Advanced Transition Metal Chemistry_Inorganic Reaction Mechanisms

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Module - 11
Lecture - 52
Electron-Transfer Processes

Hello everyone. Once again, I welcome you all to MSB lecture series on Transition Metal Chemistry. This is going to be the fifty-second lecture and this is going to be the last lecture as far as Inorganic Reaction Mechanisms are concerned. So, once after completing this one, I shall move on to another important topic about interpretation of data when you make a compound.

That means spectroscopic methods and how to use spectroscopic methods to characterise coordination compounds and organometallic compounds. And also, when you perform a reaction, when we get the product, whether product is in pure form; if not, if we get mixture of products, in what ratio we got mixture of products; and of course, for separation, you have to use the separation techniques and purification methods to get ultra-pure product for analytical and spectral analysis.

So, those things we shall discuss but let me continue from where I had stopped to conclude Inorganic Reaction Mechanism topic. So, continue with again Electron-Transfer Processes. Before I concluded my previous lecture, I showed you a table of data; let me go back to that data again.

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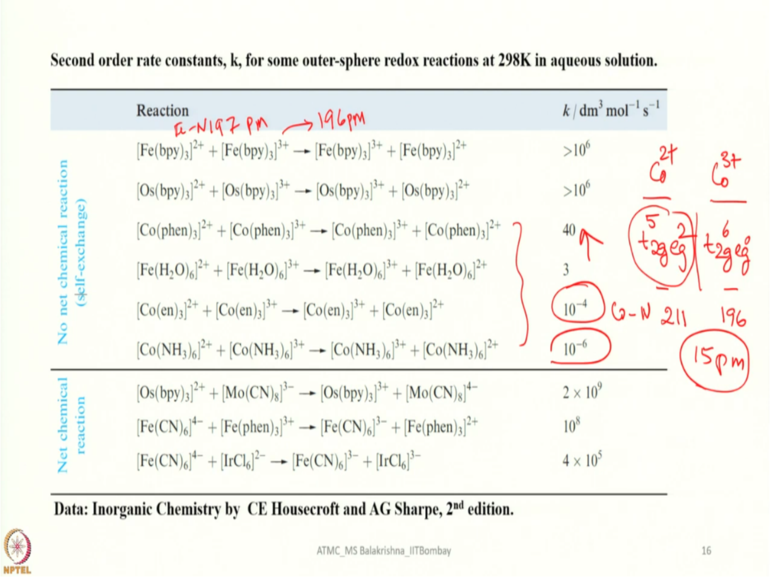

Second order rate constants, k, for some outer-sphere redox reactions at 298K in aqueous solution.

	Reaction	k / $dm^3 mol^{-1} s^{-1}$
No net chemical reaction (self-exchange)	$[Fe(bpy)_3]^{2+} + [Fe(bpy)_3]^{3+} \rightarrow [Fe(bpy)_3]^{3+} + [Fe(bpy)_3]^{2+}$	$>10^6$
	$[Os(bpy)_3]^{2+} + [Os(bpy)_3]^{3+} \rightarrow [Os(bpy)_3]^{3+} + [Os(bpy)_3]^{2+}$	$>10^6$
	$[Co(phen)_3]^{2+} + [Co(phen)_3]^{3+} \rightarrow [Co(phen)_3]^{3+} + [Co(phen)_3]^{2+}$	40
	$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightarrow [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$	3
	$[Co(en)_3]^{2+} + [Co(en)_3]^{3+} \rightarrow [Co(en)_3]^{3+} + [Co(en)_3]^{2+}$	10^{-4}
	$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$	10^{-6}
Net chemical reaction	$[Os(bpy)_3]^{2+} + [Mo(CN)_8]^{3-} \rightarrow [Os(bpy)_3]^{3+} + [Mo(CN)_8]^{4-}$	2×10^9
	$[Fe(CN)_6]^{4-} + [Fe(phen)_3]^{3+} \rightarrow [Fe(CN)_6]^{3-} + [Fe(phen)_3]^{2+}$	10^8
	$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$	4×10^5

Data: Inorganic Chemistry by CE Housecroft and AG Sharpe, 2nd edition.

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You can see here, the second order rate constants, k for some outer-sphere redox reactions carried out at 298 K in an aqueous solution are listed here. The rates of outer-sphere self-exchange reactions vary considerably. Fastest reactions listed here in the chart are between 2 low spin complexes which differ only in the presence of an extra non-bonding electron in that t_{2g} orbital of the complex containing the lower oxidation state metal.

So, that means the difference is only 1 extra electron in t_{2g} because one is in +2 state, other one is +3 state. Other than that, both are low spin complexes because they are under the influence of a strong field ligand. For example, if you take bipyridine, phenanthroline or ethylenediamine, something like that, such low spin complex pairs have similar bond lengths in their ground state; this is very important.

When we consider very similar low spin pair of complexes for performing outer-sphere redox transfer process, so, they will be having very similar bond lengths in that ground states. If we consider iron to nitrogen bond distances, in the first case, here it is 197; and 197 for 2+; here it is 197 pm. And whereas, in this case, it is 196 picometre. That means very marginal difference is there. And I would say, there is no difference at all.

If we consider estimated standard deviation, even if it is plus or minus 2, so, both of them look alike. So, such pairs, low spin complex pairs, where bond lengths are very similar, what happens, the rate of the process can be very rapid, because we have to spend less activation energy to prepare these two species having very similar bond parameters to do electron transfer process.

So, in a pair of low- and high-spin complexes, if we consider, bond lengths vary significantly. In that case, what happens, we have to arrive at a transient or encounter state where we have to bring them; one where we have the longer bond length in case of high spin complex; and in case of low spin complex, where shorter bond length. Where the bond length is shorter, we have to stretch it; and where the bond length is shorter, we have to contract it.

When the short one is there, we have to elongate it; when long is there, we have to make it smaller. So, in that case what happens, for example, if we consider typical cases of octahedral complexes where we have say $t_{2g}^6e_g^2$ one case; and another one is t_{2g}^5 and e_g^0. So, that means here if you consider, we are considering say cobalt 2+ and we are considering cobalt 3+.

So, in this case what happens, if you consider hexaamminecobalt 2+ and hexaamminecobalt 3+, one is a high spin complex; one is a low spin complex. And here, if you look into the cobalt to nitrogen bond distance, it is 211 here; whereas here, 196. You can see, the difference is remarkable; so, that means about 15 picometre difference is there. So, that means here, alteration is very essential in order to transfer electron to complete the redox process.

And as a result, you can see here, the typical case here, you can see the rate. The implications of differing bond lengths and spin states and the mechanism of self-exchange reactions can be used using Franck-Condon principle. That means, when we talk about outer-sphere mechanism, Franck-Condon principle has to be kept in mind. And I shall tell you what is Franck-Condon principle and how one can bring that concept in case of outer-sphere mechanism.

So, reactants must approach closely for the electron to migrate from reductant to oxidant. This is very important here because we are not involving a bridging species. So, however, when we perform this kind of electron tunnelling or electron transfer and there Franck-Condon principle imposes restriction. What is that condition that is imposed by Franck-Condon principle in outer-sphere mechanism?

So, during electron transfer, nuclei are essentially stationary, so, electron transfer between this one, cobalt 2+, cobalt 3+ taking place, it is not easy. So, that means you can see how to modify now. According to Franck-Condon principle between these two species having a remarkable difference in bond parameters, it is not very easy; it can only occur. So, between such cases, such species involving outer-sphere mechanism, electron transfer can only occur with vibrationally excited states with identical structure.

So, we have to look for excited states in case of both the species to have relatively similar bond parameters, bond lengths. This reductant oxidant pair is called the encounter or precursor complex. That means, when we have dissimilarities in the bond lengths of 2 species between which electron transfer has to occur, we have to prepare them to have a moderate or very similar bond distances in both the species.

This we have to prepare for eventually electron transfer. And such intermediate or transient state we generate are essentially called as encounter or precursor complex. Same terminology we were also using in case of water exchange reactions if you recall. A molecular electronic transition is much faster than a molecular vibration. The greater the change in bond lengths required to reach the encounter complex, the slower the rate of electron transfer.

So, data here given in this table shows that the self-exchange reaction between hexaamminecobalt 2+ having $t_{2g}^5e_g^2$ electronic configuration and hexaamminecobalt 3+ having $t_{2g}^6e_g^0$ electronic configuration is relatively slow. Why that between trisbipyridyl iron 2+ and trisbipyridyl iron 3+ is very fast? Because you can draw conclusion simply by looking into bond parameters.

So, bond parameters are similar in case of iron(II), iron(III) species; whereas, in case of cobalt(II) and cobalt(III) species with amine ligands, bond parameters are distinctly different. This data shows that the self-exchange between hexaamminecobalt 2+ and hexaamminecobalt 3+, or between trisethylenediamine cobalt 2+ and trisethylenediamene cobalt 3+ is relatively low in both the cases, we can see here; this is also relatively slow here.

So, self-exchange between trisphenanthroline cobalt 2+ and cobalt 3+ is much faster relatively compared to that one if we go here. So, that means why this is different, is much faster than the same between hexamine and trisethylenediamene complexes although all processes are between high spin and low spin complexes. If we consider all the 3 cases here, in all these cases we have, cobalt 2+ has $t_{2g}^5e_g^2$, and low spin complex has t_{2g}^6 and e_g^0.

And they have in all 3 cases distinctly different; but whereas, in case of phenanthroline ligand, why the rate is little faster? Now we have to analyse. This is consistent with the ability of phenanthroline ligand. So, use pi orbitals to facilitate the intermolecular migration of electron from one species or one ligand to another. And phenanthroline complexes tend to exhibit fast rates of self-exchange processes.

So, here the pi bonding nature in phenanthroline is responsible for enhancing the rate of electron transfer. All self-exchange reactions involve cationic species in aqueous solutions. The rates of these reactions typically not affected by the nature of concentration of the anion present in solution. So, that means, as long as we have cationic species what happens, rate is not affected, is independent of concentration of the anion present in solution. So, the concentration of anionic species present in the solution has little influence on the rate as long as we have another counter cationic species in the reaction sphere.

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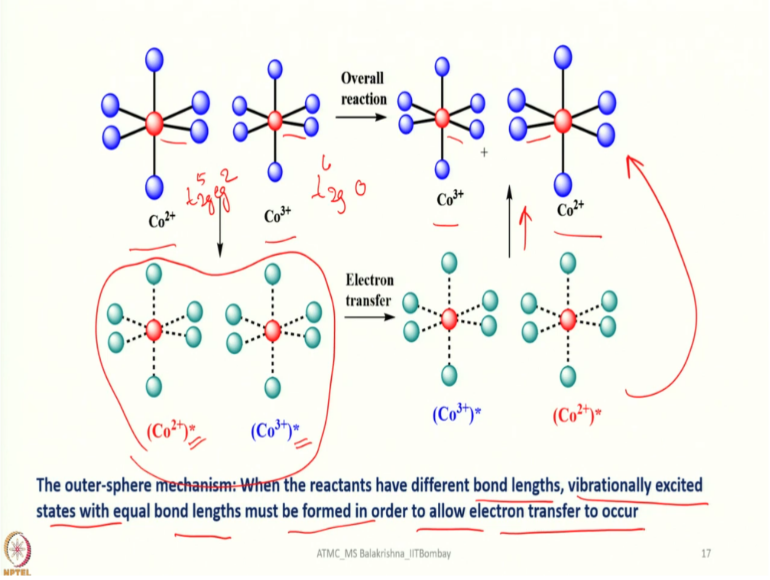

The outer-sphere mechanism: When the reactants have different bond lengths, vibrationally excited states with equal bond lengths must be formed in order to allow electron transfer to occur

So, now let us look into the intermediate or encounter species that is needed for this self-exchange reaction. You can see here, cobalt 2+ is shown here and cobalt 3+ is shown here; again cobalt 3+ and cobalt 2+ are there. Can you see any difference between these two species? So, one is $t_{2g}^5e_g^2$, this is $t_{2g}^5e_g^2$, and this is $t_{2g}^6e_g^0$, cobalt 3+. So, can you see any difference when you look into the diagrams as shown here?

Of course, here you can see, bonds are little shorter here compared to this one. This is obvious. Once the process is over, now this one is elongated and this is shortened. So, this is the overall redox reaction, but it has to go through this intermediate here. This is electron transfer for that one. This process has to generate encounter species or precursor species, something like this.

You can see here; this indicates that the transient species here or transient state in which you can see both of them have similar bond parameters. This is where energy is needed; activation energy to prepare both the complexes to look alike, so that electron transfer can be completed. Once the electron transfer is completed, they will revert back to this one. This is how you can represent pictorially the transient state where both the species, reductant and oxidant have similar bond distances.

So, outer-sphere mechanism: When the reactants have different bond lengths, vibrationally excited states with equal bond lengths must be formed in order to allow electron transfer to occur; this you should bear in mind.

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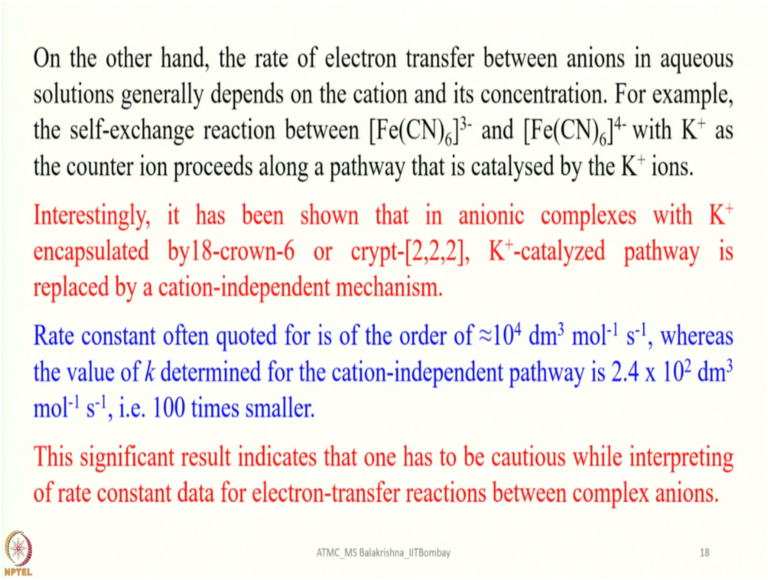

On the other hand, the rate of electron transfer between anions in aqueous solutions generally depends on the cation and its concentration. For example, the self-exchange reaction between $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ with K^+ as the counter ion proceeds along a pathway that is catalysed by the K^+ ions.

Interestingly, it has been shown that in anionic complexes with K^+ encapsulated by18-crown-6 or crypt-[2,2,2], K^+-catalyzed pathway is replaced by a cation-independent mechanism.

Rate constant often quoted for is of the order of $\approx 10^4$ dm^3 mol^{-1} s^{-1}, whereas the value of *k* determined for the cation-independent pathway is 2.4×10^2 dm^3 mol^{-1} s^{-1}, i.e. 100 times smaller.

This significant result indicates that one has to be cautious while interpreting of rate constant data for electron-transfer reactions between complex anions.

So, on the other hand, the rate of electron transfer between anions in aqueous solution generally depend on the cation and its concentration. As I mentioned, it has less influence, less affected by the concentration of anionic species, but what is important is the cation and its concentration.

For example, in a typical self-exchange reaction, if you consider between hexacyanoferrate 3- and hexacyanoferrate 4- with K^+ as the counter ion, proceeds along a pathway that is catalysed by the K^+ ions; that means here, in such self-exchange reactions, cations play a major role and they catalyse and they make this or facilitate this process through their catalytic activity. So, interestingly, it has been shown through experiments that in anionic complexes with K^+, you add 18-crown-6 ether or cryptand 2,2,2 so that potassium cation can be encapsulated.

Once potassium cation is encapsulated with this kind of multidentate ligands what happens, its activity is arrested, its mobility is arrested. When you arrest the mobility of cation while performing a redox process by trapping or encapsulating using 18-crown ether or cryptand, then what happens? Now, the rate of electron transfer will be independent of cation mechanism.

So, that means here, it has a tremendous influence on the rate; rate probably decreases. So, the rate constant often quoted is of the order of 10^4 decimetre cube per mole per second, whereas the value of k determined for the cation independent pathway is only 2.4×10^2. So, that means you can see now, when potassium, the cation was encapsulated and its mobility is arrested once, then it is no longer can catalyse redox process.

In that case, the rate constant is 100 times smaller. So, this indicates the significance of cation and its mobility. In order to make the reaction more facile, one should not think of trapping the cation using encapsulating crown ether or cryptand. That is needed to stabilise and crystallise the molecule; that is a different thing. Whereas, in this process, one has to bear in mind how a cation influences rate of the reaction and also what would happen if the cation is free or cation is encapsulated.

The significant result indicates that one has to be cautious while interpreting of rate constant data for electron transfer reactions between complexes. That means one has to analytically think and evaluate every species present in a particular reaction before arriving at any conclusion is what the lesson, these points are telling us.

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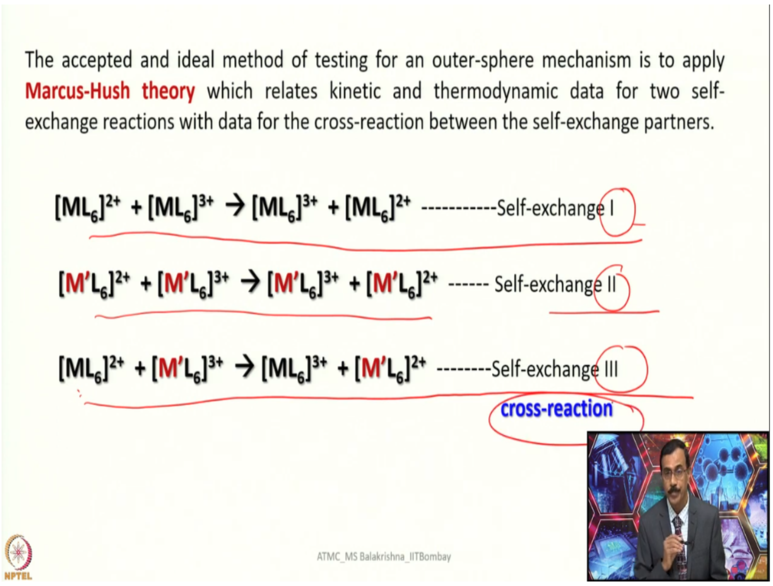

The accepted and ideal method of testing for an outer-sphere mechanism is to apply **Marcus-Hush theory** which relates kinetic and thermodynamic data for two self-exchange reactions with data for the cross-reaction between the self-exchange partners.

$[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$ -----------Self-exchange I

$[M'L_6]^{2+} + [M'L_6]^{3+} \rightarrow [M'L_6]^{3+} + [M'L_6]^{2+}$ ------ Self-exchange II

$[ML_6]^{2+} + [M'L_6]^{3+} \rightarrow [ML_6]^{3+} + [M'L_6]^{2+}$ --------Self-exchange III

cross-reaction

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The accepted and ideal method of testing for an outer-sphere mechanism is to apply Marcus-Hush theory; so, one more theory comes into picture; which relates kinetic and thermodynamic data for 2 self-exchange reactions with data for the cross-reaction between the self-exchange partners. That means we can perform two reactions and look into the cross-reaction between those two independent reactions to arrive at their information about outer-sphere mechanism.

That is about Marcus-Hush theory. So, for example, let us look into first reaction here. We are doing here self-exchange. Here, both of them are not labelled here; both the species are not labelled. We are doing this reaction. And we are also performing another reaction where both the species are labelled. Now, we are doing the reaction that is required for redox process; one is labelled, one is not labelled; and this is called as, let us call self-exchange 1, self-exchange 2 and self-exchange 3. This is called cross-reaction.

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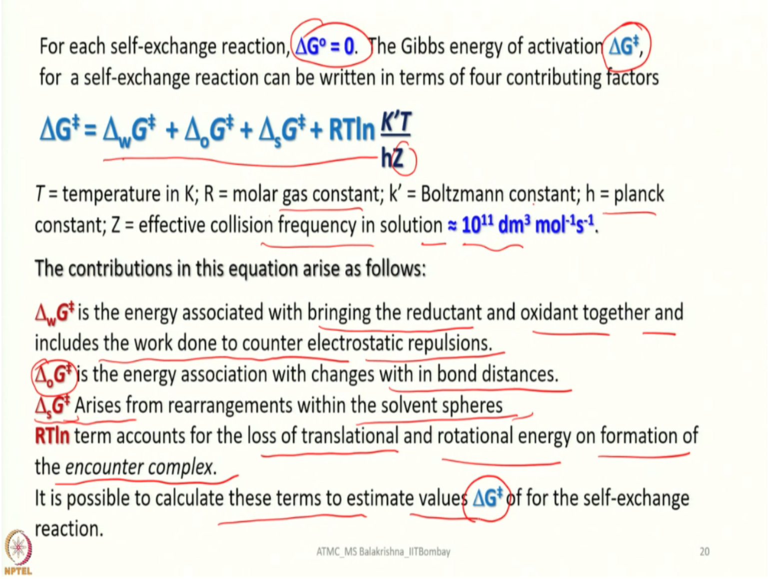

For each self-exchange reaction, $\Delta G^{o} = 0$. The Gibbs energy of activation $\Delta G^{\ddagger}$, for a self-exchange reaction can be written in terms of four contributing factors

$$\Delta G^{\ddagger} = \Delta_w G^{\ddagger} + \Delta_o G^{\ddagger} + \Delta_s G^{\ddagger} + RT\ln\frac{K'T}{hZ}$$

T = temperature in K; R = molar gas constant; k' = Boltzmann constant; h = planck constant; Z = effective collision frequency in solution $\approx 10^{11}\ dm^3\ mol^{-1}s^{-1}$.

The contributions in this equation arise as follows:

$\Delta_w G^{\ddagger}$ is the energy associated with bringing the reductant and oxidant together and includes the work done to counter electrostatic repulsions.

$\Delta_o G^{\ddagger}$ is the energy association with changes with in bond distances.

$\Delta_s G^{\ddagger}$ Arises from rearrangements within the solvent spheres

RTln term accounts for the loss of translational and rotational energy on formation of the *encounter complex*.

It is possible to calculate these terms to estimate values $\Delta G^{\ddagger}$ of for the self-exchange reaction.

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So, now, for each self-exchange reaction, this is 0. So, the Gibbs energy of activation then can be given for this reaction using this following expression here. So, that means here, towards Gibbs energy of activation, 4 terms contribute. Which are those? So, of course, the temperature T is there in Kelvin; you are familiar that R is molar gas constant; and K' prime what we have is Boltzmann constant; and h is Planck constant; Z in the term refers to effective collision frequency in solution; this is in the order of 10^{11}.

So, that means the contributions in this equation arise as follows. If you look into the first term, $\Delta_w G^{\#}$ is the energy associated with bringing the reductant and oxidant together and includes the work done to counter electrostatic repulsion. That means, when you are bringing 2 cations, you have to compensate the repulsion that try to keep away these two ions. That means work has to be done to counter electrostatic repulsion.

This also included in this one. Besides bringing these two species together in their solvent second coordination sphere, work is also done to counter electrostatic repulsion that would try to keep these two ions away from each other. And $\Delta_o G$ is the energy associated with changes with bond distances. A long distance is there in the high spin complex that has to be shortened and the low spin complex has to be elongated.

So, work done to bring to optimum bond parameters is represented by this term. And then $\Delta_s G$ arises from rearrangements within solvent spheres. This will be referring to solvent contribution in this process. And then, RTln term accounts for the loss of translation and rotational energy on formation of the encounter complex. The energy lost during this formation of encounter complex where we have the optimum bond parameters. So, that is represented by RTln. So, it is possible to calculate these key terms to estimate this one for a self-exchange reaction.

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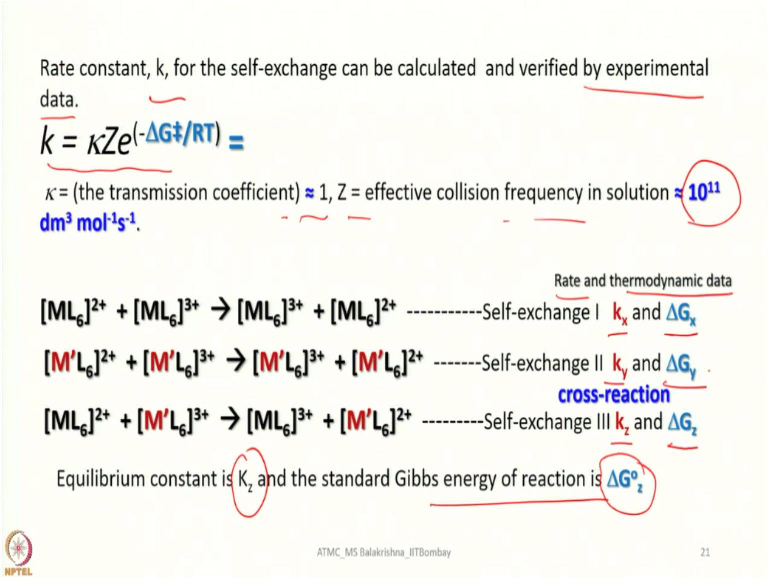

Rate constant, k, for the self-exchange can be calculated and verified by experimental data.

$$k = \kappa Z e^{(-\Delta G‡/RT)} =$$

κ = (the transmission coefficient) ≈ 1, Z = effective collision frequency in solution ≈ 10^{11} $dm^3\ mol^{-1}s^{-1}$.

Rate and thermodynamic data

$[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$ ----------Self-exchange I k_x and ΔG_x

$[M'L_6]^{2+} + [M'L_6]^{3+} \rightarrow [M'L_6]^{3+} + [M'L_6]^{2+}$ -------Self-exchange II k_y and ΔG_y

cross-reaction

$[ML_6]^{2+} + [M'L_6]^{3+} \rightarrow [ML_6]^{3+} + [M'L_6]^{2+}$ ---------Self-exchange III k_z and ΔG_z

Equilibrium constant is K_z and the standard Gibbs energy of reaction is ΔG^o_z

So, the rate constant k for the self-exchange can be calculated and verified by experimental data as we have now experimental techniques available for different rate for any given redox process. The term represents this one, k equals this term is there. Of course, K, the transmission coefficient which is always equal to 1. And Z is effective collision frequency in the order of 10^{11}.

Now, the rate and thermodynamic data are given by k_x and ΔG_x for self-exchange reaction 1; and k_y and ΔG_y for self-exchange reaction 2; and for the cross-reaction, corresponding rate is k_z and thermodynamic data is ΔG_z. So, equilibrium constant is K_z and standard Gibbs energy of reaction for this cross-reaction is ΔG_z^o. So, now we have defined all the terms involved in this equation.

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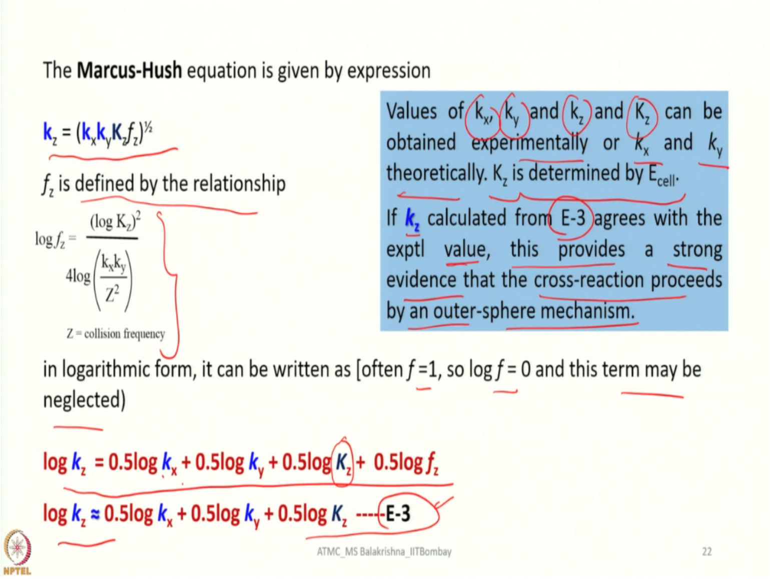

The **Marcus-Hush** equation is given by expression

$k_z = (k_x k_y K_z f_z)^{½}$

f_z is defined by the relationship

$$\log f_z = \frac{(\log K_z)^2}{4\log\left(\frac{k_x k_y}{Z^2}\right)}$$

Z = collision frequency

Values of k_x, k_y and k_z and K_z can be obtained experimentally or k_x and k_y theoretically. K_z is determined by E_{cell}.

If k_z calculated from E-3 agrees with the exptl value, this provides a strong evidence that the cross-reaction proceeds by an outer-sphere mechanism.

in logarithmic form, it can be written as [often f =1, so log f = 0 and this term may be neglected)

$$\log k_z = 0.5\log k_x + 0.5\log k_y + 0.5\log K_z + 0.5\log f_z$$

$$\log k_z \approx 0.5\log k_x + 0.5\log k_y + 0.5\log K_z \text{ ----E-3}$$

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So, this Marcus-Hush equation is given by expression, this expression here. And of course, f_z is defined by a relationship something like this. And in logarithmic form, it can be written as often f = 1, so, log f becomes 0 and this term may be neglected. So, if you neglect this term, then it would eventually end up in this format here, log k_z equals rate of cross-reaction equals 0.5 log k_x + 0.5 log k_y + 0.5 log k_z.

So, you should remember I had given in different colour; this is equilibrium constant, this is rate constant. And then, similarly, if you call this one as equation 3, so, values of k_x, k_y and k_z and K_z, rate and equilibrium can be obtained experimentally; or k_x and k_y can be obtained theoretically and K_z is determined by E_{cell}. If k_z is calculated from this value agrees with the exponential value, this provides a strong evidence that the cross-reaction proceeds by an outer-sphere mechanism.

So, this is all about Marcus-Hush equation and its utility in cross examining a reaction to confirm that yes, whether it follows an outer-sphere mechanism or not. So, with this, I am almost completed discussion on Inorganic Reaction Mechanism. Few other things I would have brought into picture; as I mentioned, because of time constraint and I have several other things to discuss in next 8 lectures, I am stopping at this juncture. So, now, quickly, for a couple of minutes, let us look into some problems.

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Some problems for you to enjoy
Inorganic Reaction Mechanisms

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And I leave those problems for you to solve with enough information I have given in these 5, 6 lectures on Inorganic Reaction Mechanism. If I give a couple of problems, you should be able to solve it without any problem.

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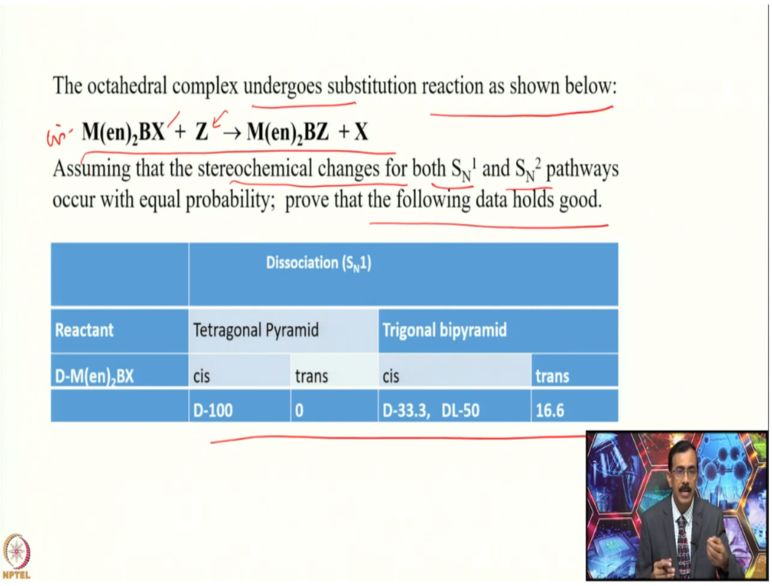

The octahedral complex undergoes substitution reaction as shown below:

$M(en)_2BX + Z \rightarrow M(en)_2BZ + X$

Assuming that the stereochemical changes for both S_N^1 and S_N^2 pathways occur with equal probability; prove that the following data holds good.

	Dissociation (S_N1)			
Reactant	Tetragonal Pyramid		Trigonal bipyramid	
D-$M(en)_2BX$	cis	trans	cis	trans
	D-100	0	D-33.3, DL-50	16.6

So, now, the first problem is, the octahedral complex undergoes substitution reaction as shown below: Cal. 1, where I have used; you should remember this is an optically active compound and Z is the entering ligand and X is the leaving ligand. And then, we get a compound like that assuming that stereochemical changes for both S_N^1 and S_N^2 pathways.

That means we have to consider dissociative mechanism as well as associative mechanism; and there are equal possibilities there. So, that means 50% for dissociative and 50% for associative pathway. Prove that the following data holds good. So, keeping the probability of undergoing dissociative pathway and associated pathway is 50% each, so, this data is given. Now, we have to look into the validity of data by solving this problem.

For this, what you should do is, you take this one. Take this compound; this is cis compound of course, otherwise, it is not optically active. It is a trans compound, it is not optically active. You have to consider only cis here. Then you go for first dissociative pathway. In the dissociative pathway, what we should do is, we should look for square pyramidal geometry and trigonal bipyramidal geometry as I have shown.

And then look into the percentage what would happen to here; optical activity retention is there, racemisation is there, or you get a trans compound. And then, go for associative pathway. There you have to think of pentagonal bipyramidal geometry and how many intermediates we can think of when ligand is approaching from different directions. And then you should be able to solve and verify the data given here.

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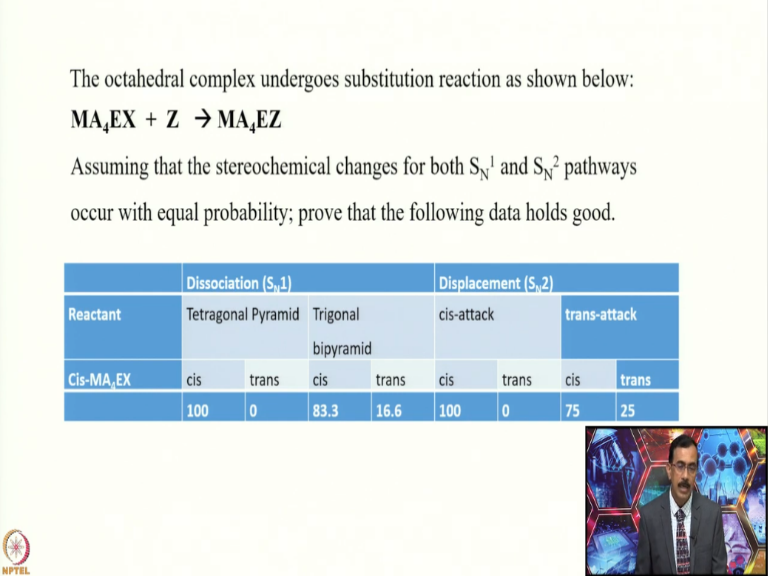

The octahedral complex undergoes substitution reaction as shown below:

$MA_4EX + Z \rightarrow MA_4EZ$

Assuming that the stereochemical changes for both S_N^1 and S_N^2 pathways occur with equal probability; prove that the following data holds good.

	Dissociation (S_N1)				Displacement (S_N2)			
Reactant	Tetragonal Pyramid		Trigonal bipyramid		cis-attack		trans-attack	
Cis-MA_4EX	cis	trans	cis	trans	cis	trans	cis	trans
	100	0	83.3	16.6	100	0	75	25

And similar problem I also given here for a simple cis compound here. And it is a cis compound now; it is not an optically active compound. Now, the data also I have given. You have to see here the consequences.

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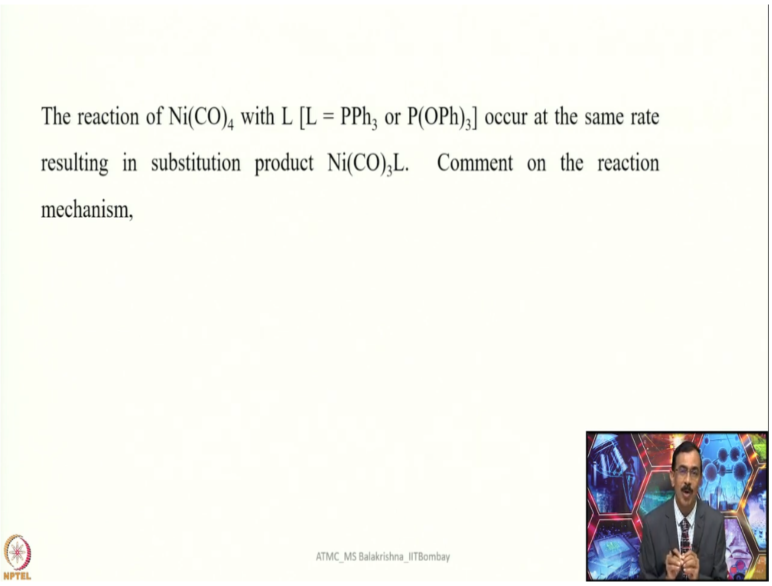

The reaction of $Ni(CO)_4$ with L [L = PPh_3 or $P(OPh)_3$] occur at the same rate resulting in substitution product $Ni(CO)_3L$. Comment on the reaction mechanism,

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Now, one more reaction; the reaction of $Ni(CO)_4$ with L; L = PPh_3 or $P(OPh)_3$ occur at the same rate resulting in substitution product $Ni(CO)_3L$. Comment on the reaction mechanism. So, read the question carefully. For example, if you have not heard of this question, you think that you cannot answer; but if you read couple of times, you will understand the reaction, what is the content in it and what is the question, so that you should be able to answer.

The reaction of nickel tetracarbonyl with L, where L is triphenylphosphine or triphenyl phosphite, occur at the same rate, resulting in substituted product $Ni(CO)_3L$. Comment on the reaction; so, statement is already made that whether you displace carbon monoxide, 1 carbon monoxide with triphenylphosphine or triphenyl phosphite, the rate is same. So, rate is same means what happens? Here it is independent of entering ligand.

It is independent of entering ligand and rate determining step is the dissociation of 1 ligand. So, that is equally in both the cases. That means it follows dissociative pathway and S_N^1 mechanism. So, it is so simple. The answer is there in the question itself. So, one has to read; one should not read between the lines; one should read the question properly so that answer is there, answer will pop out immediately.

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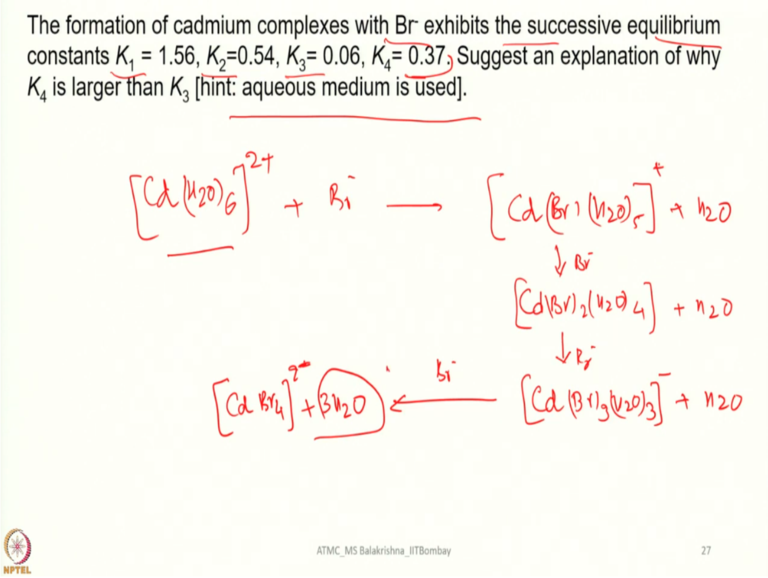

The formation of cadmium complexes with Br^- exhibits the successive equilibrium constants $K_1 = 1.56$, $K_2 = 0.54$, $K_3 = 0.06$, $K_4 = 0.37$. Suggest an explanation of why K_4 is larger than K_3 [hint: aqueous medium is used].

One more interesting question. The formation of cadmium complexes with bromide exhibits the successive equilibrium constants $K_1 = 1.56$; $K_2 = 0.54$; K_3, 0.06; and $K_4 = 0.37$. Suggest an explanation of why K_4 is larger than K_3? Why the formation is very facile for the last one? And what is the hint? Aqueous medium is used. That means, say, if I am adding bromine; here you should remember the hint, aqueous medium.

In the aqueous medium, if you take cadmium, it will be hexaaquacadmium 2+. If it is hexaaquacadmium 2+ is there, you take to begin with $[Cd(H_2O)_6]^{2+}$ add bromide. What would happen? What you get is $[Cd(H_2O)_5Br]^+$; and H_2O comes out. So, this is given. So, next one is similarly; so, this will give you next another this one; $[Cd(H_2O)_4Br_2]$ and H_2O of course after Br is added.

So, next it will give, one more Br is added, $[Cd(H_2O)_3Br_3]^-$, plus H_2O. So, now this one, just look into here; this is where the catch. You add another bromide, what would happen? $[CdBr_4]^{2-}$ + 3 H_2O. So, $3H_2O$ means here entropy increases dramatically. So, the reason is increase in entropy here in this one. So, that is the reason there is a marked difference is there. So, you should be able to see these things.

And what you should remember is, this is the one, to begin with, yes, I am performing bromide substitution on hexaaqua compound. And again, when you go for halides, halides are, you are not going to make hexabromo, so, here, only tetrabromo species is stable; beyond that, it cannot go. So, that means, when the last bromide is coming, the fourth one is coming, 3 equivalents of water is coming out. So, that means entropy is increasing.

So, that is the reason. So, this is how you can explain. So, let me stop here. Like that, many interesting problems are there in Shriver and Atkins book and also in C.E. Housecroft and A. G. Sharpe book and many other books. Please look into it and solve these problems and enjoy learning. If you learn chemistry through problems, chemistry is not a problem. Have an excellent time and thank you for your kind attention.