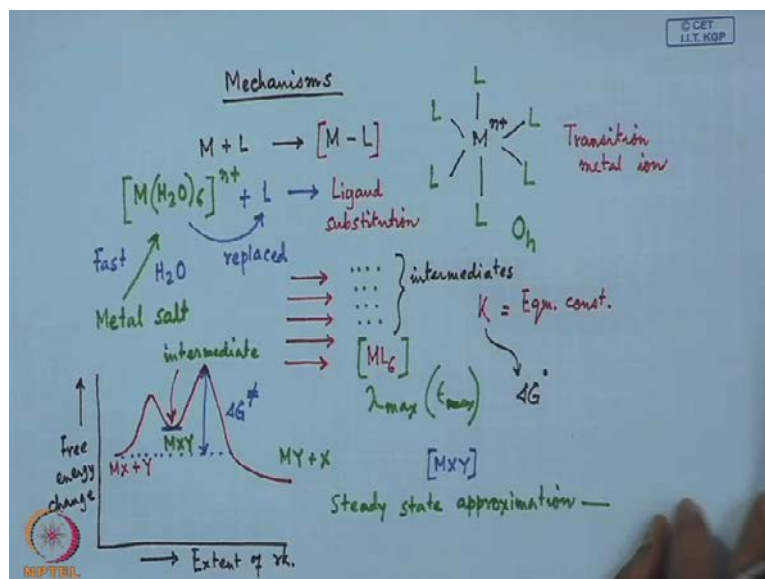


Coordination Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 36
Reaction Mechanism – II

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Good evening everybody. So, today we will just talk with the mechanisms, where we can see that how a particular complex formation reaction is taking place with the formation of at least one metal ligand bond. So, the second part of these reaction mechanisms, we will be considering on the equilibrium formation of the complexes.

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Reaction Mechanisms - II

We have been considering the equilibrium formation of the Complexes.

Rate is important for understanding the chemistry of metal complexes.

Inert: species that are unstable but survive for minutes or more

Labile: species that react more rapidly than inert complexes

 4/2013

So, when we add metal ion and the ligand to each other, we find that the corresponding metal ligand bond is formed and depending upon its corresponding co-ordination number requirement of the metal ion, if the metal ion present is in some oxidation states with plus 2 or plus 3 and if it binds to, say six ligand groups and these ligand groups will occupy the metal ion at six different positions in a three-dimensional array.

If these 6 positions are occupying a particular octahedral geometry, we get a corresponding octahedral complex. Depending upon these, that means if we can have, so this, the first step if 1 M is reacting with 1 L, we are getting M L species forming, but what actually happening, it is basically nothing but some sort of ligand substitution reactions. Because we all know now that whenever a metal salt is available in the solid state and if we dissolve this metal salt in aqua's medium, and that means water is given over there. So, we get the corresponding hexa aqua complex immediately. So, this reaction is very fast and sometimes it is very difficult to monitor this very fast reaction. But when we get some different metal complex apart from this hexa aqua compound, which is always present in solution of water, we use these ligands. So this L is given. So, one after another; that means, all six water molecules will be replaced by these L groups. So, they are all replaced and basically what we get there is the corresponding ligand.

That means, one particular ligand was water molecule and that water molecule will be replaced by the new ligand L. It can be ammonia, it can be methylene diamine or it can

be any other sulphur bearing or any other type of ligand. So, we get a ligand substitution reaction. For such six ligands to occupy 1 2 3 4 5 6, we get therefore all six steps, so all six steps, we can have a, ultimately we can have a corresponding $M L_6$ species. So, if we can monitor the corresponding concentration of either the free metal salt or the aqua complex in solution and if we know the corresponding concentration of the ligand, we all know that the equilibrium constant for the formation or the equilibrium formation constant k can be found out. So, that we also know. Depending upon the nature of the ligand and its corresponding equivalating behaviour, if they are equivalating, the stability constant of the metal complexes, so this k we get as the corresponding equilibrium constant.

If that particular k , which has some relation with the corresponding thermodynamic stability of the complex, we consider it as the corresponding compound is stable, if the k value is pretty high. That means, what we can find out is, we will find out the concentration of the metal complex form. If this compound, because most of the cases what we study in these octahedral complexes of $M n$ plus is the corresponding metal complexes of transition metal ions. So, if this is a transition metal ion; that means, that particular transition metal ion would be called. If we can monitor the corresponding formation of this $M L$ or $M L_6$ compound by looking at the corresponding lambda max value for the formation of this particular $M L_s$ species, and its corresponding epsilon max, the molar absorptivity of that particular compound.

So, we can find out this corresponding concentration of this $M L_6$ species concentration of the M is known and concentration of added L is also known. So, that gives rise to the corresponding equilibrium constants. So, equilibrium constant tells us that how the stability of the corresponding compound is forming due to the corresponding ligand substitution reaction by stepwise replacement of all the six water molecules by these ligands. So, when we consider these as the equilibrium formation of these complexes, the reaction mechanism will not tell us how quickly they are forming or how quickly the equilibrium is achieved for the formation of this particular $M L_6$ species. So, we will just utilise something what we consider as the rate; that means, the rate of the reaction at which whether the rate is very fast or the rate is very slow at particular rate, the metal ion is reacting with the ligands. So, the rate is important in understanding the corresponding mechanism and the chemistry of these transition metal complexes.

So, in particular case, if we just consider that if we want to understand the corresponding electronic structure at the same time and the intermediates, so if these $M-L$ is forming over there, so the other steps what we have utilised is the corresponding stepwise replacement of the water molecules by L. So, these species, we can consider as some intermediates also. So, if they are our intermediates, then how the intermediate is achieved and through that intermediate, how the ultimate product or the final product is formed, that we can find out. So, the explanation for any reaction, if we consider the corresponding reaction co-ordinate; that means, the free energy change for the reaction which will also tell us about the corresponding free energy change, because this k value, the equilibrium constant value is dependent on the corresponding free energy change for the reaction.

So, if we have the free energy change for that particular reaction, so if we have the free energy change along this axis and the extent of reaction on the other axis and if we just consider that the reaction is approaching through this path, where $M-H_2O$ or $M-x$ is there; that means, $M-x$ is reacting with y is nothing but our L and x is nothing but our water molecule. Then at this particular point, we have is stabilised part and if this particular stabilised part is can be detected, so we have the corresponding stability of that intermediates. So, intermediate has some sufficient stability what we can measure and in this particular case, whether $M-x$ plus y or $M-y$ directly can form over there and that tells us how quickly this intermediate is formed and then we have $M-y$ plus x , ultimate product; that means, $M-L$ is forming.

So, this particular case; that means, the amount of activation what we get from there is nothing but the free energy of activation, which is different and not formed the free energy change. How we get this free energy of activation is that, basically the activation barrier. So, for this particular reaction, whether it is a replacement of the water molecule by L or replacement of x by y , we see that it crosses one small hump and it approaches to some intermediate. That means, when this intermediate is formed, it has sufficient stability and it can be detected at this particular point. So, if some suitable technique is available, we can detect the presence of $M-x-y$ through some kinetic experiment. Then this $M-x-y$, further crosses another hump, where this particular energy of activation is required to proceed the reaction from the left to right, which is the corresponding energy barrier for the reaction to go from left to right to produce $M-y$ plus x . So, this is a

different form, where we do not have any intermediate step. But if intermediate is there and if the intermediate can be detected, we have the corresponding reaction co-ordinate for the determination of the formation of M_y .

So, we can have the concentration of the intermediates. So, how we get that? So, we have the corresponding concentration of $M_x y$. So, we can have a corresponding steady state approximation. We call it as a steady state approximation, where we consider about the corresponding concentration of the intermediate. In which case, we will find that the concentration of the intermediate is assumed to be small.

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Conc. of the intermediate is assumed to be small and essentially unchanging during much of the reaction.

Kinetic Experiments

- i) Order of the reaction — power of the reactant concentration in the differential equation that describes the rx.
- ii) rate constant — speed of the reaction
- iii) free energy of activation — study the rx. at diff. temps.
- iv) enthalpy (or heat) of activation —
- v) entropy of activation — interpretation

pressure dependence

Reaction Mechanism & Energy Surface

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So, that is the corresponding approximation for the steady state, which is reached for the conversion to the product is assumed to be small and essentially unchanging or not changing, during much of the reaction or during the codes of this particular reaction.

So, these are the things and we can have certain kinetic experiments to get this kinetic data. So, what are those kinetic experiments? So, in our hand, we can have kinetic experiments. So, we should have certain parameters which we can be detected. In the first case, what we can find out from a particular type f kinetic experiment is the order of the reaction. So, in that case, we have the concentration of the metal ion, the concentration of the ligand and the concentration of the metal complex form. If we have the corresponding reactant concentration, so how we find out? The order is basically depending on the power of the reactant concentration.

So, how it is dependent on the rate of the reaction? So, power of the reactant concentration, if it is the ligand substitution reaction on the aqua complex, it is the concentration of the aqua complex. In the differential equation, power of the reactant concentration in the differential equation, that describe the reaction. So, if we have some power depends on the reaction, then how this power is related to the corresponding reactant concentration and that will tell us the order of the reaction.

Then, once we know the order of the reaction, then we can find out the rate of the reaction or the rate constant we can determine. So, the rate constant, how quickly the reaction is taking place; that means, the speed of the reaction. So, the speed of the reaction, we can determine and then how we find out the corresponding hump? That means, the barrier of the reaction what we want to cross is therefore, the free energy of activation. So, we have the free energy of activation and will follow the Arrhenius equation. That Arrhenius equation will tell us that the rate of the reaction; that means, the speeding of the reaction can take place at every 10 degree centigrade temperature change to double to triple. So, the rate we can increase in that order in most of these reactions.

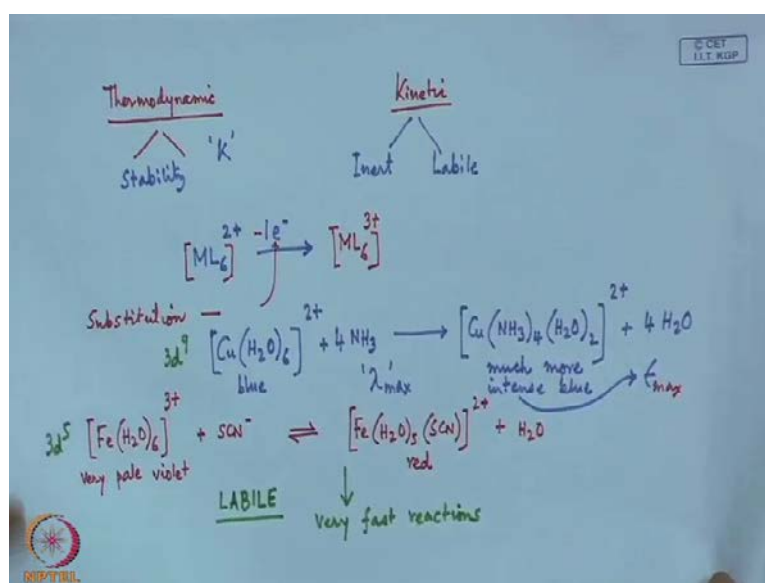
So, how we can find out the free energy of activation? We can find out by measuring or studying the reaction at different temperatures. So, study the reactions at different temperatures. That basically gives us the corresponding free energy of activation. Then we can have another important parameter that we can determine is the heat of activation. It is the free energy and we all know the free energy, that ΔG , the change in free energy has two components. One is the ΔH term and another is the $-T\Delta S$ term. So, the enthalpy or the heat term or the ΔH term is the corresponding thing what we can find out. So enthalpy or heat of activation.

So, heat of activation also we can determine from this study. Lastly, once we can have this enthalpy, we can also determine the entropy of activation. So, if we determine all these together, then we can find out, because in some cases also, we have other dependences also. That means, the pressure dependence, if there is a change in the pressure while going from left to right, we get the corresponding pressure dependence of any particular reaction. So, if we get all these values in our hand and we can further interpret all these data, so we can have the interpretation, which gives us the corresponding reaction mechanism and along with the corresponding energy surface of the reaction. That means, we get the corresponding energy surface. So, depending upon

the corresponding rate of the reaction rate constant, when we find out, we have the speed of the reaction.

Because, we find that while we go for the corresponding substitution of the water molecule by some ligand, we see that, in some cases the speed of the reaction is very high and immediately we can substitute all the water molecules by some these ligands.

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So, we can have, depending upon the corresponding kinetic parameter, we can have the thermodynamic terms. So, the thermodynamic quantity for the reaction and the kinetic quantity for the reaction is are of two types. So, in terms of the corresponding k values, once if we face the corresponding formation constant, if the formation constant is pretty high, the magnitude of the formation constant is pretty high, we can say that the corresponding stability of the complex is also very high. So, we talk about the corresponding stability of the complex. So, one can be very stable, very much stable or have a high stability and one can have the low stability for the corresponding thermodynamic parameter depending upon the k value.

Similarly, for this is corresponding substitution reactions, how quickly the corresponding species is reacting with some other ligand and we can have two types of these complexes. One can be inert complex and another can be labile complex. So, we can have these two terms for the thermodynamic stability and unstability and the kinetic term, we can have the inert form and the labile form of these complexes. So, we find

that, when we take a particular compound as the inert complex, which is a particular metal ligand assembly or species that are unstable, but survive for minutes or more, if in solution, a transit species is formed and has some survival time of a minute or more, we can consider particular compound is inert. But when this particular compound reacts more rapidly than inert complexes, we call them as a very labile complex. So, some of these water molecules, which are surrounding the metals centres or the corresponding aqua complexes, so from the periodic table depending upon the different metal ions, we can have the corresponding rapid exchange of these water molecules.

Because, these water molecules can go from the bulk; that means, from the reaction medium and from the surroundings and then it can go and bind to the metal ion. So, depending upon the charge of the metal ion and its size, the corresponding size of these metal ions, the rate of these substitution reactions can also take place. Most of these aqua complexes are labile in nature, if they are from alkali and alkaline or metal ion. But for some transition metal ions, we will find them as them very inert complexes.

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Variations in reactivity

- Reaction types – substitution, dissociation, addition and redox reactions, reactions of coordinated ligands.
- Equilibrium constants for substitution reactions.
- Kinetic vs. thermodynamic stability of the metal complexes
- Measuring rates of water exchange in aquo metal ions.

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So, we have two types of these complexes. While checking the reactivity of these complexes, we will find that there are the reaction types. So, while talking about these inert and labile complexes, but before proceeding to that will find that what are the different reaction types we can consider. While will talking about the substitution reaction; that means, one ligand is getting substituted by the other.

Then, the disassociation reaction means, the ligand is getting disassociated from the metal environment. Then the addition reaction; that means, if this is the corresponding opposite reaction of the disassociation; that means, we can add one particular ligand to the corresponding species, if it is $M L_6$ type. After disassociation, we get $M L_5$ compound and then after addition, we again get back the corresponding $M L_6$ or $M L_5$ type of compound.

Then, there are something which we considered as the redox reactions. That means, when the metal centre has surrounding ligands; that means, $M L_6$ species is there, but it can transfer one electron to some other species or it can accept the one electron to it. That means, the redox reactions can take place. So, if we have $M L_6$ which is 2 plus, so apart from these ligand substitution, ligand dissociation addition reaction, but also if it goes for one electron elimination or one electron loss, then there will be something; that means, some other species should be available, which can take up this electron.

So, some other species which will be available in the reaction medium or it can be simply the electrode for any electro chemical system like cyclic (()) system or the (()) metric system giving rise to $M L_6$ 3 plus and this electron transfer can take place between these two species, which is $M L_6$. So, both of them are $M L_6$, but only change in the corresponding oxidation state of the central metal ion. So, we get the redox reactions and for that redox reactions, we can have all these values whatever we are seeing for the corresponding substitution or the addition or their limits in reaction for the metal complex. Then will find some of these reactions, where the coordinated ligand, which is bound to the metal centre is undergoing some sort of reaction, that these, some organic transformations or some redox reactions or any other type of reactions or some addition reactions on some coordinated ligand, which is being facilitated due to the corresponding reactions with that of the metal centre.

So, we found out that the equilibrium constants for substitution reactions. So, the thermodynamic parameter what we are talking about is the corresponding determination of the equilibrium constants, if we consider that the reaction is taking place for the corresponding substitution reactions. Then we can have the kinetic process versus thermodynamic stability of the metal complexes. So, the kinetic stability or inertness and thermodynamic stability or the corresponding instability or this opposite of that stable compound of these corresponding metal complexes, can be classified in terms of two

different terms. One is related to the kinetic term and another is related to the thermodynamic term.

Once a substitution reaction is very easier, very fast substitution reactions, we can measure for measuring the rates of water exchange reactions in aqua metal ions. So sometimes, if we can monitor it by some enema technique or in some cases by isotope effect; that means, the water molecules, which are being utilised, they are isotopically levelled. That means, O 17 or O 18 of water molecules can levelled and we can find out the corresponding exchange reaction with that of our parent aqua complexes.

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Labile vs. Inert

General Rules:

- For 2+ ion, d metals are moderately labile particularly d^{10} (Hg^{2+} , Zn^{2+})
- Strong field d^3 and d^6 octahedral complexes are inert, i.e., Cr(III) and Co(III)

- Increasing Ligand Field Stabilization Energy improves inertness

- 2nd and 3rd row metals are generally more inert

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So, we find that we get two different types of these compounds. One is labile and another is inert. So, how we get this particular reaction for this? If we talk about the substitution reaction and that substitution reaction, what we find for particular copper compound, which is hexa aqua. So, we have in our hand the cupric copper, copper in plus 2 oxidation state, which is blue in colour. When we add ammonia, the incoming ligand for the substitution of these water molecules, we find that immediately 4 ammonia molecules can react quickly with this copper centre giving 4 NH_3 whole 4 H_2O whole 2 2 plus with the removal of 4 water molecules, which were already bound to the metal centre.

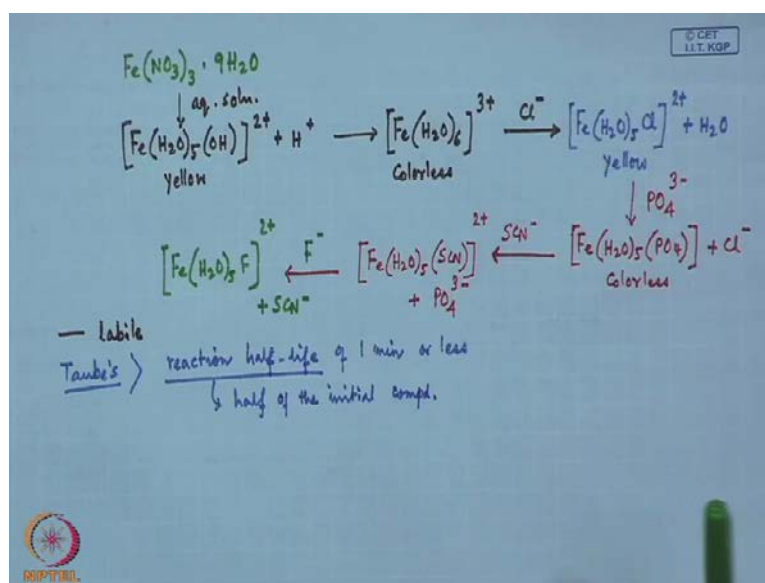
So, this blue colour is getting intensified and which is much more intense blue. So, if there is a change in the corresponding lambda values, a slight change in lambda values

with change in corresponding epsilon value; that means, the intensity is changing and the molar absorptivity is changing, and that means epsilon max is changing. So, by looking at the corresponding lambda max for this compound and epsilon max for this compound, we can monitor the corresponding formation of this particular reaction very quickly. So, with time if we can monitor the corresponding growth of this particular lambda max value for this tetra amine dioco compound of copper, we can find out the corresponding rate of the reaction. So, this particular reaction is a very first reaction. So, immediately this reaction can take place with some time, which is some milliseconds only.

Similarly, if another colour changing critrestic reaction, which immediately shows us the corresponding ligand substitution reaction for these water molecules occupying the octahedral positions around the iron in the fake state is that and it has a pale violate colour. So, very pale, which is light colour, very pale violet in colour, which when reacts with thiocyanate ion and this reaction is in true sense is reversible in nature. We get with the attachment of one thiocyanate group to the iron centre with replacement of 1 water molecule with the elimination of that water molecule. So, there is a critristic colour change. If we get attachment of only one such thiocyanate group to the iron site, that basically gives us the corresponding reaction for that and this red colour formation is very fast. We get this sort of reaction or the previous reactions and these are very fast reactions. These are very fast reactions. So, this particular compound and this iron compound, both of them are aqua compounds.

So, aqua compounds having a particular electronic configuration, which is $3d^9$. This is $3d^9$ and this is $3d^5$. So, these two electronic configurations can tell us they have very first reactions for ligand substitution reactions. Therefore, they are kinetically labiled complexes. So, the complexes which we are talking here, they are labile in nature.

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So, for such reactions, what we find that, if we just start from the solid compound like ferric nitrate having 9 water of crystallizations, and that ferric nitrate, when we make an aqua solution, it gives us $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ at a particular pH value, otherwise, it is all hex aqua, plus H^+ , which is slightly yellow in colour. This basically gives us $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, which is almost colourless or very pale violet. So, this particular one, so if we just go for this, this is a typical acid based type of reaction. So, on the complex also, we find some acid based type of reaction because the water molecule which is bound to the corresponding ferric centre; this is ferric centre, where in plus 3 oxidation state, it polarises the corresponding OH bond. The $\text{p}K_a$ value of this particular water molecule is getting lowered and we get for the corresponding deprotonation and proton is being lost from the medium and we get the corresponding species in this form. So, it is some sort of acid based type of reaction. When it reacts with say some chloride ion, when the chloride ion is supplying to these, so we get another compound because most of these compounds what we are talking over here, they are all labile compound.

So, here also we have again $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ and one water molecule will be replaced by the incoming Cl^- . So, this is basically a substitution reaction using Cl^- with the elimination of one water molecule, which is again going back to the same colour, which is yellow. Then if we can add some other anion, which is highly charged, that is the phosphate anion. So, when phosphate anion is added, we get $[\text{Fe}(\text{H}_2\text{O})_5(\text{PO}_4)]^{3-}$,

an electro neutral form of the ferric ion and which is again colourless plus removal of this chloride ion.

What we have seen in our previous reaction, that this particular or these particular species is reacting with thiocyanate, at this particular point, the thiocyanate is forming a strong bond with the iron site. So, if we add thiocyanate ion over here, we get the red compound $\text{Fe}(\text{H}_2\text{O})_5\text{SCN}^{2+}$ plus plus removal of the phosphate anion part and this further can react with fluoride anion.

Unlike this chloride anion, but it can have stronger binding affinity. So, you have $\text{Fe}(\text{H}_2\text{O})_5\text{F}^{2+}$ plus plus SCN^- . So, we have given some examples of these metal complexes and their corresponding ligand substitution reactions one after another. How we get these reactions because if we can monitor that what is forming over there and whether some intermediate is forming during all these reactions, so if we are able to monitor the corresponding λ_{max} values; that means, the UV-vis spectra for monitoring the formation of the different species, we find that all of these compounds are labile in nature. That means, the ligand exchange reaction takes place at the time of mixing of the solutions; that means, whenever we add fluoride to this particular solution, the thiocyanate will immediately be kept out from the medium and forming the corresponding hexa-aqua iron 3 plus compound.

So, at the time of the mixing, this is forming. So, the labile complex, therefore, we can define as the Nobel laureate Henry Taube definition. So, Taube defined this labile complex is that, when the reaction half-life for these of 1 minute or less. Reaction half-life is nothing but is the time of disappearance of half of the initial compound. So, time required to disappear half of the initial compound. So, when the reaction half-life is 1 minute or less, we get the corresponding compound as the corresponding labile complex.

So, we just can have the corresponding definition for this labile will be in our hand. So, not only this ferric ion, but several other compounds in high-oxidation state also, that transition metal ions are moderately labile, particularly in detail when we do not have any ligand free stabilisation energy for mercuric ion or zinc 2 plus ion. So, if we have water molecule surrounding this mercury or mercuric ion or zinc 2 ion, they exchange very rapidly with a bulk water molecules or some other ligand groups also. So, they are the good examples of labile complexes. But the corresponding compounds of other

groups; that means, the strong field d^3 and d^6 octahedral complexes which are having large crystal field stabilisation or the ligand field stabilisation energies of $-12 \Delta_o$ in octahedral geometry or $-24 \Delta_o$ in typical octahedral geometry, they provide something where the compound is not reacting very fast. They are called inert or robust compound, because they will react more slowly. So, if we are able to make any cobalt compound in $+3$; that means, we have prepared hexa-amine cobalt 3 compound.


Definitely it can react with the acid to give you the corresponding hexa-aqua compound of cobalt in the trivalent state. So, the thermodynamic stability of this compound is there, but its reactivity pattern is different. It will not react easily with the proton available in the medium. That is why it can be easily crystallised for some time. That means, if the solution stability of the compound is there, then only we can crystallise in the solid state. Otherwise, that compound will decompose in our time. So, increasing the LFSC values improves the inertness.

So, for these two; that means, these d^3 and d^6 octahedral complexes, the LFSC values are there. LFSC values are pretty high and that is why it has the corresponding inertness into the system. Compared to the first and first row transition metal ions, the second row and the third row transition metals are genuinely more inert. That means, we know the corresponding splitting is more; that means, the ligand field splitting is more. So, if we move from iron to ruthenium to osmium, similarly, from nickel to palladium to platinum, we will find that both ruthenium and osmium as well as palladium and platinum can show more inert complexes.

So, while we study the kinetic of these complexes, we will find that the good choice would be the compound from the second and the third row element. That means, we can immediately find that the ruthenium and osmium cases or for palladium and platinum cases, we can measure the corresponding rate of the reaction very easily, because most of the compounds available from there are inert in nature.

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Associative vs. Dissociative Reactions



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So, will talk about that different associative versus dissociative reactions. Before we finalise these things; that means, we go for this associative and dissociative reactions, after completing the corresponding reaction, when we consider these as how we get these inert compounds.

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Inert complexes - react more slowly

$3d^8$ $[\text{Ni}(\text{CN})_4]^{2-} + 4 \text{}^{14}\text{CN}^- \rightarrow [\text{Ni}(\text{}^{14}\text{CN})_4]^{2-} + 4 \text{CN}^-$ $t_{1/2} < 1 \text{ min}$ exchanges rapidly - labile
 Ni^{2+} sq. pl. 25°C
 0.1 M

$3d^3$ $[\text{Cr}(\text{CN})_6]^{3-} + 6 \text{}^{14}\text{CN}^- \rightarrow [\text{Cr}(\text{}^{14}\text{CN})_6]^{3-} + 6 \text{CN}^-$ $t_{1/2} = 24 \text{ d}$
inert \rightarrow stable

$[\text{Fe}(\text{H}_2\text{O})_5\text{F}]^{2+}$ \leftarrow 'k' large - thermodynamically stable

$3d^6$ $[\text{Co}(\text{NH}_3)_6]^{3+} + 6 \text{H}_3\text{O}^+ \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{3+} + 6 \text{NH}_4^+$ ($\Delta G^\circ < 0$)
labile
unstable in acid medium / reaction is very slow - 'inert'



So, the inert compounds are nothing but they are reacting slowly. So, inert complexes are those which react more slowly and we also call them as the robust compound. So, we

have apart from the corresponding stability, in terms of the corresponding thermodynamic term.

So, the d^8 configuration, the $3d^8$ configuration is square planer geometry, such as tetra-sano nickelet, potassium tetra-sano nickelet or ammonium tetra-sano nickelet is there. If we consider that, just like water exchange reaction, if we can also monitor the exchange of these attached cyanide groups with the levelled cyanide, where carbon is radio levelled with ^{14}C , carbon 14. So, with this what will find that the substitution for this radio levelled cyanide can take place, but more slowly with the elimination of 4 normal cyanide. In this particular case, the huplife as per Henry Taube's definition is less than 1 minute. So, this particular reaction is also very fast. So, we have the exchange. So, this exchange, what is taking place the cyanide exchange is quite rapid. It exchanges rapidly. So, at temperature of 25 degree centigrade utilising the metal ion and the ligand concentration at 0.1 molar, we find that the corresponding $t_{1/2}$ value is less than 1 minute. It is basically giving the reaction and it exchanges quite rapidly. Therefore, we consider this as a labile complex.

So, we find that this particular one is for something, where this Ni^{2+} is giving us a square planer complex and this is basically a stable complex. So, from the thermodynamic point of view, we get a stable compound, which is a very stable one we all know. But when we talk about the corresponding exchange reaction with a radio levelled cyanide, we find that it exchanges quite rapidly and from kinetic point of view, it is a labile complex.

Similarly, when we find that in case of another cyanide complex, which is hexa sano chromium, which when exchanges with 4 radio levelled cyanide, we get $^{14}C_n^{6+}$ whole $^{63}Cr^{3+}$ minus plus $^{63}Cr^{3+}$ minus. In this particular case, our $t_{1/2}$ is 24 d. So, this $t_{1/2}$ basically tells us that this particular compound, which is getting exchanged with this $^{14}C_n^{6+}$ is now inert. That we have seen also, that a particular type of electron configuration, which is $3d^3$, and here it is $3d^8$. So, for $3d^8$ in square planer geometry, what we expect that it also can give rise to some inert compound. But this particular inert compound, we are not getting in case of nickel, but expectedly we can have these for palladium and platinum compound. But in case of chromium, for the first transition series element, it is kinetically inert compound. So, we get basically a compound like this, which is inert.

Similarly, another example we can have and what we have seen just now also, that this Frodo compound also we have seen that this is a labile compound because it exchanges quite rapidly. It removes the thiocyanate group from the coordinate sphere of the iron, but it has large equilibrium constant of formation. Because when we find out the corresponding k value, it has a large value of the corresponding equilibrium formation constant. That means it is thermodynamically stable. It is not unstable. It is thermodynamically a stable compound, but it is kinetically labile.

So, what we just told you also, that when we have the corresponding species; that means, hexa amine cobalt 3 plus, which when reacting with acid, which is protonated one, H_3O^+ plus. So, this proton will go and bind with this ammonia molecules. This particular one, when reacts with ammonia molecule, so is unstable in acid, in acid medium. So, it is unstable in acid medium; that means, thermodynamically since this is stable, but this is unstable.

So, these two things are going, in some cases, not in the same direction. But what about its corresponding kinetic term? It is unstable in acid medium; that means, if we put in the acid medium, it definitely can go for the corresponding decomposition to give us a corresponding hexaaqua compound with 6 ammonium ion and ΔG° is negative; that means, it is spontaneous also. So, the formation of this particular one; that means, slowly it can form the corresponding hexaaqua compound, but it is unstable in acid medium. That means, it gives us that idea that it will decompose slowly with the acid, but the reaction is very slow. That means, it is reacting slowly with the acid available in the medium; that means, this particular compound, which is in $3d^6$ electronic configuration is kinetically inert. It is unstable thermodynamically, but kinetically it is inert. So, next day we will just consider about the other reaction mechanisms.

Thank you very much.