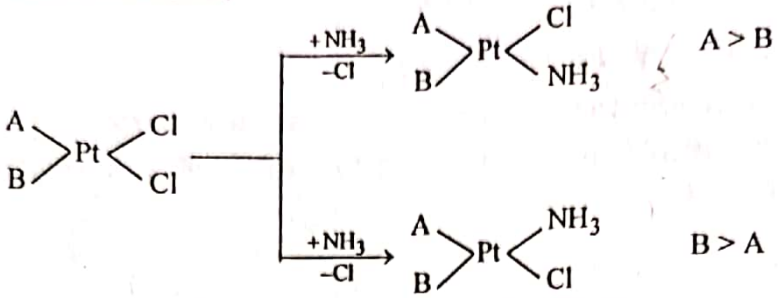
(Not found)

In reaction (i) and (ii) the observed isomer is the one that forms by substitution of a ligand trans to a Cl^- ion. The phenominon of such type of substitution is called trans effect. Groups like Cl^- which direct the incoming ligand to occupy the position trans to them are called trans directing groups.

The trans effect of a group coordinated to a metal ion/atom is the tendency of that group to direct an incoming group to occupy the position trans to that group.

Trans effect may also be defined as the labilization of ligand (trans to certain other ligands) or effect of a ligand on the rate of replacement of a group lying trans to it.

Trans effect may be shown as follows :



A) B)) cl

The approximate decreasing order of trans effect of ligands is shown below.
This series is called trans directing series.

CN^-, CO, NO, C_2H_4 > PR_3, H^- > CH_3^- > C_6H_5, $SC(NH_2)_2$, SR_2 > SO_3H^- > NO_2^-, I^-, SCN^- > Br^- > Cl^- > *py* > RNH_2, NH_3 > OH^- > H_2O

The ligands (CN^-, CO, NO, C_2H_4 etc) lying at the high end are powerful trans directors. These have vacant π or π^* orbitals which can accept electrons from metal orbital to form metal-ligand π-bond ($d\pi$–$d\pi$ or $d\pi$–$p\pi$ bond). These ligands are called π-bonding ligands. The trans effect of the ligands increases with the increase of their ability to form metal-ligand π-bond.

The ligands like (*py*, NH_3, OH^-, H_2O etc.) lying at the low end are very poor trans director. These ligands do not have capability to π-bonding. The trans effect of these ligands increases with increase in their plarisability. e.g.,

— Polarisability increase →

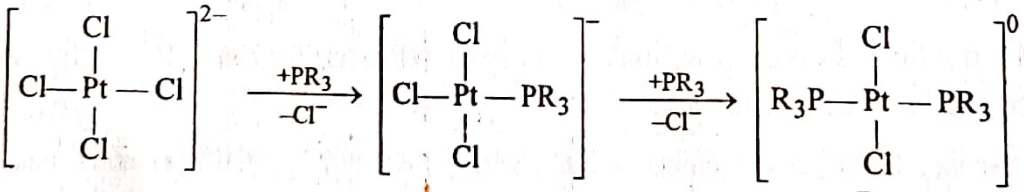
$Cl^- < Br^- < I^-$

— Trans effect increases →

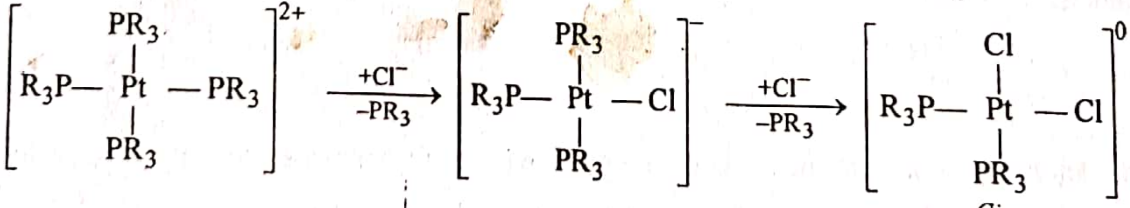
Uses of Trans Effect

(1) Synthesis of *cis*- and *trans*-$[PtCl_2(PR_3)_2]^0$

$PR_3 > Cl^-$



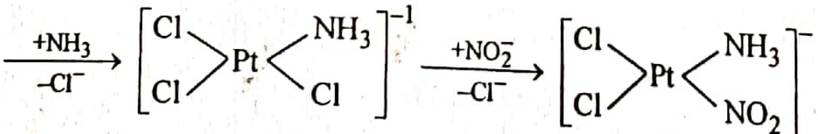
Trans–



Cis–

(2) Synthesis of *Cis*- and *Trans*-$[PtCl_2(NO_2)(NH_3)]^-$

$NO_2^- > Cl^- > NH_3$



Cis–

As the polarisibility (or *trans* effect) of L increases the Pt-X bond length increases and bond strength decreases.

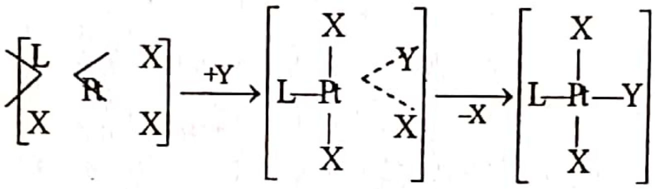
(2) π-Bonding Theory

Polarisation theory explains the effect of the ligand which do not have ability of forming π-bond with Pt(II). This theory do not explain the effect of the ligands like CN^-, CO, C_2H_4, PR_3 which have ability to form π-bonding with Pt(II).

High *trans* effect ligands like CN^-, CO, PR_3, C_2H_4 etc. which have vacant π or π* orbitals withdraw a pair of electrons from the *d*-orbitals of Pt(II) (d_{xz} or d_{yz}) to form metal-ligand π bond ($d\pi - d\pi$ or $d\pi - p\pi$ bond).

In $[PtLX_3]$ type complex (L is the π-bonding ligand), the d_{xz} or d_{yz} orbitals of Pt(II) with a pair of electrons overlaps with empty π or π* orbital to form π bond ($d\pi - d\pi$ or $d\pi - p\pi$ bond). The formation of the π-bond increases the electron density in the direction of L and dimenishes in the direction of X trans to L. The Pt-X bond, therefore, is weakened and rate of substitution of X trans to L by other ligand increases.

The π-acceptor ligands increases the stability of species (Trigonal bipyramidal transition state or intermediate) in which both the incoming ligand Y and the outgoing ligand X are simultaneously bound to Pt(II). The incoming ligand Y enters into he direction in which electron density on Pt(II) is diminished to form 5 coordinated transition state PtX_3LY. The five cordinated transition state has trigonal bipyramidal structure in which the two X which are *cis* to L forms the apexes.



The *dπ-pπ* and *dπ-dπ* bonding is shown below:

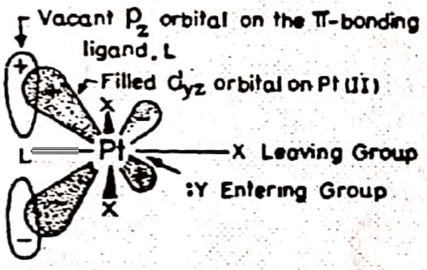


Fig. Formation of *dπ—dπ* bond in *tbp* 5-coordinated activated complex formed during the substitution reaction in Pt(II) square-planar complex, $PtLX_3$:
$PtLX_3 + Y \longrightarrow PtLX_3Y + X$.

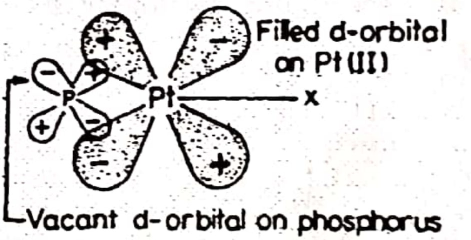
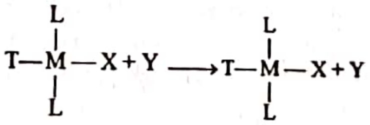


Fig. Schematic representation of R_3P-Pt double bond.

The Rate Law for Nucleophilic Substitution in a Square Planar Complex

The first step in elucidating a mechanism for a reaction is to determine the rate law experimentally. The reaction of interest here may be represented as in which Y is the entering nucleophilic ligand, X is the leaving ligand, and T is the non labile ligand trans to X. Kineticists try to simplify their experiments as much as possible and one way to do that in this case is



$$T-\overset{\overset{L}{|}}{\underset{\underset{L}{|}}{M}}-X + Y \longrightarrow T-\overset{\overset{L}{|}}{\underset{\underset{L}{|}}{M}}-X + Y$$

to run the reaction under pseudo first-order conditions. Practically, this means that the concentration of Y is made large compared to that of the starting complex so that changes in [Y] will be insignificant during the course of the reaction ([Y] = constant). For reactions in which reverse processes are insignificant, the observed pseudo first-order rate law for square planar substitution is. The rate law for the reaction is:

$$\text{rate} = d[ML_2TX]/dt = k_1[ML_2TX] + k_2\,[ML_2TX][Y] \qquad ...(1)$$

This expression may be rearranged to give:

$$\text{rate} = (k_1 + k_2[\text{Y}])\,[\text{ML}_2\text{TX}] = k_{\text{obs}}\,[\text{ML}_2\text{TX}] \qquad \ldots(2)$$

and

$$k_{\text{obs}} = k_1 + k_2[\text{Y}] \qquad \ldots(3)$$

From equation (3) we can see that by repeating the reaction at various concentrations of Y, we can obtain both k_1 and k_2 because a plot of k_{obs} against [Y] will give a straight line with k_1 as the intercept and k_2 as the slope.

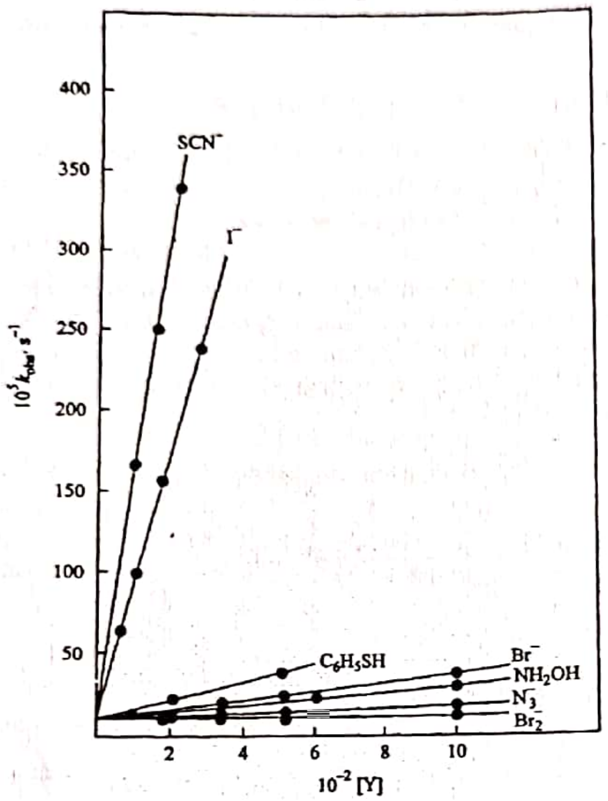


Fig. Rate constants (k_{obs}, s^{-1}) as a function of nucleophile concentration ([Y]) for reaction of *trans*-[Pt(Py)$_2$Cl$_2$] with various nucleophiles in methanol at 30 °C. [From Belluco, U.; Cattalini, L.; Basolo, F.; Pearson, R. G.; Turoco, A. *J. Am. chem. Soc.* 1965, *87*, 241–246. Used with permission.]

Mechanism of Nucleophilic Substitution in Square Planar Complexes

In developing a detailed view of the overall process of nucleophilic substitution in square planar complexes, we can a nucleophile Y attacks a 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 metal *d* orbitals and from the bodnign electrons. It may coordinate to the metal through an empty p_z orbital to form a square pyramidal species (following figure). Electronic repulsions, as well as steric factors, slow the attack somewhat. Once formed, the square pyramidal species will undergo a transformation to a trigonal bipyramidal structure. It will have three ligands (Y, T, and X) in its equatorial plane, and two of the groups 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.

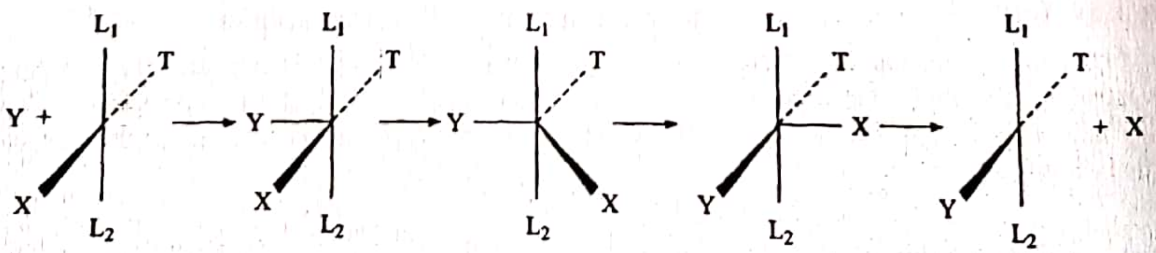


Fig. Mechanism for nucleophilic substitution in square planar ML_1L_2XT complexes.

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, i.e., at the transition state (following figure). In contrast, the term *Intermediate* implies that a species has a detectable lifetime (although it may be short) and that it is at least somewhat more stable than any activated complexes that form along the reaction pathway (following figure).

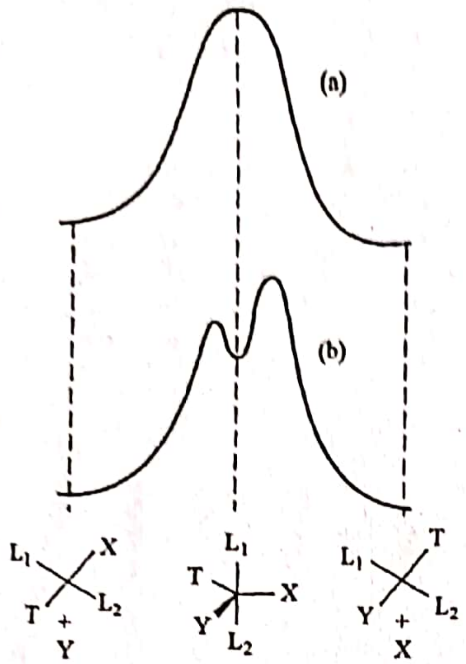


Fig. Reaction coordinate/energy profile for a square planar substitution reaction having (a) a trigonal bipyramidal activate complex and (b) a trigonal bipyramidal intermediate. [From Burdett, J. K. *Inorg. Chem.* 1977, *16*, 3013–3025. Used with permission.]

To derive an explanation for the trans effect, we should now ask how the ligand T in above figure is able to dramtically increase the reaction rate and induce the departure of X in preference to itself or the cis ligands. There are two possible modes by which *T* can enhance the rate of the reaction.

It can either destabilize the ground state by weakening the metal-ligand bond trans to itself or it can somehow stabilize the transition state. Either mode (or a combination of the two) serves to speed the reaction because the activation energy, E_a (the difference in energy between the ground and transition states) is reduced.

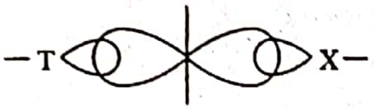


Fig. Competition of trans ligand (T) and leaving group (X) for a metal p_x orbital in a square planar complex.

The extent to which a ligand affects the bond trans to itself in a complex is termed the *trans influence.* It can be assessed by looking at ground state properties such as bond lengths, coupling constants, and stretching frequencies. The effect of T on the 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 (above figure). If T forms a strong bond to M, the M—X bond is weakened because the p_x orbital is not as available to X. The net effect is to destabilize the substrate and thereby to reduce E_a. 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:

$$H^- > PR_3 > SCN^- > I^-, CH_3^-, CO, CN^- > Br^- > Cl^- > NH_3 > OH$$

Two ligands in the above list, CO and 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 decrease in the order shown:

$$C_2H_2, CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$$

The high positions of CO, CN^-, and C_2H_2 in this series suggest 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 favor an equatorial position in the trigonal bipyramidal activated complex or intermediate that forms in the reaction. Provides an explanation for the labilization 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.

It is quite likely that both σ and π factors contribute to the order of ligands in the trans effect series, but there is a wide spectrum of opinion regarding the relative importance of each factor.

UNIT-XI Electron Transfer Reactions

These are oxidation-reduction (redox) reactions in which an electron passes from one complex to another. Electron-transfer reactions may involove substitution of one or more ligands in the first-or inner-coordination spheres of either reactants or products, but this is not necessary. An example of an elrctron-transfer reaction is given by Eq. (i).

$$Fe^{2+}(aq) + Ce^{4+}(aq) \longrightarrow Fe^{3+}(aq) + Ce^{3+}(aq) \qquad \ldots(i)$$

in which the aqua ion of Ce^{IV} is reduced by the aqua ion of Fe^{II}.

An electron-transfer reaction may take place so that there is actually no net chemical change, as Reaction (ii).

$$[{}^*Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} = [{}^*Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-} \qquad \ldots(ii)$$

Such reactions are called self-exchange reactions. Self-exchange reactions can only be followed by using isotopic tracers or certain magnetic resonance techniques. These reactions are of interest because there is no change in free energy as a consequence of recation, and the free energy profile is symmetrical.

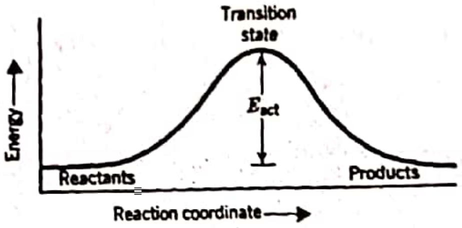


Figure : Free energy versus reaction co-ordinate for a self-exchange reaction.The profile is symmetical because the reactnts and products are identical. For other elrectron transfer reactions known as cross reactions the products are at a lower energy than reactants in proportion to the electrochemical potential ($\Delta G = -nFE$) for the reaction.

The Classification of Redox Reactions

In the 1950s, Henry Taube identified two mechanisms of redox reactions. One is the inner-sphere mechanism, which includes atom transfer processes. In an inner-sphere mechanism, the coordination spheres of the reactants share a ligand transitorily and form a bridged intermediate activated complex. The other is an outer-sphere mechanism, which includes many simple electron transfers. In an outer-sphere mechanism, the complexes come into contact without sharing a bridging ligand.

Outer Sphere Mechanisms

In this type of reaction bonds are neither made nor broken. Consider the reaction:

$$[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)6]^{3-} + [Mo(CN)8]^{4-}$$

The rate of the reaction is faster than cyanide exchange for either reactant so we consider the process to consist of electron transfer from one stable complex to another with no breaking of Fe—CN or Mo—CN bonds.

Anouter sphere electron transfer may be represmted as follows:

$$\begin{aligned} O + R &\longrightarrow [O\text{----}R] \\ [O\text{----}R] &\longrightarrow [O\text{----}R]^* \\ [O\text{----}R]^* &\longrightarrow [O^-\text{----}R^+] \\ [O^-\text{----}R^+] &\longrightarrow O^- + R^+ \end{aligned}$$

First the oxidant (O) and reductant (R) come together to form a precursor complex. Activation of the precursor complex, which includes reorganization of solvent molecules and changes in metal-ligand bond lengths must occur before electron transfer can take place. The final step is the dissociation of the ion pair into product ions.

This mechanism is certain to be correct when both complexes participating in the reaction undergo ligand substitution reactions more slowly than they participte in electron-transfer reactions. An example is the reaction shown in Reaction (iii).

$$[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \rightleftharpoons [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-} \qquad \ldots(iii)$$

where both reactants are "inert twoards substituion ($t_{1/2} > 1$ ms), but the redox reaction is fast ($k = 10^5$ L mol^{-1} s^{-1}). Clearly, the electron-transfer process is not constrained to wait for substitution to take place or it would be itself as slow as substitution. The outer-sphere mechanism is also correct when no ligand is capable of serving as a bridging ligand.

There is a pre equilibrium constant, K_{OS}, in which the outer sphere complex (or ion pair) is formed (reaction (iv).

$$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} = [Fe(CN)_6]^{4-}/[IrCl_6]^{2-} \qquad K_{os} \qquad \ldots(iv)$$

$$[Fe(CN)_6]^{4-}/[IrCl_6]^{2-} \longrightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-} \qquad K_{et} \qquad \ldots(v)$$

The encounter (outer-sphere complex or ion pair) between the reactants brings them to within the internuclear separation required for electron transfer. The electron-transfer step takes place within this outer-sphere complex, only after metal-ligand bond lengths have been altered enough to allow the electron transfer to take place adiabatically (without further change in energy). R. Marcus recognized that the electron transfer should be adiabatic, because electron motion should be faster than nuclear motion. In other words, the electron transfer takes place quickly, once internuclear distances have become appropriately adjusted. For the complex that is being oxidized, (metal-ligand distances in the activated complex must generally become shorter, because of the higher oxidation state that is to exist on the metal upon oxidation. The complex being reduced must achieve longer metal-ligand bond distances in the activated complex, in anticipation of the lower oxidation state that develops at the metal upon reduction.

Self Exchange Reactions : The redox reactions in which not net chemical change occurs during electron transfer, are called self exchange reactions. Some example of self exchange reactions are given in the following table:

Table : Rate constants for some Self-Exchange Reactions that proceed via outer-sphere mechanism.

Reactants	**Rate Constants** **($L\ mol^{-1}\ s^{-1}$)**
$[Fe(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{3+}$ $[Mn(CN)_6]^{3-}$, $[Mn(CN)_6]^{4-}$ $[Mo(CN)_8]^{3-}$, $[Mo(CN)_8]^{4-}$ $[W(CN)_8]^{3-}$, $[W(CN)_8]^{4-}$ $[IrCl_6]^{2-}$, $[IrCl_6]^{3-}$ $[Os(bpy)_3]^{2+}$ $[Os(bpy)_3]^{3+}$	$10^4 - 10^6$
$[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$	7.4×10^2
$[MnO_4]^-$, $[MnO_4]^{2-}$	3×10^3
$[Co(en)_3]^{2+}$, $[Co(en)_3]^{3+}$ $[Co(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$ $[Co(C_2O_4)_3]^{3-}$, $[Co(C_2O_4)_3]^{4-}$	$\sim 10^{-4}$

For the case of Self-exchange reactions, the transition state must be symmetrical; the two halves of the activated complex must be identical. (The lengthening of metal-ligand bonds that is required of the complex undergoing reduction is equal to the shortening of the metal-ligand bond that is required of the complex undergoing oxidation. After all, self-exchange simply transforms one reactant into the other, with no net chemical change. Furthermore, it can be shown that an unsymmetrical transition state would correspond to a higher activation energy and, therefore, would not lie along the preferred reaction path.

In the seven fastest reactions of above table there is very little difference in the metal-ligand bond lengths in the two reacting complexes. Thus, very little energy of bond stretching and bond compressing is needed to achieve the symmetrical transition state. For the MnO_4^-/MnO_4^{2-} pair the bond length difference is somewhat greater, and for the last three reactions thee is a considerable differece between the two reactants in metal-ligand bond distance.

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

$$[Co^*(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+} \longrightarrow [Co^*(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}$$

The second-order rate constant for this slow reaction is 10^{-6} M s^{-1}. The Co—N bond length in Co(III) is 1.935(15) Å while in Co(II) it is 2.114(9) Å, a difference of 0.178 Å. Considerable elongation of the Co(III)—N bond and compression of the Co(II)—N bond is necesary before electron transfer can occur. In contrast, the self-exchange rate constatn for the $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{2+}$ couple is 8.2×10^2 $M^{-1}s^{-1}$ and the Ru—N bond length difference is 0.04(6) Å. This musch faster for the ruthenium exchange is consitent 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 d^6 complex to a high-spin d^7 complex while ruthenium remains low spin in both the oxidized and reduced form. It has been argued that the cobalt reaction is anomalously slow because it is spin forbidden; however, recent work does not support this hypothesis.

It should be noted that not all self-exchange reactions between Co(III) and Co(II) are slow. The nature of the bound ligand has a significant influence on the reaction rate. In particular, ligand with π systems provide easy passage of electrons. For $[Co(phen)_3]^{3+}/[Co(phen)_3]^{2+}$ exchange, for example, k is 40 $M^{-1}\ s^{-1}$, many orders of magnitude faster than for the cobalt ammine system.

Cross Reactions : Electron-transfer reactions between dissimilar complexes are called cross reactions.

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

For cross reactions there is a net decrease in free energy, and the free energy profile is not symmetrical. A linear free energy relationship exists for such reactions, and the faster reactions tend to be those for which the free energy change is most favorable. Marcus and Hush derived the relationship.

$$k_{12} = [k_{11}k_{22}K_{12}f]^{1/2} \qquad \text{...(A)}$$

This equation allows the calculation of the rate constatn for a cross reaction (k_{12}) from the two appropriate self-exchange rate constants (k_{11} and k_{22}) and the equilibrium constant for the overall cross reaction (K_{12}). The constant f in equation is a statistical and steric factor that is usually about 1. The linear free energy relationship arises because the rate of reaction (as measured by k_{12}) depends on the net free energy change of the reaction (as measured by K_{12}). In fact, it is a general result that the faster cross reactions are those with the larger equilibrium constants. Thus rate constants for cross reactions are generally higher than those for the comparable self-exchanges.

As a specific example, consider the cross reaction.

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

for which k_{12} is sought. The equilibrium constant K_{12} for above reaction is 1.0×10^2. The self-exchange reactions that apply are

$$[Fe(CN)_6]^{4-} + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Fe(CN)_6]^{4-} \qquad k_{11}$$

$$[Mo(CN)_8]^{3-} + [Mo(CN)_8]^{4-} \longrightarrow [Mo(CN)_8]^{4-} + [Mo(CN)_8]^{3-} \qquad k_{22}$$

Values for the self-exchange rate constants are $k_{11} = 7.4 \times 10^2\ L\ mol^{-1}\ s^{-1}$ and $k_{22} = 3.0 \times 10^4\ L\ mol^{-1}\ s^{-1}$. Substitution of these values into Eqation (A), and using a value for f of 0.85 yields the prediction that k_{12} should be about $4 \times 10^4\ L\ mol^{-1}\ s^{-1}$. The value that is obtained experimentally is $3 \times 10^4\ L\ mol^{-1}\ s^{-1}$.

The Marcus equation connects thermodynamics and kinetics, as shown by the dependence of k_{12} on K_{12}: As K_{12} increases, the reaction increases. Thus outer sphere reactions which are thermodynamically more favorable tend to proceed faster than those which are less favorable.

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 complete theory reveals that rate increases rapidly with increasing spontaneity, reaching a maximum when the change in free energy is equal to the sum of reorganization energies, and then decreases as the driving force increases further.

Calculated and Observed Rate constant for outer sphere cross reaction.

Reaction	log K_{12}	k_{12obsd} ($M^{-1}\ s^{-1}$)	$k_{12calcd}$ ($M^{-1}\ s^{-1}$)
$Ru(NH_3)_6^{2+} + Ru(NH_3)_5py^{3+}$	4.40	1.4×10^6	4×10^6
$Ru(NH_3)_5py^{2+} + Ru(NH_3)_4(bpy)^{3+}$	3.39	1.1×10^8	4×10^7
$Ru(NH_3)_6^{2+} + Co(phen)_3^{3+}$	5.42	1.5×10^4	1×10^5
$Ru(NH_3)_5py^2 + Co(phen)_3^{3+}$	1.01	2.0×10^3	1×10^4
$V_{aq}^{2+} + Co(en)_3^{3+}$	0.25	5.8×10^{-4}	7×10^{-4}
$V_{aq}^{2+} + Ru(NH_3)_6^{3+}$	5.19	1.3×10^3	1×10^3
$V_{aq}^{2+} + Fe_{aq}^{3+}$	16.90	1.8×10^4	2×10^6
$Fe_{aq}^{2+} + Os(bpy)_3^{3+}$	1.53	1.4×10^3	5×10^5
$Fe_{aq}^{2+} + Fe(bpy)_3^{3+}$	3.90	2.7×10^4	6×10^6
$Ru(NH_3)_6^{2+} + Fe_{aq}^{3+}$	11.23	3.4×10^5	2×10^6
$Ru(en)_3^{2+} + Fe_{aq}^{3+}$	9.40	8.4×10^4	4×10^5

$Mo(CN)_8^{4-} + IrCl_6^{2-}$	2.18	1.9×10^6	8×10^5
$Mo(CN)_8^{4-} + MnO_4^-$	–4.07	2.7×10^2	6×10^1
$Mo(CN)_8^{4-} + HMnO_4$	8.48	1.9×10^7	2×10^7
$Fe(CN)_6^{4-} + IrCl_6^{2-}$	4.08	3.8×10^5	1×10^6
$Fe(CN)_6^{4-} + Mo(CN)_8^{3-}$	2.00	3.0×10^4	4×10^4
$Fe(CN)_6^{4-} + MnO_4^-$	3.40	1.7×10^5	6×10^4

The Concepts Needed to Discuss Outer-Sphere Processes

The analysis of the outer-sphere mehanism depends on two concepts. One is the Born-oppenheimer approximation, which implies that electron distribution can be calculated by assuming that the nuclei are stationary at a given location. This separation of the motion of electrons and nuclei is based on the great difference of mass of electrons and nuclei, and hence the former's ability to respond almost instantaneously to rearrangements of nuclei and, conversely, for the nuclei to respond only sluggishly to movement of the electrons. If we assume that the nuclei are fixed in the intermediate (transition-state) configuration, we can picture the wavefunction of the migrating electron as distributed over both centres. it is also energetically more economical for ion-ligand bond lengths to adjust to intermediate values, and then for electron transfer to take place, than for electron transfer to occur at reactant bond lengths (as would be the case in photo-effected electron transfer, which is subject to the Frank-Condon principle). The second concept we need is that electron transfer is most facile when the nuclei in the two complexes have positions that ensure that the electron has the same energy on each site. It follows from these two points that the rate of electron transfer, and the activation energy for the process, is governed by the ability of nuclei to adopt arrangements that achieve this matching of energies.

To understand how an outer-sphere reaction occurs, we consider the exchange reaction

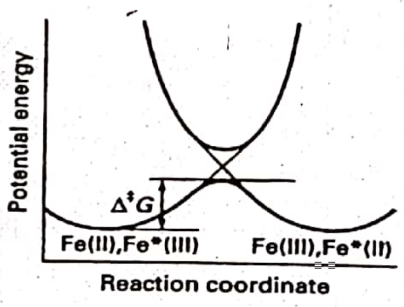
$$[Fe(OH_2)_6]^{2+} + [Fe^*(OH_2)_6]^{3+} \longrightarrow [Fe(OH_2)_6]^{3+} + [Fe^*(OH_2)_6]^{2+}$$

where the * indicates a radioactive isotope of iron that acts as a tracer. The second-order rate constatn is 3.0 L mol^{-1} s^{-1} at 25°C and the activation energy is 32 kJ mol^{-1}. With the two theoretical points in mind we must consider the following three factors. First, bond lengths in Fe(II) are longer than those in Fe(III). Hence a part of the activation energy will arise from their adjustment to a common value in both complexes. This adjustment requires a change in Gibbs energy that is called the **inner-sphere rearrangement energy,** $\Delta^{\ddagger}G_{IS}$. Second, the solvent immediately outside the coordination sphere must be recorganized, which results in a change in Gibbs energy called the **outer-sphere reorganization energy,** $\Delta^{\ddagger}G_{OS}$. Thirdly, there is the electrostatic interaction energy between the two reactants, $\Delta^{\ddagger}G_{ES}$. The total activation Gibbs energy is therefore

$$\Delta^{\ddagger}G = \Delta^{\ddagger}G_{IS} + \Delta^{\ddagger}G_{OS} + \Delta^{\ddagger}G_{ES}$$

The Potential Energy Curves for Reaction

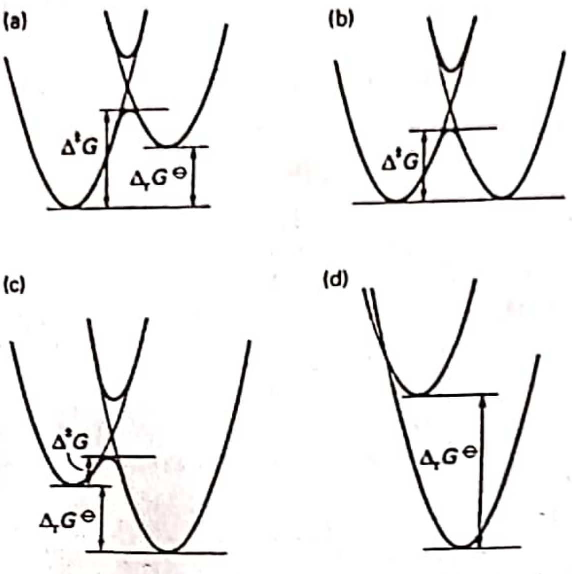
The reactants initially have their normal bond lengths for Fe(II) and Fe(III), respectively, and the reaction corresponds to motion in which the Fe(II) bonds shorten and the Fe(III) bond ssimultaneously lengthen. The potential energy curve for the products of this symmetrical freaction is the same as fo the reactants, the only difference being the interchange of the roles of the two Fe atoms. We have assumed that the metal-ligand stretching motions resemble a harmonic vibration and so have drawn them as parabolas.



A simplified reaction profile for electron exchange in a symmetrical reaction. On the left of the graph, the nuclear coordinates correspond to Fe(II) and Fe*(III); on the right, the ligands and solvent molecules have adjusted locations and the nuclear coordinates correspond to Fe(III) and Fe*(II), where * denotes the isotope label.

The activation complex is located at the intersection of the two curves. However, the noncrossing rule states that molecular potential energy curves of states of the same symmetry do not cross but instead split into an upper and a lower curve (as seen in figure). The noncrossing rule implies that, if the reactants in their ground states slowly distort, then they follow the path of minimum energy and transform into products in their ground states.

More general redox reactions correspond to a nonzero reaction Gibbs energy, so the parabolas representing the reactants and the products lie at different heights. If the product surface is higher (figure a), then the crossing point moves up and the reaction has a higher activation energy. Conversely, moving the product curve down (figure c) leads to lower crossing points and lower activation energy, at least until the crossing begins to occur at the left. At the extreme of exergonic reaction (figure d), the crossing point rises and rates may become slower again.



The effect on the activation energy of a change of reaction Gibbs energy for electron transfer when the shape of the potential surfaces remains constant (corresponding to equal self-exchange rates).

Inner Sphere Mechanism

Inner sphere reactions are more complicated than outer sphere reactions because in addition to electron transfer bonds are broken and 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 coworkers. Their system involved the reduction of cobalt(III) (in $[Co(NH_3)_5Cl]^{2+}$) by chromium (II) (in $[Cr(H_2O)_6]^{2+}$) and was specifically chosen because (1) both Co(III) and Cr(III) form inert complexes and (2) the complexes of Co(II) and Cr(II) are labile. Under these circumstances the chlorine atom, while remaining firmly attached to the inert Co(III) ion, can displace a water molecule from the labile Cr(II) complex to form a bridged intermediate:

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow [(H_3N)_5Co{-}Cl{-}Cr(OH_2)_5]^{4+} + H_2O$$

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

$$[(H_3N)_5Co{-}Cl{-}Cr(OH_2)_5]^{4+} \longrightarrow [(H_3N)_5Co]^{2+} + [ClCr(OH_2)_5]^{2+}$$

The five-coordinate cobalt(II) species presumably immediately picks up a water molecule to fill its sixth coordination position and then hydrolyzes rapidly to $[Co(H_2O)_6]^{2+}$.

$$[Co(NH_3)_5]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(H_2O)]^{2+}$$

$$[Co(NH_3)_5(H_2O)]^{2+} + 5H_3O^+ \longrightarrow [Co(H_2O)_6]^{2+} + 5NH_4^+$$

Formally, such an inner sphere reaction consists of the transfer of a chlorine atom from cobalt to chromium, decreasing the oxidation state of the former but increasing that of the latter. In addition to the self-consistency of the above model (inert and labile species) and the observed formation of achlorochromium complex.

The overall reaction is

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

Good bridging ligands are those with more than one pair of electrons available to donate to the two metal centers; they include:

$$Br^-,\ I^-,\ SO_4^{2-},\ NCS^-,\ PO_4^{3-},\ CH_3COO^-$$

$$:\ddot{\underset{..}{Cl}}:^- \quad :S{-}C\equiv N:^- \quad :N\equiv N: \quad :\underset{..}{\overset{..}{N}}=N=\underset{..}{\overset{..}{N}}:^- \quad :C\equiv N:^-$$

An inner-sphere reaction can be regarded as the outcome of three steps:

1. Formation of the bridged (μ) complex:

$$M^{II}L_6 + XM^{III}L'_5 \longrightarrow L_5M^{II}{-}X{-}M'^{III}L'_5 + L$$

2. Electron transfer:

$$L_5M^{II}{-}X{-}M'^{III}L'_5 \longrightarrow L_5M^{III}{-}X{-}M'^{II}L'_5$$

3. Decomposition of the successor complex into final products:

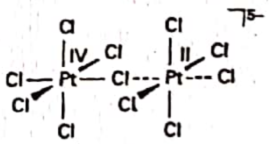
$$L_5M^{III}{-}X{-}M'^{II}L'_5 \longrightarrow \text{products}$$

The rate-determining step of the overall reaction may be any one of these processes, but the most common one is the electron-transfer step. Reactions in which break-up of the successor complex is rate-determining are common only if the configuration of both metal ions after electron transfer results in substitutional inertness—but then an inert binuclear complex is a characteristic product. A good example is the reduction of $[RuCl(NH_3)_5]^{2+}$ by $[Cr(OH_2)_6]^{2+}$ in which the rate-determining step is the dissociation of $[Ru^{II}(NH_3)_5(\mu{-}Cl)Cr^{III}(OH_2)_5]^{4+}$. Reactions in which the formation of the bridged complex is rate-determining tend to be quite similar for a series of partners of a given species. For example, the oxidation of V^{2+} (aq) proceeds at more or less the same rate for a long series of Co(III) oxidants with different bridging ligands. The explanation is that the rate-determining step is the substitution of an H_2O molecule from the coordination sphere of V(II).

The reactions that result the change of oxidation number by ± 1, are called one-equivalent processes. Similarly, reactions that result in the change of oxidation number by ± 2 are often called two-equivalent processes and may resemble nucleophilic substitution. This resemblance can be seen by considering the reaction.

$$[Pt^{II}Cl_4]^{2-} + [{}^*Pt^{IV}Cl_6]^{2-} \longrightarrow [Pt^{IV}Cl_6]^{2-} + [Pt^{II}Cl_4]^{2-}$$

which occurs through a Cl^- bridge. The reaction depends on the transfer of a Cl^- ion in the break-up of the successor complex.



In reactions between Cr^{2+} and CrX^{2+} and between Cr^{2+} and $Co(NH_3)_5X^{2+}$, which are inner sphere, the rates decrease as X is varied in the order $I^- > Br^- > Cl^- > F^-$. This seems reasonable if ability to "conduct" the transferred electron is associated with polarizability of the bridging group, and it appeared that this order might even be considered diagnostic of the mechanism. However, the opposite order is found for the $Fe^{2+}/Co(NH_3)_5X^{2+}$ and for the $Eu^{2+}/Co(NH_3)_5X^{2+}$ reactions. Moreover, the $Eu^{2+}/Cr(H_2O)_5X^{2+}$ reactions give the order first mentioned, thus showing that the order is not simply a function of the reducing ion used. The order must, of course, be determined by the relative stabilities of transition states with different X, and the variation in reactivity order has been rationalized on this basis.

There are now a number of cases (e.g., those of $Co(NH_3)_5X^{2+}$ with $[Co(CN)_5]^{3-}$, where X = F^-, CN^-, NO_3^-, and NO_2^-, and that of Cr^{2+} with $[IrCl_6]^{2-}$) in which the electron transfer is known to take place by both inner and outer sphere pathways.

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 reduction of $[Co(NH_3)_5Cl]^{2+}$ is about 10^{10} faster than the reduction of $[Co(NH_3)_6]^{3+}$. The bound ammonia ligand has no nonbonding pairs of electrons to donate to a second metal. Thus the reduction of the hexaammine 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 importatn 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 intimate 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 wtih respect to each reactant).

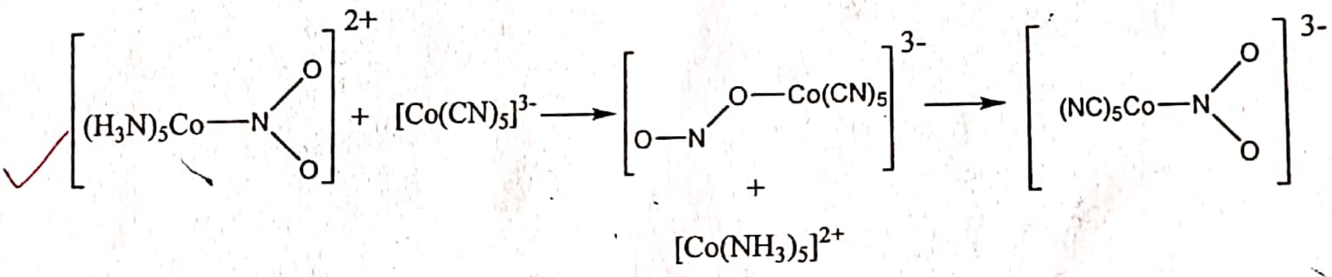
$$\text{rate} = k\,[\text{oxidant}]\,[\text{reductant}]$$

Furthermore, although the chloro ligand in equation 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 stablized its original complex more than the newly formed complex, failure of its transfer would be no surprise. For example:

$$[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} \longrightarrow [Fe(CN)_6]^{4-} + [Co(CN)_5]^{2-}$$

Presumably the C-bound cyano group stabilizes the d^6 (Fe^{2+}) configuration of $[Fe(CN)_6]^{4-}$ more than the N-bound cyano group would stabilize a d^6 (Co^{3+}) configuration in $[Co(CN)_5(NC)]^{3-}$.

If the bridging ligand contains only one atom (e.g., Cl^-), both metal atoms of the complex must be bound to it. However, if the bridging ligand contains more than one atom (e.g., SCN^-), the two metal atoms may or may not be bound 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:



In the above instance the kinetically favored nitrito complex isomerizes to the thermodynamically favored nitro complex in seconds.

Mixed Valence Complexes

Theoretical treatments of electron transfer between two transition metal ions in solution are complicated by contributions arising from solvent reorganization and by transfer pathway uncertainties. If, however, the reducing and oxidizing agents are separated by a bridge within a single bimetallic complex, there will be no solvent molecules between the metal ions and the pathway will be defined. Furthermore, electron transfer over various distances can be studied by varying the lengths of the bridge and this can provide some insight into important biological processes. Complexes that contain a metal atom in more than one oxidation insight into important biological processes. Complexes that contain a metal atom in more than one oxidation state are referred to as mixed valence complexes. 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 unti is best represented as two $+2\frac{1}{2}$ ions.

$$M^{2\frac{1}{2}+} \text{-------------} M^{2\frac{1}{2}+}$$

Of greater interest are systems in which modest coupling exists beween metal centers, for in these it is possible to photolytically induce electron transfer.

One photoactive system which has been extensively studied is a bimetallic complex of Ru^{2+}/Ru^{3+} in which 4,4'-bipyridine functions as the bridge.

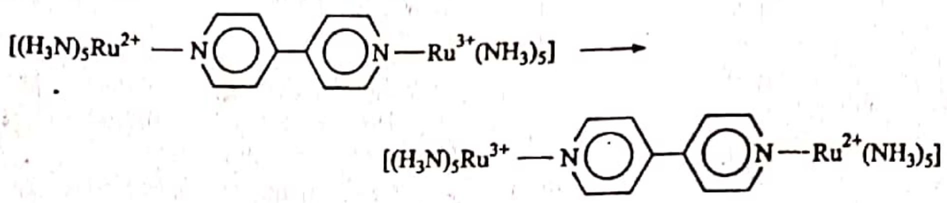
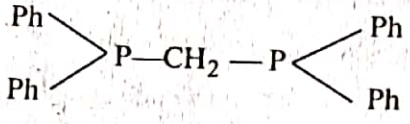
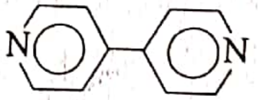
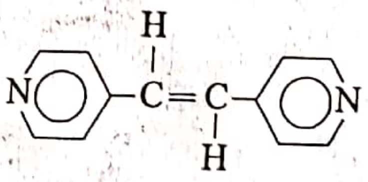


Table : Calculated rate constants for electron transfer in $[Ru(bpy)_2Cl]_2L—L$ complexes and distance (*r*) separgtina the metal centers.

L—L	r_1 Å	$k_r\,s^{-1}$
	6.8	3×10^9
	7.1	1×10^8
	6.0	6×10^{10}
	11.3	1×10^8
	13.8	2×10^7