Basics in Inorganic Chemistry
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Lecture – 11
Application of CFSE: Spinel and J-T Distortion

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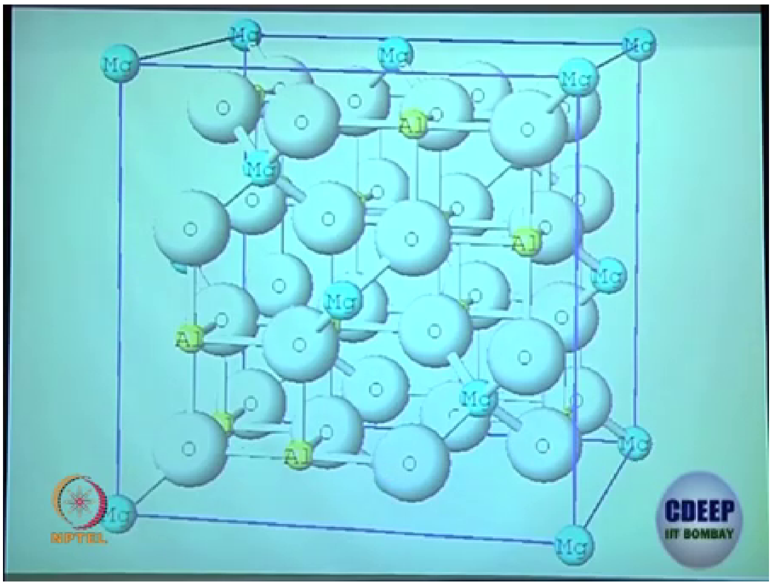

Now, this is the topic today we are going to discuss Spinel.

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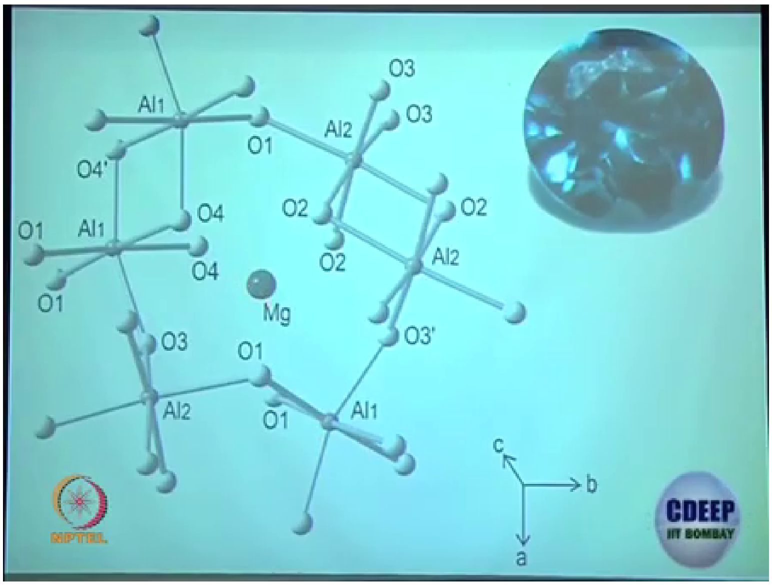

Spinel are the ones which is let us say this nice looking gem looking thing or gem basically magnesium aluminum oxide.

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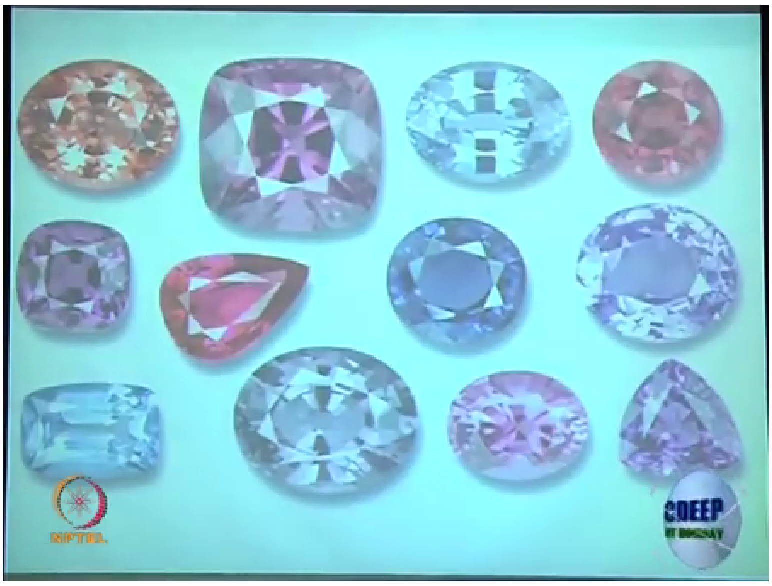

It is beautiful in colour ok; of course, colour comes from you know where the colour is coming from those transition ok.

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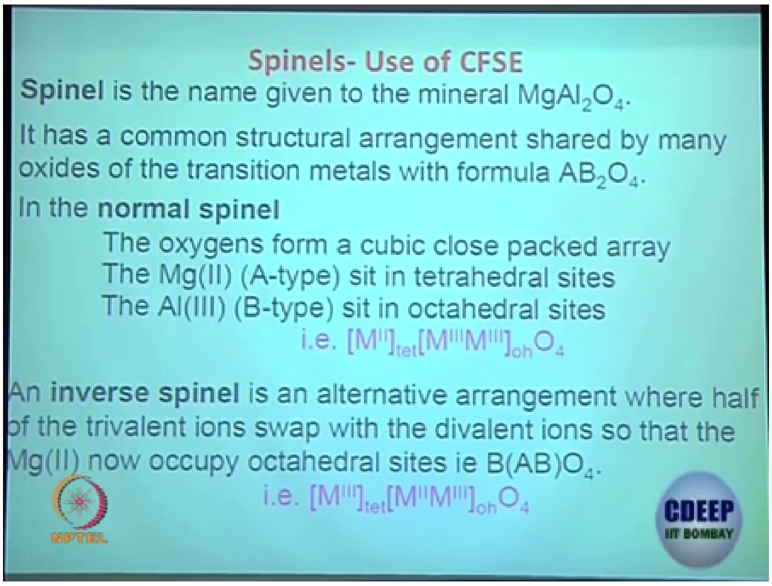

Spinels- Use of CFSE

Spinel is the name given to the mineral $MgAl_2O_4$.

It has a common structural arrangement shared by many oxides of the transition metals with formula AB_2O_4.

In the **normal spinel**

The oxygens form a cubic close packed array
The Mg(II) (A-type) sit in tetrahedral sites
The Al(III) (B-type) sit in octahedral sites

i.e. $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$

An **inverse spinel** is an alternative arrangement where half of the trivalent ions swap with the divalent ions so that the Mg(II) now occupy octahedral sites ie $B(AB)O_4$.

i.e. $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$

Now, definition in spinel is very simple. You can have either same metal or different metal it could be let us say Fe 3 O 4, CO 3 O 4 or it could be MgAl 2 O 4. Three metal should be there, two of them should be the same as you see at least two of them has to be the will be the same usually speaking again or one is different MgAl 2 O 4 something like that. Now, AB 2 O 4 is the general formula for spinel.

The normal spinel are the one, there are two type of spinel as I said – normal there would be abnormal two spinel or inverse spinel. Now, we do not say abnormal inverse spinel. Normal spinel are the one where you have this electronic configuration it is always going to be O 4, 4 oxides are there; that means, minus 8; each oxide minus 2, 4 of the oxide will be minus 8. Now, minus 8 means you have almost one possibility in realistic possibility 3 plus 3 plus 2. Of course, other possibilities are there. Those are less likely never happens for spinel.

So, 3 plus 3 plus 2, since it is 3 plus in the normal behaviour or normal spinel cases you would expect the octahedral geometry or octahedral geometry will be preferred by 3 plus and tetrahedral geometry will be preferred by 2 plus. Let us look at the you know over here magnesium aluminium. This is octahedral, you can see 1 2 3 4 5 6; each aluminium is octahedral. You look at magnesium it is having 4 ligands it is in tetrahedral. I think most likely 1, 2 maybe 3 and 4. Magnesium is in tetrahedral geometry, aluminium is in octahedral geometry.

Yes. So, over here this is further showing you that 1 2 3 4. So, one of them; so, it is a little bit complicated looking thing, but if you go by unit cell if you break down the complex structure and look at the core of it each of the metal ions AB 2 O 4 both the B will be in octahedral geometry ok. Sometime it is just not clear by looking one glance at it ok. You have to just look it little bit carefully you will be able to understand where it is.

And, these are usually the crystal structures. So, there should not be any ambiguity, you just have to look it carefully. So, both the octahedral will be in plus both the plus 3 oxidation metal will be in octahedral state and the one which is 2 2 plus will be in tetrahedral geometry and 4 oxides are there. If this is the case this is normal spinel.

If other way around if one of these octahedral M III plus has to be pushed out from this octahedral side to tetrahedral side that will be called inverse spinel. So, all it depends on whether one of these M III plus will be in octahedral side or tetrahedral side that is it. Of course, always there will be one metal III plus which is in octahedral side, this is common.

The second metal III plus whether it is exchanging with this other metal that is what you need to see. Is it clear? Normal spinel, normal behaviour; III plus should be octahedral right it is a privileged class III plus higher oxidation state, octahedral should be right. It is a high charge, everything should be ligand should be interacting more and so on, that is like normal behaviour if it is other way around octahedral site is coming out and tetrahedral is going into the octahedral 1 or 2 plus is going into the octahedral one this is when it is called inverse spinel, inverse spinel normal spinel.

Now, when what is the criteria? Simply, you have to see metal this metal in III plus whether it prefer prefers octahedral or metal II plus, what it prefers. Let me show you.

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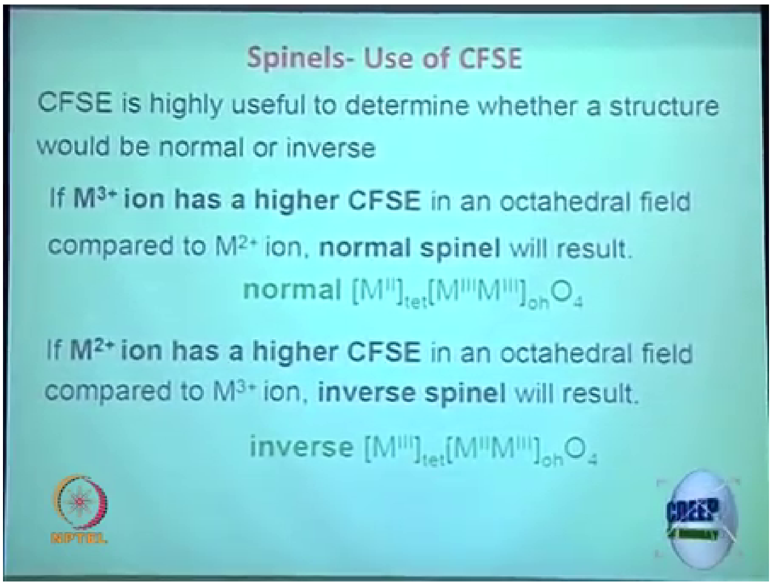

Spinels- Use of CFSE

CFSE is highly useful to determine whether a structure would be normal or inverse

If **M^{3+} ion has a higher CFSE** in an octahedral field compared to M^{2+} ion, **normal spinel** will result.

normal $[M^{II}]_{tet}[M^{III}M^{III}]_{oh}O_4$

If **M^{2+} ion has a higher CFSE** in an octahedral field compared to M^{3+} ion, **inverse spinel** will result.

inverse $[M^{III}]_{tet}[M^{II}M^{III}]_{oh}O_4$

So, M 3 plus ion as when M 3 plus ion has a higher crystal filled stabilization energy compared to M 2 plus ion then this is a normal spinel ok. If M 2 plus ion has a higher CFSE then it is inverse spinel. So, you do not have to really look at the tetrahedral; you do not have to look at the tetrahedral. You take the metal ion M 3 plus M 2 plus for a given metal ion you find out M 3 plus and M 2 plus, their CFSE separate CFSE; if M 3 plus is more then normal, if M 3 plus is less having less CFSE compared to M 2 plus then it is inverse. Just read these two lines.

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So, expectation is M 3 plus M octahedral and this is usually going to be high spin should have high CFSE. Of course, opposite is true M 2 plus octahedral high spin should have low CFSE; CFSE calculation we have learned how to do; if this is done, normal; opposite – inverse; normal spinel, inverse spinel. Do not mix up with calculation of octahedral versus tetrahedral. Sometime people end up doing that they go into wrong direction.

So, you have to just calculate octahedral site stabilization energy like how much stabilization is there. So, that is what it is written M 3 plus ion has a higher CFSE in an octahedral filled compared to M 2 plus ion in normal spinel and so on. Do not calculate for the M 3 plus in tetrahedral ok.

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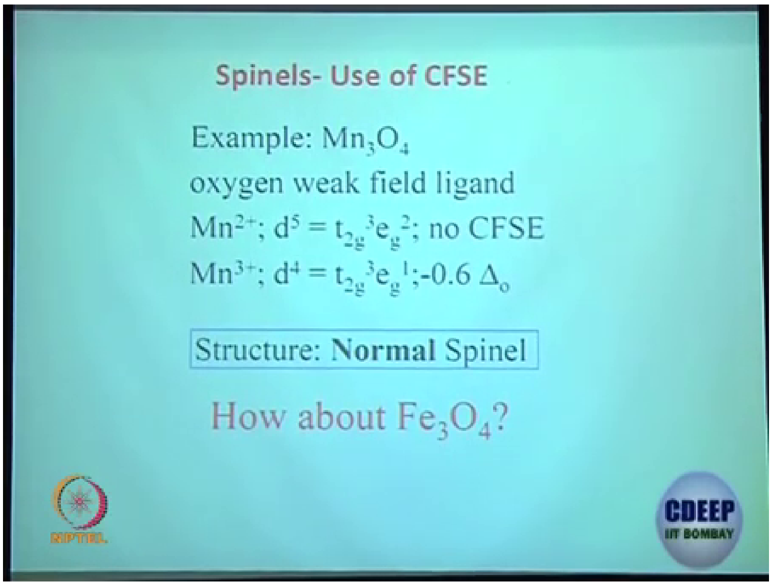

Spinels- Use of CFSE

Example: Mn_3O_4

oxygen weak field ligand

Mn^{2+}; $d^5 = t_{2g}^3 e_g^2$; no CFSE

Mn^{3+}; $d^4 = t_{2g}^3 e_g^1$;-0.6 Δ_o

Structure: **Normal** Spinel

How about Fe_3O_4?

Student: (Refer Time 08:24).

Yeah.

Student: (Refer Time 08:26).

So, this is where I mean yes then how will you conclude right. So, you have to step figure out the stability of M 3 plus versus M 2 plus right. This other otherwise it will get confused what will be will be comparing with right CFSE for tetrahedral is usually low 4 lines of delta O what to calculate ok. So, let me give you an example. It will be clearer.

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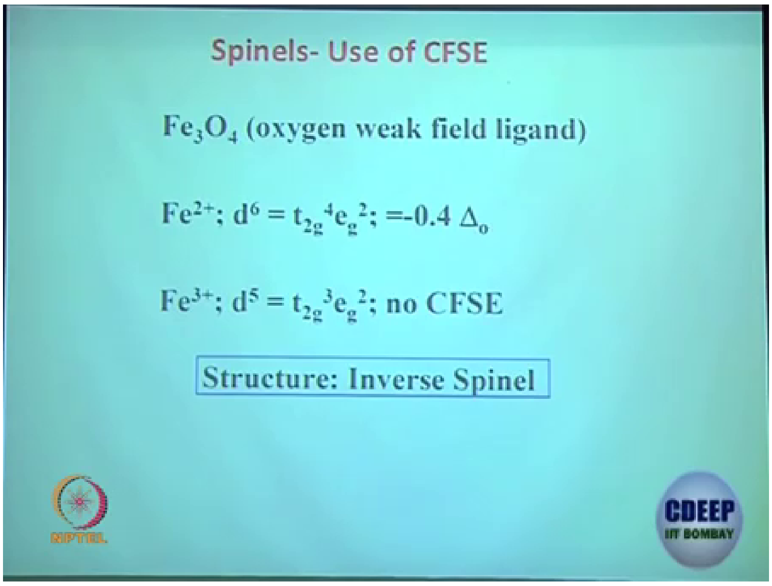

Spinels- Use of CFSE

Fe_3O_4 (oxygen weak field ligand)

Fe^{2+}; $d^6 = t_{2g}^4 e_g^2$; $= -0.4\ \Delta_o$

Fe^{3+}; $d^5 = t_{2g}^3 e_g^2$; no CFSE

Structure: Inverse Spinel

Student: Sir.

Yeah.

Student: I CFSE means more negative (Refer Time 09:05).

More negatives. See any in terms of energy in chemistry, physics everywhere energy means the one which is having low CFSE low anything low repulsion is stable, low energy I mean it is stable anything low would be stabilized. It is like as I was I think I was trying to say it is like home feeling. You want to feel home everybody wants to belong somewhere and that is why they want to go right. So, always low stability should be maximum

Student: Sir.

Yeah.

Student: (Refer Time 09:43).

No, that is the splitting.

Student: delta (Refer Time 09:55).

Delta. So, that is the splitting we were comparing; when we are not changing anything ligand keeping constant metal oxidation state varying metal with a higher oxidation state will have higher splitting. That is somewhat true here, but I mean we are not saying that extent to which. We are trying to tell here is M 3 plus M 2 plus yes you are partially right M 3 plus M 2 plus you just calculate the CFSE ok.

Let me give you this example. Hopefully things will be clear ok. Mn 3 O 4 Mn 3 O 4 of course, here oxygen usually always I mean not always again there will be one example which is other way. Usually oxides for these cases are going to be the weak filled ligand, it is a weak filled ligand. Now, unless the metal is very high you know very high oxidation state or so, oxide will be the weak filled ligand ok.

You do not have to worry about the oxide too much except in one question which will come. Manganese 2 plus d 5 since it is weak filled ligand it is a high spin that is what I was saying high spin. Now, high spin is 0 CFSE manganese 3 4 3 plus d 4 is t 2g 3 e g 1. So, you are going to get net minus 0.6 delta 0, that is what you have calculated right should be minus 12 minus 6. So, sorry plus 6 minus 12 plus 6 it is minus 6 dq.

Now, this is the normal spinel how about Fe 3 O 4, can you calculate Fe 3 O 4? Whoever is trying to calculate try give yourself 1 minute Fe 3 O 4. Fe 3 plus and Fe 2 plus tries whoever got it hold on for a minute. Inverse spinel yes, that is the correct answer. Just I will in a moment I am looking for something. So, I hope you have got this right Fe 2 plus d 6 t 2g 4 e g 2 high spin 3 and 2 cancels out 3 over here and 2 over here cancels out so, minus 4. It is easy, right? Over here 3 and 2, 0 CFSE right.

Now, Fe 3 as you can see is having less CFSE compared to Fe 2 so, that is it; so, inverse spinel. Do not only request is do not complicate too much. You think, but for calculation do this because if you end up calculating tetrahedral Fe 3 plus k tetrahedral Fe 2 plus k tetrahedral it is going nowhere ok. It is the simple thing higher oxidation state should try to stay in the octahedral side.

The moment higher oxidation state becomes less favourable compared to the lower oxidation state switch of the power happens. It is just the BJP and Congress you have to pick up one of them in the centre, not the local or democratic or republican you do not have any choice ok.

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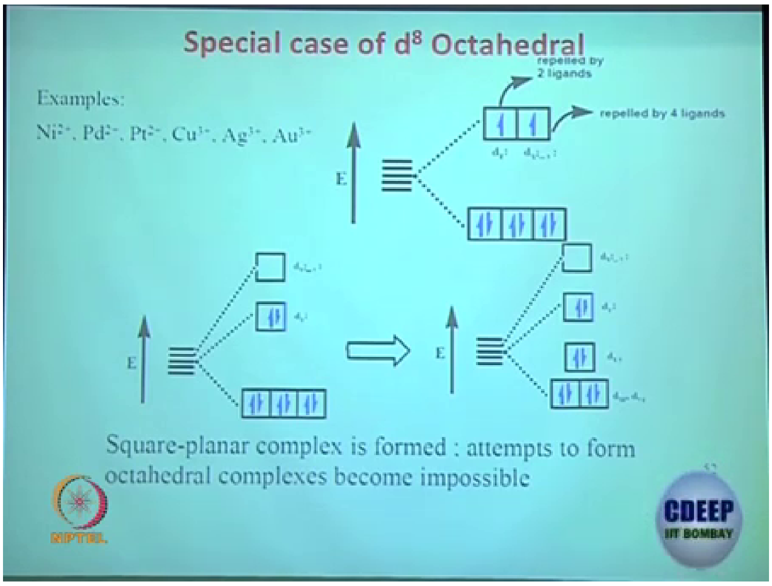

Special case of d^8 Octahedral

Examples:

Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{3+}, Ag^{3+}, Au^{3+}

Square-planar complex is formed : attempts to form octahedral complexes become impossible

Now, so, this is the special case special case of d 8 octahedral right. So, what is the special case? We are eluding before that these d g 2 orbital are the one getting repelled by 2 electrons. This is a d 8 electronic configuration as you can see t 2g 6 e g 2 and this is the one repelled by 4 ligands that is unfair. That is what happens is z orbital try to stabilize to minimize the energy to gain more energy.

So, you start with an octahedral situation, but you see d 8 you go blank. d 8 octahedral will tend to form square planar geometry because the z you will see square planar complex is form because z will get destabilized a sorry stabilized. z is getting stabilized as you can see z orbital will get destabilized. This is an unfavourable situation. This is a situation which cannot be tolerated. This is 2 ligands refilling 4 ligands refilling right. This is the unique situation one – one unique situation. Same electron repelled by one electron repelled by 2, one electron repelled by 4.

In order to bring some sort of calmness to the system z orbital will stabilize if you want to stabilize x 2 y 2 orbital, then the problem becomes; stabilization means repulsion is less that is the stabilization repulsion less is the stabilization. If you want to stabilize d x 2 y 2 orbital then you have to elongate 4 of the ligands, stabilisation means you know reducing the repulsion.

If you are stabilizing z square then you just need to take out those axial ligands. Take it was here two axial ligands were here, you pull it out. So, z will be stabilized d z square will be stabilized of course, further it will be stabilized any z component there will get stabilized. So, d xz will be stabilized, d yz will be stabilized. This is the scenario where square planar complex goes. d 8 octahedral usually will be I mean if it is possible always it will go to the square planar situation that is also true. d 8 d 8 tetrahedral or d 8 4 ligands are not tetrahedral d 8 configuration 4 ligands are going to be square planar ok. This is where you see iron, cobalt, nickel; nickel is nickel 2 plus d 8 is square planar alright. Now, this is one scenario.

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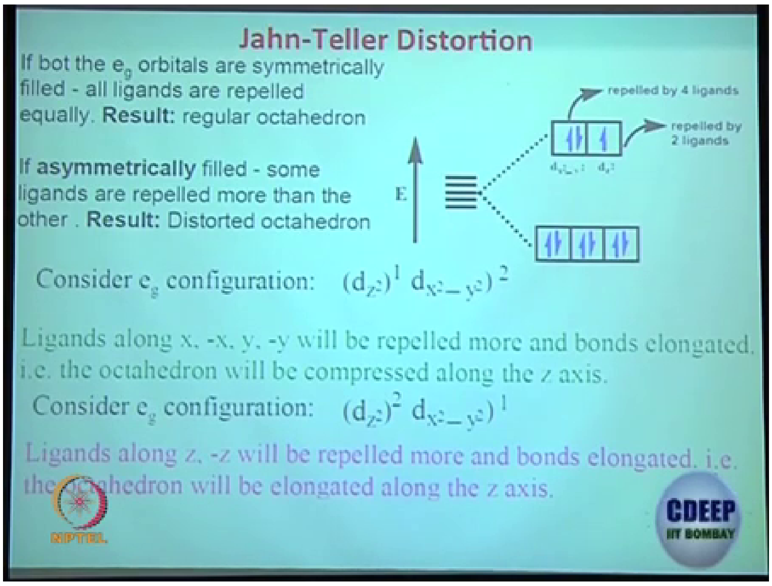

Jahn-Teller Distortion

If bot the e_g orbitals are symmetrically filled - all ligands are repelled equally. **Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other . **Result:** Distorted octahedron

Consider e_g configuration: $(d_{z^2})^1\ d_{x^2-y^2})^2$

Ligands along x, -x, y, -y will be repelled more and bonds elongated, i.e. the octahedron will be compressed along the z axis.

Consider e_g configuration: $(d_{z^2})^2\ d_{x^2-y^2})^1$

Ligands along z, -z will be repelled more and bonds elongated, i.e. the octahedron will be elongated along the z axis.

Our other scenario is that e g orbital is unsymmetrically filled. So, you can see that majority of the syllabus is biased towards octahedral ok. Tetrahedral not too much, but that is because octahedral is favoured octahedral is historically more important and that is how most of the study has been done. And, it is a common geometry more common geometry I would say.

Now, this is the Jahn-Teller distortion of course, you can some people pronounce at differently in British in England you will go pronounced differently, US it will pronounce differently Jahn-Teller some people tell some people tell Jahn-Teller whatever it is it is the same thing J-T distortion.

So, what we see if this one is unsymmetrically filled what are the situation when it is e g 3 or e g 1 that is the only two possibilities. e g 2 will be symmetrically filled, e g 4 will be symmetrically filled e g 1 or e g 3. If it is filled then again you are having some sort of a problem; what is the problem that is what we are coming to. Let me go to the picture ok.

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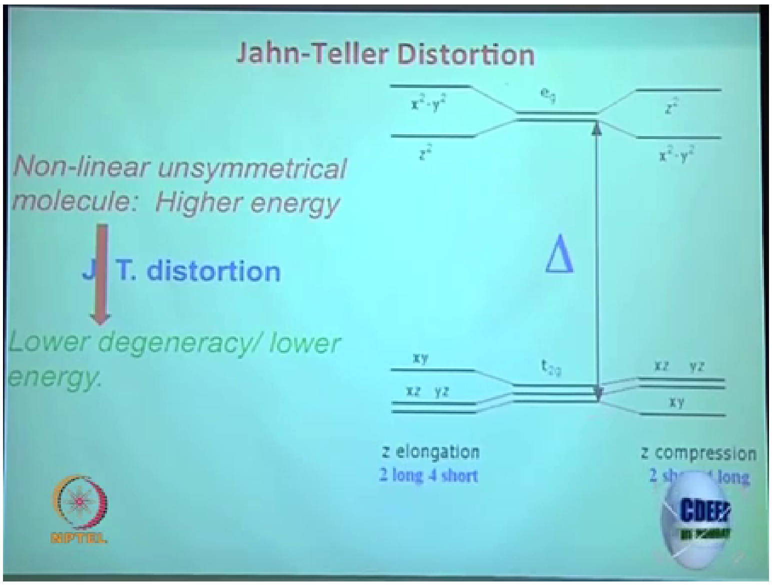

Jahn-Teller Distortion

Non-linear unsymmetrical molecule: Higher energy

J. T. distortion

Lower degeneracy/ lower energy.

This is what is Jahn-Teller distortion. If of course, t 2g is completely filled completely filled or symmetrically filled, either t 2g is t 2g 3 e g 1 or t 2g 6 e g 3 all these configuration.

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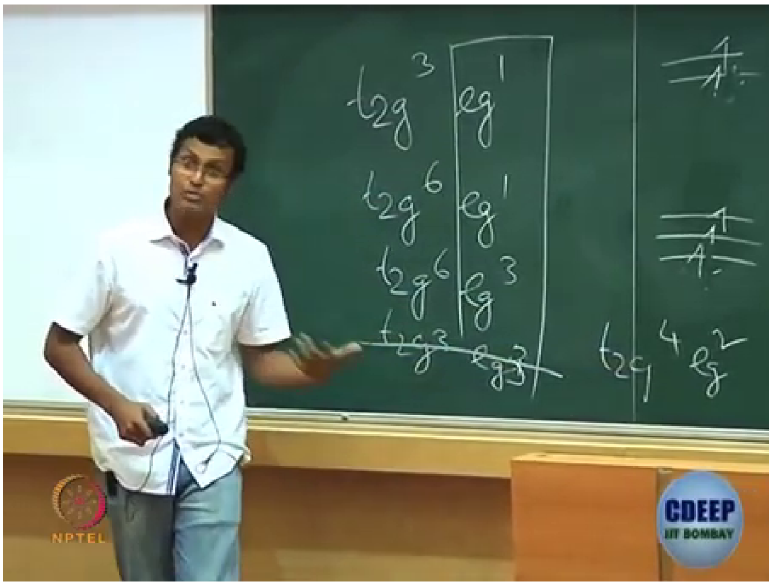

So, what are the configuration? t 2g 3 e g 1, t 2g 6 e g 1 t 2g 6 e g 3. So, wherever unsymmetrical situations are possible of course, t 2g 3 e g 3 is not possible right t 2g 3 e g 3 is not possible because it would be t 2g 4 t 2g 3 e g 4 is not possible. So, this sort of thing you should be able to recognize very quickly t 2g 3 e g 4 actually should be t 2g 4 e g 2 right.

Student: Why?

Why means it is a stabilisation you look at.

Student: (Refer Time 19:58).

Very good question right. So, t 2g 3 e g sorry e g this is did I say 3 everything I will say this is correct 3 plus 3, 6; 4 plus 2 6. Now, t 2g 3 e g 2 this is the t 2g 3 e g 2 high spin if you are say. Now, how it can be going over there because it is giving more energy or destabilizing the system. This sixth electron should come here say the always filling rules anywhere I mean you read spin principle you did whatever other principle system has to be stabilized.

When two scenarios are there system goes for stabilization, but when high spin low spin situation is there because high spin is accessible it goes for high spin or it can go through low spin. Here after filling out 1 2 3 if it is high spin 4 5 6th electron will come back from here, it is home right, it is stable. So, t 2g 3 e g 3 is not a valid configuration, it is t 2g for e g 2. It is invalid; I mean literally it is possible for an excited state. If you excite t 2g 4 e g 2 then it can come to t 2g 3 e g 3. This is usually all we are talking about is ground state electronic configuration ok. Any confusion on that? No, hopefully not.

Now, J-T Jahn Jahn-Teller distortion t 2g t 2g either fully filled or half filled t 2g 6 or t 2g 3. Here it has to be unsymmetrically filled means e g 2 and 4 is out of question e g 1 or e g 3, two orbitals are there ok. What can happen two scenarios are there either d g 2 can be stabilized or d x 2 y 2 can be stabilized.

Now, stabilisation again stabilization means what? Stabilization means repulsion is less stabilization means less repulsive. Less repulsion when it can happen? When ligand is not coming? If z square is stabilizing; that means, along that direction ligands are far. So, this will be too long this that will be.

(Refer Slide Time 22:55)

So, the left hand scenario this is a base for octahedral scenario we are drawing. This is the equatorial plane axial was here. Now, it this is let say normal scenario if I want to say that dz square orbital is stabilized; that means, this ligand is not this is the j dz square orbital reaction right. So, that means, ligand is not coming close to this dz square orbital. This is where the dz square orbital is right.

So, it is not coming close; that means, it is going far and that is how dz square can be stabilized; that means, two of them two of the ligands should be at a longer distance and four of them at a shorter distance or relatively shorter distance. The opposite is here when relatively speaking d x 2 y 2 is getting stabilized; that means, these are going out. Stabilized means repulsion is less ligands in the second scenario ligands will be further further away and z was over here.

So, z in this is called z in z direction getting in; this is called z out ok. It is a very very simple thing. If you just try to understand very simply do not complicate things it is that very simple. Now, as you can see z z out this is the z out, if you keep on moving more and more z out becomes your square planar right.

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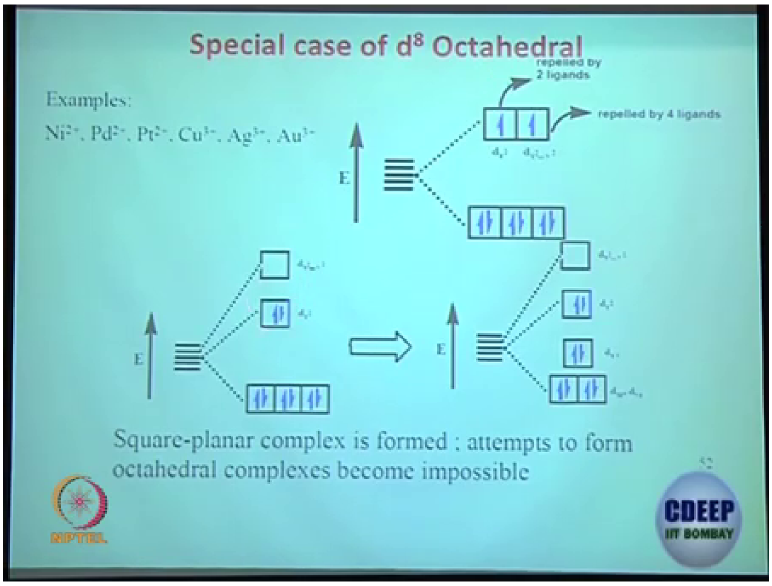

Special case of d^8 Octahedral

Examples:

Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{3+}, Ag^{3+}, Au^{3+}

Square-planar complex is formed : attempts to form octahedral complexes become impossible

So, here previous case what we were discussing. If z becomes stabilized more more more here, so that it is you are taking too far from the metal center, octahedral is no longer octahedral it is becoming square planet ok. So, z in and z out. Yeah?

Student: (Refer Time: 25:26).

Sorry.

Student: (Refer Time: 25:30). So, why they are instead of pulling that (Refer Time: 25:35)?

No, these are having same energy right.

Student: Yeah, instead of x and.

No, these are see these are degenerate you cannot dictate the term. You cannot tell who is where you want it is just this is just for nomenclature sake I have written just to you know just to tell you or just to write you something I have written. Which one is dz 2 or which one is dx 2 you do not know. It is same energy right degenerate means same energy 5d orbitals before crystal filled theory we used to think that same energy we do not discriminate right. So, this is just representation sake.

Student: (Refer Time: 26:20).

Not all the cases, but when it is unsymmetrically filled then it is becoming a problem. See three four scenarios are there e g orbital. Why e g orbital is getting part perturbed, why t 2 g not? Because those are the one you can see these are the outside. If you see the splitting wise those are the one facing the maximum of the ligand repulsion right in e g 4 configurations are there e g 1, e g 2, e g 3, e g 4.

e g 2 scenario we have already discussed. e g 2 scenario is the one where we are getting most often we are getting that d 8 t 2g 6 e g 2, e g 2 that is a d 8 electronic configuration it tends to go for a square planar one. Fine, you remained with e g 1 or e g 3. e g 1 and e g 3 scenario we are trying to discuss here.

So, when it is symmetrically or full filled then usually we do not get bothered it is you know other way one way or the other it is just the same I mean you know it is completely full so, nothing to really compare with. But, in this scenario when you have unsymmetrical spilling then you have the chance of splitting. See similar split the extent of splitting you can see is not the same here again.

Of course, usually speaking these are the one e g are the one which are going to face the ligand directly and thereby splitting starts over there and then of course, sometime it also get affected t 2 g gets affected. That is where we have we were showing initially we did not split it initially we when we were discussing t 2g 6 e g 2. We were showing that d z 2 is getting stabilized when it is getting further stabilized and this then it is going to get split further ok.

So, look at the slide almost in every book it has been written really well. If you have any confusion, please come back or discuss with your friends. So, z in and z out; this is z out z out means z you are pulling out stabilisation happening ok.

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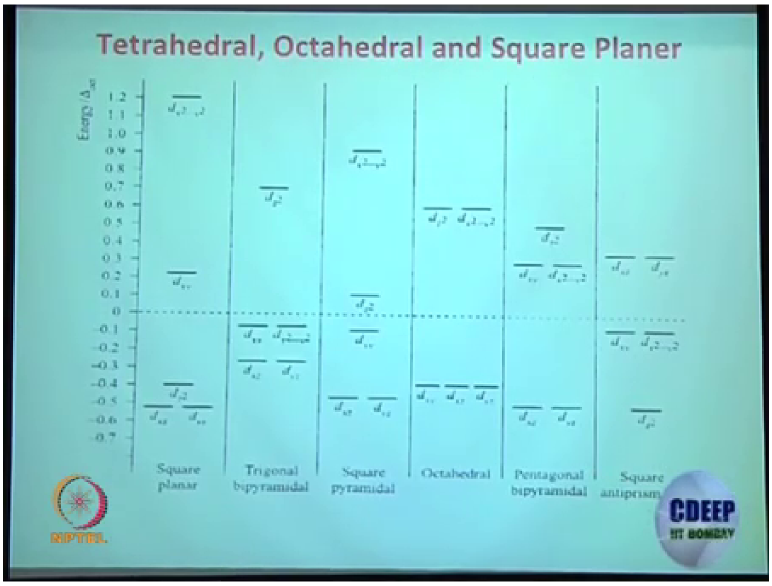

Tetrahedral, Octahedral and Square Planer

Now, this is a slide which is mostly left for you to digest little bit square planar geometry. So, if you want to memorize sometimes things can be problematic. We want to read you mainly let say octahedral 3, 2. Octahedral, where is tetrahedral? Tetrahedral is not given here, anyway. The geometry and thereby they are splitting; how they are going to split. This is not all of them is part of the syllabus again. This is just a overview giving an idea how ligands are coming, how d orbitals are getting perturbed.

Which direction d orbitals are is located and then from which direction ligands are coming. Of course, that is what going to determine what is their geometry. If it is a square planar where it is coming you know; if it is a trigonal by pyramidal or tbp 3 of them in the equatorial plane triangle one from the top, one from the below. So, which are the orbitals going to get affected in to what extent and so on.

So, these are these are these are in the book or may not necessarily we have to read it. You are, but you are supposed to read octahedral, tetrahedral, square planar. I think for fun you can look at that try to justify a little bit ok. So, that is it for this chapter.