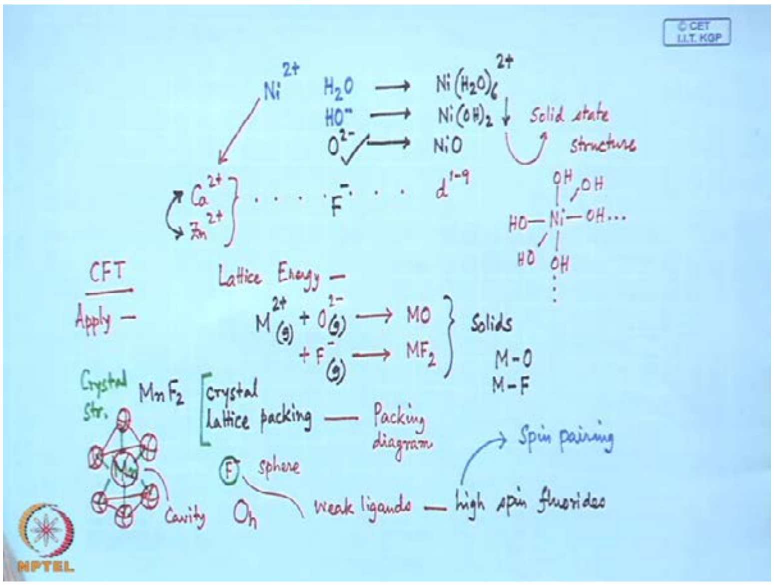
Coordination Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 27
Application of CFT

(Refer Slide Time: 00:32)

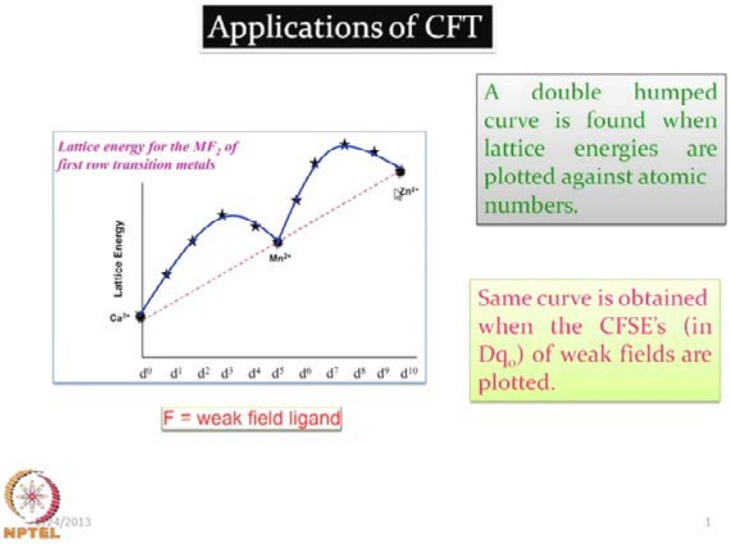


Good evening everybody. So, today we will see how we can utilize the crystal field theory in various applications. So, so far we have seen that a particular metal center if it is present say nickel two plus, and the other species which is around this particular nickel center. It can be our simple water molecules, it can be the hydroxide ion when we get then nickel hydroxides. So, these species basically including the corresponding w deep water species like the oxide anion.

So, these three species as aligned, they can interact with the metal center giving rise to some complex form which we all known now that Hexaco nickel two anion or simple nickel hydroxide, what we encounter in analytical chemistry and it is precipitating out also as well as nickel oxide. So, if we change these environments and if we next compare this nickel two ion say calcium 2 plus or zinc 2 plus, because these 2 ions without having any d electron in it can interact with these molecules or some other ligand rules in a similar fashion where they can also interact with the water molecule, they can give rise to the corresponding hydroxides as well as oxides.

So, in today’s class what we will see that how these interactions are completely different when a particular metal ion have no d electron in it is orbital’s and when the metal ion has some d electrons in it. So, we will apply basically whatever we have learned. So, far related to the crystal field theory where the point charges; we are considering the metal center as the point charge. And the ligands are also point charge of negative magnitude or some negative end of the dipolar units which are interacting, so that particular aspects of this theory. How we can apply to some of our problems related to the interactions of these species or the formation of these species?

(Refer Slide Time: 03:19)



Applications of CFT

A double humped curve is found when lattice energies are plotted against atomic numbers.

Same curve is obtained when the CFSE’s (in Dq_o) of weak fields are plotted.

F = weak field ligand

So, we will see how we can apply this crystal field theory for certain basic energetic of the system and the thermodynamics? How we can control with respect to this crystal field theory? Because whatever we get we just one after another because after calcium we know that we can start the entered first tenison’s series elements from scandium titanium and all these. So, when we start from filling up all these metal ions with some d electron configuration from d 1 to d 9. When it is detain we get the zinc 2 ion. So, due to the presence of these d electrons in the system their interaction in terms of the corresponding crystal field which is forming around these species. That means, in the solid state because since these are precipitating out; we can separate it out in the solid state and it has some corresponding structure.

So, both nickel hydroxide and nickel oxide can have a solid state structure where we will see that how this nickel is sitting. Whether it is in some octahedral crystal field like that of our hexaco nickel two ion or in some other form. Where these ligands have been changed from water to hydroxide ion or they are forming some polymeric species. Where these OH group can form basic interaction with the second metal center.

So that means, see that how we can apply this things and where they energetic for the system or some thermodynamic parameters into heavy with the variation of this occupation of this orbital's by the d electrons. So, first of this example would be the corresponding lattice energy parameter. So, what we know that the lattice energy we can calculate out and applying the bond Hayward circle. We know that how we can calculate the corresponding energy parameter in terms of the corresponding lattice formation. So, when this metal ion present say m 2 plus in the gaseous state with some of these species like these oxide anion or say fluoride anion, so when... So, when they are acting with certain of these anion like o two minus or f minus they giving rise to the formation of the corresponding oxide or the fluoride. So, they have certain specific solid state structure also. So, the molecular solid's are formed where the interaction between this metal center with that of oxygen or metal center of florin.

How they can vary if we vary these entire series from say calcium to zinc? If the whole thing is dependent on the presence of the d electron; these metal ions. We will see the interaction with calcium due to the formation of calcium oxide or calcium fluoride. We do not see any effect at the some contribution or the crystal field contribution towards the lattice energy term. That the entire bond hay ward cycle, if we see that there are certain state to get it back to the complete cyclic process. Where the individual states are involve for some energy values. And once a step we can consider it as the corresponding state where the crystal field can contributes some amount of energy to the entire lattice energy term. So, whether this particular calcium can contribute some amount of these to the lattice energy or the vanadium chromium manganese or iron, that means that those who are containing some d electrons.

And now, we all know now that is very familiar to us now that whenever some electron is going to this d orbital's. We have the high spin electron configuration and low spin electron configuration. If these two configurations can interact with these ions; they are also in the gaseous state. They do interact differently with these anions during the formation of these solid states. We see that some interaction can we have depending upon not only the energy parameter. But also sometime we can have some important idea about the corresponding metal oxygen and metal florin bond distances because it cannot. So, some liner relationship as we move from left to right. That means, beyond the corresponding transition series to the end of the transition series. That will some signatures some indications that crystal field theory. And the corresponding crystal field stabilization energy is basically contributing some amount of energy to the entire energy term.

So, if we plot a very simple plot, just simply write in the any 5 chance. There is ax axis will be plotting the corresponding occupancy of the different d levels straight way. We can plot on d 0 which is calcium. That means, we can see the effect of this particular metal ion where we do not have any d electron present in it to up to zinc where the same situation is prevailing. But the only different is that here we do not have any d electron in three d level. But here all the three d levels are field having an electronic configuration of three d tin to zinc 2 plus, so in this particular case like metal oxides or hydroxides or any other solid chlorides bromides.

The example has been taken for m f to the metallic di fluoride of first root transition metal ions. That means, like calcium we can have the vanadium. We can have the chromium. We can have the manganese fluoride. We can have the nickel fluoride. We can have the copper fluoride and up to we can have the zinc fluoride. So, it is consideration of the corresponding bond hay ward cycle related to the calculation of lattice energy term for all the fluorides starting from calcium to zinc. So, these - these eleven elements if we can consider and if we plot them in this fashion; we see that the occupation of these d levels do contribute differently towards the lattice energy term for these transition metal ions.

So, when you go from d 1 to up to d 2 to d three; it again drops at d four. And it again come back to the linear straight line, these red dotted line will be related to the corresponding lattice energy increase where we do not have any crystal field contribution. That is why it is falling on a straight line which is monotonically increasing from calcium to manganese manganese to zinc. That means manganese two plus will not. So, any such contribution towards the lattice energy term though it is a transition metal ion. But its electronic configuration which is 3 d 5; if it is in the high spin situation. That means, all the 5 d orbital’s are singly occupied. That means, they are evenly distributed for that electronic configuration and it gives us a corresponding spherically symmetric arrangement. So, like zinc when all are field the manganese will also. So, no effect in terms of the corresponding crystal field contribution. So, that is why we have the situation for calcium manganese and zinc which is monotonically increasing from left to right due to increase in nuclear charge only. That we have no d electron configuration this is half field d level and this is full field d level.

So, after d three when we go of to d 4; that means, one electron is going to the easy level than it is going to contribute less amount of this lattice energy compare to d three electronic configuration. So, that why this is less and d 5 is further less than the d 4 configuration. Similarly, beyond d 8 when it is spearing of when the situation is completely half field for manganese 2 plus the situation is like this calcium 2 plus. So, from here this double hump curve is again forming like this stead that is again one electron two electron and three electron and that T to G level then we have the corresponding one E G E G level and the second one is also in that E G level.

So, it is a situation where we are simply considering an octahedral crystal field where all the groups which are coming to attach to the metal ion. But what we are talking in terms of the corresponding manganese fluoride or any other fluoride that we have say manganese fluoride and the solid state packing, the crystal lattice packing. What we have the crystal lattice packing? We have to see and while we determine the corresponding crystal structures; we see that along the different axis of x y and z and along the a b c we have a typical packing. And that gives us to us a nice packing diagram for the structures. So, these packing diagrams, what they usually give us? The situation that manganese is there, but when it is nicely packed, that means is a typically example for the corresponding crystal field when we are seeing the corresponding crystal structure. This crystal structure gives us the corresponding crystal lattices and that crystal lattices packing gives us the corresponding diagram. And that crystal lattices packing gives us the corresponding packing diagram were. You see that instead of behaving as a simple anionic group this fluoride anion the f minus this f minus is basically behaving as a typical sphere like arrangement. So, is the solid sphere and we are getting something where we have this manganese which have a symmetric electronic distribution which is also sphere like. So, it is it is once sphere and we have the other spheres also like this.

So, though we have the charge for 2 fluoride anions, but when it is packed inside the crystal lattices will see that all the 6 fluoride anions are packed and within these six fluoride groups; we can generate some amount of cavity. And that cavity can nicely accommodate the corresponding positively charged di cationic species which is manganese 2 plus.

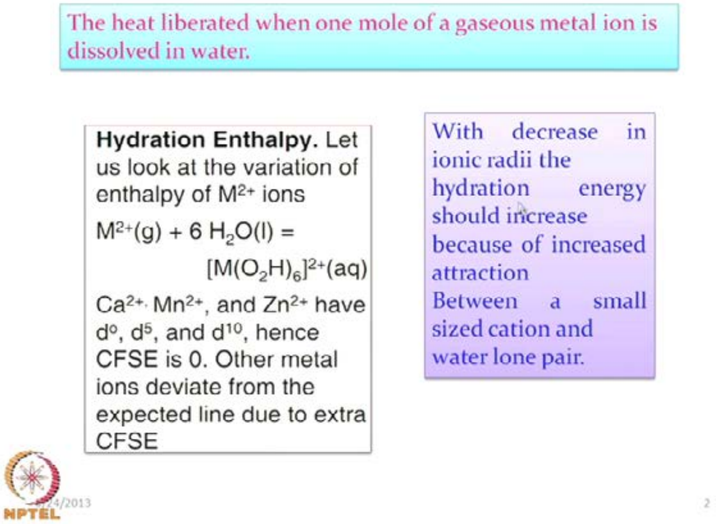
So, basically we will be getting in these crystal field diagram, and corresponding crystal field packing the cavity what is forming around manganese is giving us a corresponding octahedral crystal field due to this fluoride anions and these fluoride anions are our weak ligands. So, that all we know now we are now very well from hear with the custom with the ideas that when we have the fluoride ligands which are weak ligands. So, we will be having high spin fluorides. So, we will be getting the corresponding high spin fluorides because we do not expect any kind of spin pairing. So, this is the thing that when we get these values. So, we have a double humped curve. So, we have to be able to justify these double humped curve where we can get this values for corresponding transition from calcium to manganese 2 plus 2 zinc 2 plus.

So, we have these fluoride anions which are basically the corresponding weak field ligand and these fluoride are showing us corresponding octahedral geometry for these. And we determine these are the corresponding experimentally experimental values for the corresponding lattice energy and plot those lattice energy against the d electron configurations. So, what we get we get nothing but a doubled humped curve which we can have is found when lattice energy are plotted against atomic numbers or number of d electrons. It can be the corresponding atomic number from 20 to 30 or d 0 to d 10. If we configure them for a corresponding plot related to number of d electrons.

So, same curve we can have if we just simply consider the corresponding crystal field stabilization energies for all these transition metal ions such as for chromium such as for nickel. So, if we get these corresponding crystal field stabilization energy for nickel two plus which we have calculated in our all previous classes nicely. And if we find out that for weak field if we have a corresponding high field electronic configuration. But nickel 2 plus it will have only the corresponding high spin only or the low spin only which is t to g 6 and e g 2 configuration. And that crystal field stabilization energy in terms of d q we get the similar type of plot.

So, it is nothing but instead of if we consider that whatever amount of lattice energy contribution we are getting for the entire solid structure. But this particular part that means, which is above this red dotted line that means the double humped curve we can also get, since the plot we have not made earlier. We have the calculations in our hand for all the d electron configurations we have the CFS e’s we have calculated, so far for both the high spin configuration and the low spin configurations. So, same hallows in terms of the corresponding DQO not d q t because it is not giving us any tetrahedral geometry it is giving us only octahedral geometry. So, in that particular octahedral geometry if we plot these CFSE’s we will be getting the same double humped curve. So, it is only the contribution from the CFSE’s above this particular line which is directly connecting where we do not have any contribution for the ions like calcium 2 plus manganese 2 plus or zinc 2 plus.

(Refer Slide Time: 20:51)



The heat liberated when one mole of a gaseous metal ion is dissolved in water.

Hydration Enthalpy. Let us look at the variation of enthalpy of M^{2+} ions

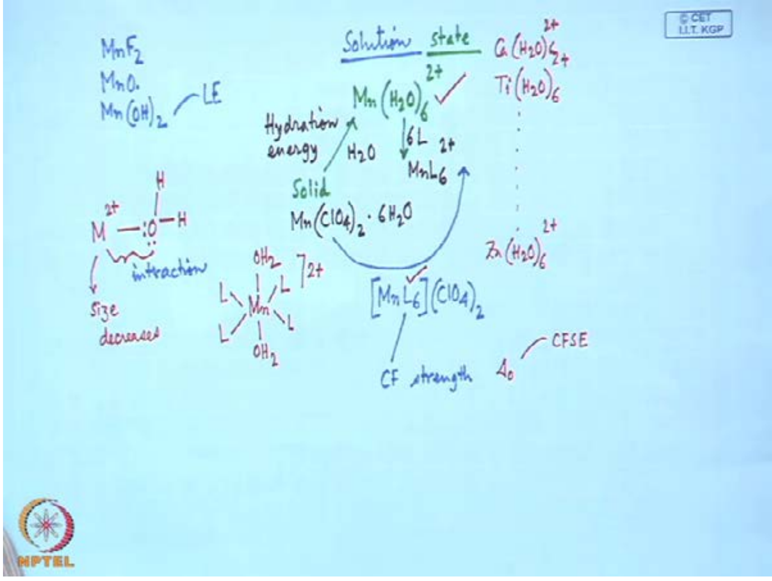
$M^{2+}(g) + 6\ H_2O(l) = [M(O_2H)_6]^{2+}(aq)$

Ca^{2+}, Mn^{2+}, and Zn^{2+} have d^o, d^5, and d^{10}, hence CFSE is 0. Other metal ions deviate from the expected line due to extra CFSE

With decrease in ionic radii the hydration energy should increase because of increased attraction Between a small sized cation and water lone pair.

So, when we see that it can also applied to the corresponding interaction with that of the metal ion with water molecule. That we have started our discussion that in the solid state what we have just seen in that the formation of M n F 2.

(Refer Slide Time: 21:11)



Similarly, we can have the corresponding formation of M n O or M n OH. And this is the corresponding solid state because in the solid state we are talking about the corresponding LE values the lattice energy values. But in solution, another thermodynamic parameter which is very important when we just see the corresponding interaction that means, the formation of manganese hexaco species where manganese is present in the by valiant state.

So, in the solution state what we have these interactions we get these interactions when we have say solid manganese chloride or manganese nitrate or manganese perchloratein our hand. So, if we have manganese per chlorate with some water of crystallizations and this solid we are dissolving in water. So, there will be the corresponding solutions and the solvation is also taking place. But what we can measure now that thermodynamic parameter which is be useful for identifying this particular interaction of the solid manganese per chlorate with water is the corresponding calculation for their hydration the reaction is our hydration.

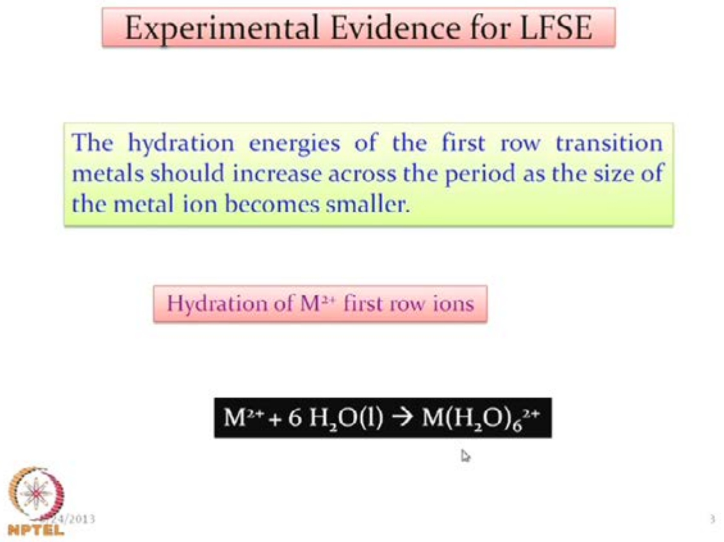
So, we can calculate the corresponding hydration energy for manganese in plus 2 oxidation state for accommodating six water molecules around this manganese 2 plus. So, it is not for manganese. But it can go like that of our the entire series because we know that all of them can. So, some interactions with these water molecules to up to zinc and also in this side we have the interaction with that of our calcium.

So, starting from calcium to zinc we can see or we can determine the corresponding hydration energy and how these hydration is getting effected due to the presence of different number of d electrons that we can see. So, from thermodynamic point of view this hydration energy, what is called this hydration energy? Hydration energy is nothing, but the amount of heat energy which can be liberated when on mole of gaseous metal ion is dissolved in waters. So, the calculations are based on the standard difference of the metal ion in the gaseous states. So, when the metal ion is present in the solution state it is basically initially hydrated one. Then the corresponding heat energy will be liberated due to the dissolution in water. So, that amount of energy we can calculate or we can think of eddies corresponding hydration energy or in terms of the corresponding delta edge values in terms of the corresponding thermodynamic parameter. We call it as a corresponding hydration enthalpy.

So, if we look at a change in the corresponding hydration enthalpy values for the different dipositive metal ions. In say first transitions series in each elements where the gaseous M 2 plus is reacting with 6 water molecules in the liquid state giving 6 water molecule connected to the m center where M H 2 O whole 62 plus which is in aqua state. That means, which is aquatic metal ion and likewise that part. We have seen just now for the lattice energy the calcium manganese and zinc in bivalent states have the corresponding no electron half field and full field d election configuration having no contribution in terms of the corresponding CFSE. But the other metal ions do deviate from this extra CFSE gain due to the presence of some odd or even number of d electrons in their orbital. So that means, apart from these metal ions other metal ions will contribute towards the hydration energy in terms of its CFSE contribution. So, what we see that with the decrease in ionic radii. The hydration energy should increase because the increase attraction between a small sized cation and water lone pair.

So, cation is very small because it is dipositive and the water lone pair we can have the corresponding interaction because the water molecule will face which is negatively charged dipolar end. That means, the oxygen ends are facing towards the metal center and we have manganese or the metal ion to the oxygen interaction and slowly the corresponding MO bond is forming. And this interaction is increasing as we have the corresponding zinc in the ionic radii. So, if the ionic radii is decreasing our hydration energy should be more.

(Refer Slide Time: 27:06)



Experimental Evidence for LFSE

The hydration energies of the first row transition metals should increase across the period as the size of the metal ion becomes smaller.

Hydration of M^{2+} first row ions

$M^{2+} + 6\,H_2O(l) \rightarrow M(H_2O)_6^{2+}$

4/2013

So, these hydration energies of the first transition should increase across period as the size of the metal ions become smaller. So, as the size of the metal ions are getting smaller and smaller these first transition hydration energies will therefore, increase because of the strong interactions. So, this is one such experimental evidence of LFSE. So, these experimental things which we can determine we can find it out the actual hydration energies. What is there for the corresponding interactions of the metal ions with the water molecules? So, this not only gives us the application of the corresponding crystal field stabilization energy. But it can also gives us corresponding idea about the corresponding experimental evidence of the corresponding stabilization.

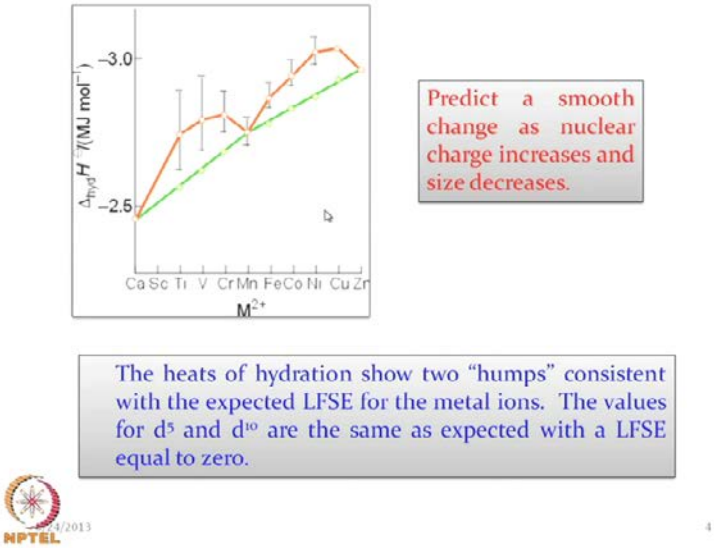
So, this basically is related to the corresponding size of these metal ions and will seeing the corresponding hydration of M 2 plus first row ions and when M 2 plus is reacting with H2O giving MH2O whole 62 plus. So, these are the very basic things what we can have that the reaction is the corresponding interactions of the water molecules with the m two plus. And these gives us some nice clue that whenever this hydration energy contribution is there. That means, whenever it dissolves some salt to this species; that means, whatever we have in the solution this is the starting point for the complexes and reaction. And when we add certain ligands to it if they are 6 in number then this manganese can form the corresponding MNL 6 species if the ligands are neutral. It will have two positive charge and whatever number of perch orated ions enhance a liberated that will now come and go for the corresponding charge neutralization and will be ending of with the corresponding MNL 6 per chlorate salt, so will add the corresponding ML 6 per chlorate salt.

So, we will have all sought of other contribution afterwards. That means, whenever we are forming the corresponding metal complex depending upon the corresponding crystal fields strength of the ligand system. We can have the different magnitudes of these crystal fields splitting or crystal fields strength and their corresponding CFSE values for this particular ligand. But the corresponding energy contributions or the energy term due to the formation of the first step. That means, the corresponding aqua complex formation most of the time we are neglecting that.

So, if it has very high energy contribution towards the formation of these species. What we will find that due to this high energy contribution and if the energy contribution towards the corresponding crystal field stabilization due to the presence of the L group or the second step of interaction. It may not possible all the time to substitute all the six water molecules from the co-ordination sphere. Instead we can have certain species like these that where we can substitute four of these water molecules by L. But 2 water molecules are still remaining there. So, this are the other possibilities for step wise removal of these water molecules by 6 L groups one after another. That is why we get the different values of the corresponding stability constants. So that is another thermodynamic parameter or thermodynamic energy contributions towards the formation of complex formations.

And these different states we will again see when we will talk about the corresponding reaction mechanisms for the formation of these complexes and their energy contributions. So, this particular interaction with six water molecules towards these M 2 plus species is the most vital and most important interaction in co-ordination chemistry.

(Refer Slide Time: 32:08)



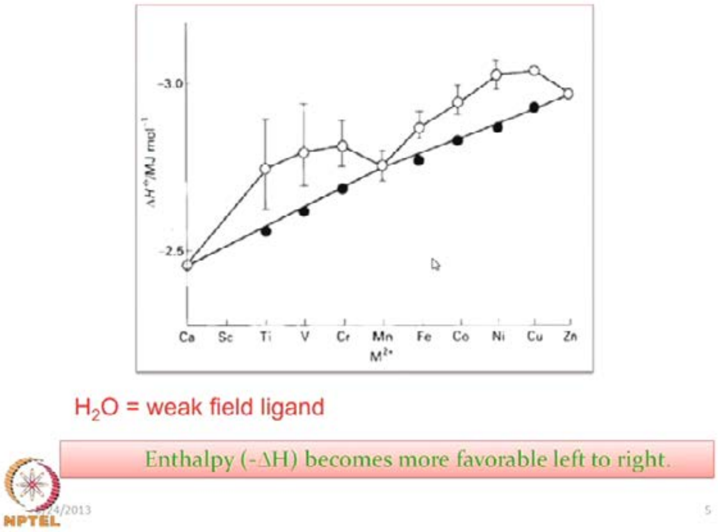
Predict a smooth change as nuclear charge increases and size decreases.

The heats of hydration show two "humps" consistent with the expected LFSE for the metal ions. The values for d^5 and d^{10} are the same as expected with a LFSE equal to zero.

So, when we see this heats of hydration again and this heats of hydrations again shows two dub humps or double humps again consistent with CFSE of the metal ions the values for d 5 and d ten are the same as expected with the CFSE equal to 0. That means, they again form like that up our lattice energy they again form in the straight line and the linearity is preserved with respective to d 0 with d 5 and d ten. So, again we can directly write down the double humped curve which is very much similarly, to that of our lattice energy. But this energy axis is only different it is the delta hydration H 0 in mille joule for mol and this particular values for this contribution is that we have the error bar. Also depending upon the measurements and depending upon the salts used. But the monotonic increase of these values for this green line which is showing that d 0 to d 5 to d 10 and if we just go for this contribution for the CFSE will be having this orange lines for this double humped curve. But if we do not get the corresponding CFSE contribution these all this values will come and will fall on the green line where we do not have any CFSE contribution for hydration.

So, what we see is that it also predates a smooth change as nuclear charge increases and size decreases. So, monotonically it is also increasing the hydration energy values that increasing as we go for increasing the nuclear charge. A nuclear charge is responsible for squeezing the size of the metal ion and the size is decreasing. And we are having more and more interaction with the N 2 plus center with that of our H2O molecule. So, as we move for M 2 plus as the size decreases this interaction with the lone pair of electrons the lone pair of electrons on this water. So, this particular interaction is basically increasing. So, as the nuclear charge is increasing the size is decreasing. So, there will be a change in the corresponding interaction and if all together 6 such bonds are forming. So, it can be multiply by 6 when the metal center is interacting at the same time almost with 6 water molecules for their contribution towards the hydration energy.

(Refer Slide Time: 35:33)



H_2O = weak field ligand

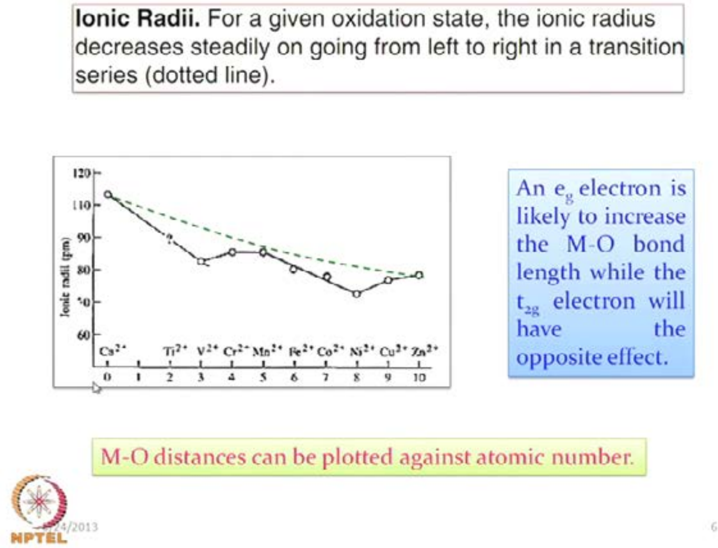
Enthalpy (-ΔH) becomes more favorable left to right.

4/2013

5

So, this basically tells us that how we can magnify the thing and how we can have this values for this contributions where H2O is again like that of our fluoride weak field ligand. So, if water is consider as the corresponding weak field ligand for this metal ions we are getting the corresponding values for the high spin configurations only. And we do not have to bother about the corresponding low spin electron configuration and the enthalpy the delta H becomes more favorable more and more favorable left to right because we are getting is in the negative end of this enthalpy, the hydration enthalpy on the negative side. So, will be gaining for this hydration of this salvation of this transition metal ions. So, salvation or the hydration of this transition metal ion is basically energy efficient process and immediately when the metal salt is dissolve in water it immediately goes for its hydration reaction.

(Refer Slide Time: 36:41)



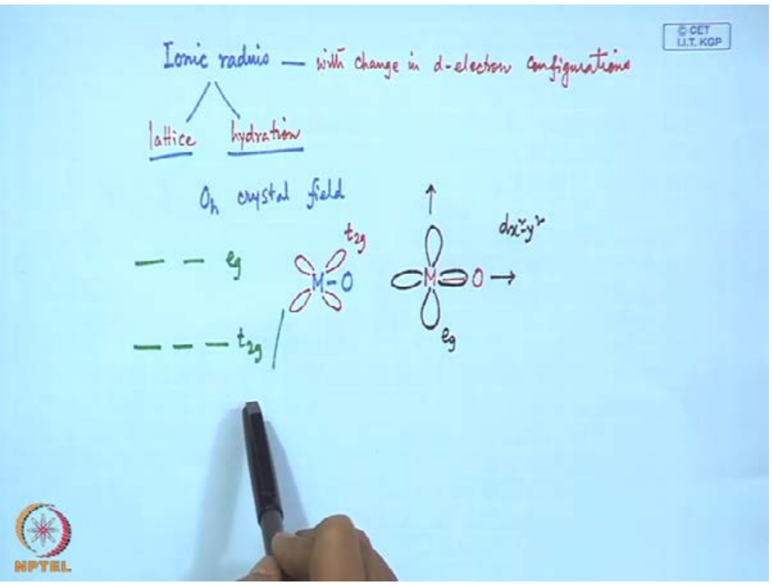
Ionic Radii. For a given oxidation state, the ionic radius decreases steadily on going from left to right in a transition series (dotted line).

An e_g electron is likely to increase the M-O bond length while the t_{2g} electron will have the opposite effect.

M-O distances can be plotted against atomic number.

Then we will see the third parameter. The first part we have seen is the lattice energy. Then hydration energy and for all this cases one particular parameter which is involved is the corresponding ionic radius.

(Refer Slide Time: 36:57)



So, how this ionic radius do contribute towards this two energy parameters what we have seen that for the corresponding lattice energy and corresponding hydration energies. So, defiantly the ionic radius us changing with the change in d electron configurations, so this contribution, that means what we see that the corresponding effect what you see in terms of the corresponding in crystal field. That ionic radius will also change with the change in d electron configuration. And that particular change also can interact for the different types of the solid space anions or the water molecules for their corresponding energy change due to lattice formation and hydration. So, for a particular oxidation state the ionic radius decreases steadily on going from left to right in a transition series.

So, we see that this is the case and we see a monotonic contraction in the size. So, ionic radius is falling. Because in other two cases the energy parameter what is changing for the hydration as well as corresponding lattice formation it is basically increasing from left to right. And the main effect for this corresponding contribution is in one case. That if there is no contribution for the d electron occupancy. We will have a monotonic decrease from calcium to zinc as the nuclear charge is increasing which is squeezing the corresponding size. And we are having a corresponding ionic radii from 113 or 114 pico meter to say. Here it is almost 80 PICO meter.

So, in this range physically 114 PICO meter to 18 PICO meter the whole thing is basically again. So, a double humped curve or in the reverse direction an the ionic radii will also will be changing with the change in number of d electrons which are present in the two levels. That means, the t 2 g level and the e g level. Why this is show? Because occupancy in these two levels where we have the t 2 g and e g electron. And if we have an octahedral crystal field; what we see that there are orbital’s which are t 2 g and e g. So, this t 2 g. So, this 2 to g set are intermediate between two ligands. So, if the ligands are facing directly from x y and z direction the orbital’s are being place between x and y between y and z and between z and x. So, these are basically of different direction. But these are basically facing the ligand direction.

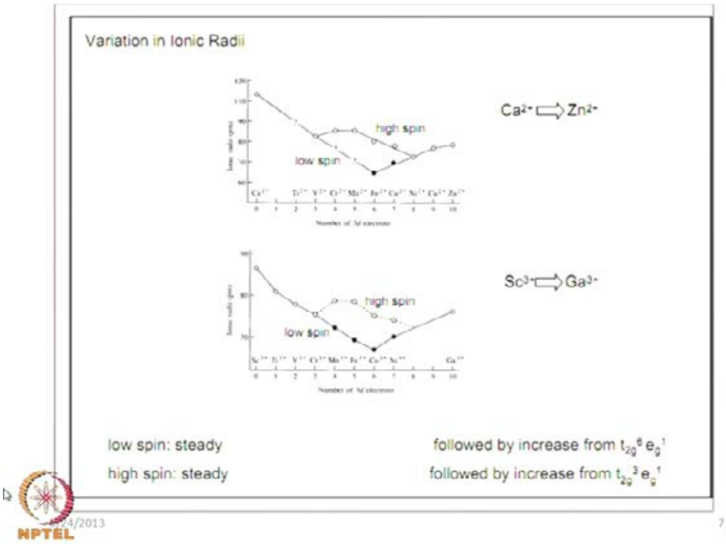
So, if we are talking in terms of the corresponding interaction with oxygen of the hydroxide ion. And if it is metal hydroxide formation or if it is hydration for the water molecule we will be seeing different effect for this particular p orbital which is facing the corresponding lone pair of electrons from the oxygen atom of the corresponding electrons in the d levels of the metal center. So, if it is in the x y direction our orbital will be like this. So, it is not directly facing the corresponding oxygen p orbital. So, this is our t 2 g set. But when this metal oxygen is there and we fine there this corresponding direct face of these orbital’s and if they are empty it will face differently and if they are filled it will fill in different way. So, this is the corresponding thing in x and y directions. So, if we have the orbital in x square minus y square direction. So, we level it as e g. So, the difference in the electronic configuration in the t 2 g level and the e level will defiantly contribute differently towards the corresponding ionic values for these metal ions.

So, what happens if an e g electron is there are that e g electron will try to increase the m o bond length which is quite obvious because this metal ion having e g electron facing the ligand orbit or the ligand p orbital or any other high d orbital directly. So, there is head to head over laps head on over lap between metal d orbital and the ligand p orbital as there is all the corresponding metal oxygen bond length will increase. But if the electron is in the t 2 g level which level is in between the metal oxygen axis. And that will have a different effector other opposite effect and that will basically decrease that corresponding metal oxygen bond length, so occupancy for this t two g level. That means, here up to this up to vanadium 2 plus ill decrease the corresponding contribution for the MO bond length. That means, it will have its corresponding say at the M will have its.

Therefore, its ionic radius and oxygen will have its for ionic radius because if we head up this 2. Then only we get the corresponding metal oxygen bond length. So, as this particular bond is decreasing. We are also getting a decreased value for say vanadium 2 plus. But when you move from vanadium 2 plus to chromium 2 plus, we put one extra electron in the e g level in the high spin configuration. And in that configuration the e g electron goes to the chromium 2 plus for d 4 electronic configuration. And that basically will increase the corresponding MO bond length and this particular change will also contribute towards the corresponding increase in the ionic radius of chromium 2 plus. So, same thing also happens that there is a monotonic decrease from manganese which is in the green line green dotted line for iron and cobalt and nickel. But again when e g occupancy there for copper 2 and zinc 2. This is e g three and this is e g four, we again loose the corresponding contribution towards the corresponding crystal field stabilization. So, depending upon the different electronic configuration with regard to t 2 g occupancy and e g occupancy we have a steady variation in the corresponding ionic radii as we move from a d 0 system to a d ten system.

So, when this is we are getting the same thing. Also we can have if we have large number of these metal complexes where it can bond to the metal hydroxide system on metal oxygen from other phonoliddonor ligand or the water distances. We can plot them against the corresponding atomic number of this or the corresponding d electronic occupancy. We get the similarly, type of plot for this m o distances at the same time.

(Refer Slide Time: 45:54)



Variation in Ionic Radii

$Ca^{2+} \Rightarrow Zn^{2+}$

$Sc^{3+} \Rightarrow Ga^{3+}$

low spin: steady followed by increase from $t_{2g}^6 e_g^1$

high spin: steady followed by increase from $t_{2g}^3 e_g^1$

So, this variation in this ionic radii can also be reflected for this two types of cation; one is the bivalent and another is the trivalent state. And we see for the low spin and the high spin case also will have different type of things. So, this is one type of things, so it us, so corresponding dotted line. So, if we move from here to here it is one hump and here to there it is another hump. Similarly, here also we have the hump up to manganese. So, this is manganese one hump and then we have the manganese another hump for the rest and. So, far we were considering for the system bond to either fluoride anion or hydroxide anion or the water molecule. That means, they are giving us only weak field crystal field as a result we have only the high spin electron configuration.

So, if we just go for the corresponding low spin electronic configuration; we do expect that straight way it is go down up to iron 2 plus which is t 2 g 6 electronic configuration. That is straight way we go up to t 2 g 6. Similarly, for trivalent also we can go down to this particular case which is cobalt three plus which is three d 6 as a result in the low spin electronic configuration. This is corresponding three d 6 or t 2 g 6 electronic configuration. So, in case of iron it is the bivalent case and case of trivalent state. It is the cobalt 3 plus having full occupancy here. It is half occupancy, full occupancy of the corresponding t 2 g set.

And this particular case it is basically going decreasing steadily up to this configuration of t 2 g 6. Then again it will increase for nickel it will increase for that nickel zinc and H all this things. And if we just plot because not all example of trivalent state can have we can go up to gallium from scandium three plus because the scandium should be the first entry for the trivalent metal ions. Because we do not have anything corresponding to calcium 2 plus or and the corresponding vanadium 2 plus scandium 2 plus is there. So, scandium 3 plus to gallium 3 plus. Again we will see simply not a double humped curve for the low spin case. We have a v shaped curve only straight down over here. Then go down up straight down over here and then again go up. So, for the low spin case there is a steady decrease of to the corresponding configuration of t 2 g 6.

And after that we increase from t 2 g 6 from one e g 1. That means, the next one is this one which is nickel three plus which is three d 7. And for the copper one also in plus three oxidation state in case of high spin also the change is very steady from one step to another. But there is a increase once the t 2 g's cell is half field. So, after t 2 g 3 basically after this particular state that where we have this one this up to the vanadium two plus which is the t 2 g 3 case. Then we have the chromium and manganese then once we go for the chromium state. It basically increasing from chromium 2 plus and for the manganese 3 plus which is also d 4 that is here it is again increasing. So, in case of bivalent state it is chromium 2 plus. In case of trivalent case it is manganese 3 plus depending upon only the electronic configuration. We can see the same effect for manganese 2 plus in high spin and for the corresponding chromium 2 plus in the corresponding high spin case.

(Refer Slide Time: 50:18)

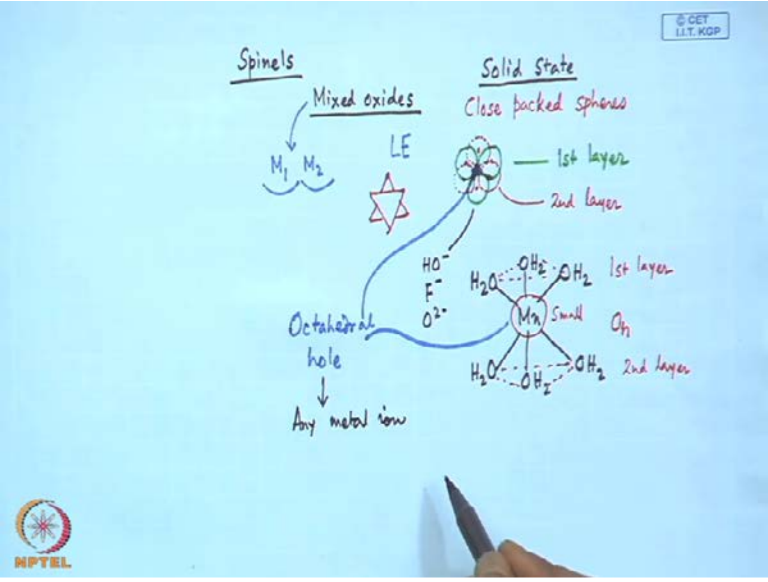
Site Preferences in Spinels

4/2013

8

Then we see some useful information related to some solid state structure which has a different name what we call as the corresponding spinels.

(Refer Slide Time: 50:31)



So, these Spinels are basically mixed oxides. So, how we treat this mixed oxides with regard to the corresponding preference for their sides. And basically we will be talking about the corresponding preference of these mixed oxide that means, we have metal ion M 1 and metal ion M 2. So, where m one will be there and where m two will be there. But before that when we are talking about the corresponding lattice energy the lattice energy values we have seen that the typical spheres where available and if we the close patten of this spheres. So, this is one layer which is the first layer and next if we have this red circles as the second layer these are the second layer.

So, what is happening due to that is whenever we are having a close packing of this spheres because this spheres can be simple HO minus F minus or O 2 minus. So, this is very much similar to that of a particular metal complex what is forming say manganese is forming. So, we have one layer one layer of ligands then we have manganese then another layer of ligands. So, if we have here; that means, manganese is bound to several of these water molecules these are all water molecules and like these thing. That means, the green circles this green circles are showing a triangular arrangement. So, we have a green triangle. So, if we take the center of this green circles. We and add up we have a circle like this. Then we if we just consider the center of the red circles the center of the red circles will be like this. So, this particular feature we can have if we take six spheres together and the center of all this six spheres are taken in this particular diagram.

So, here what we see that in this particular case what we have. So, these three are in one layer; that means, the first layer and these three are also forming another layer which is our second layer. So, if these two layers are sandwiching a particular small sphere which is small in size. That means, we have a sandy structure of one layer and second layer between this two layers. We have the trapped metal ion which is very small one and which is basically sitting inside nicely in an octahedral geometry.

So, in this particular octahedral geometry what we find the same geometry we can have if we have a close packing of spheres. So, if we have closed packed spheres in the solid state. So, whatever thing we are discussing here is based on the corresponding solid state structure. So, in the solid state structure of this hydroxides of this fluorides. And all we have the closed packed spheres and this two layers are basically forming either from hydroxide ion or the fluoride ion or the oxide ion. But at the end what is happening that we are generating something this small space a small space is nothing, but the corresponding equivalent position of this manganese.

So, due to this close packing spheres we have generated one octahedral hole. So, that octahedral hole we have generated and within that particular octahedral hole now we can put any metal ion say this manganese also. So, these gives rise to corresponding Spinel structure and how the Spinel structure can also be controlled due to the corresponding energy calculations in terms of the corresponding stabilization due to the crystal field that we will see in our next class.

Thank you very much.