Basics in Inorganic Chemistry
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Lecture – 02
Electronic Configuration of Elements

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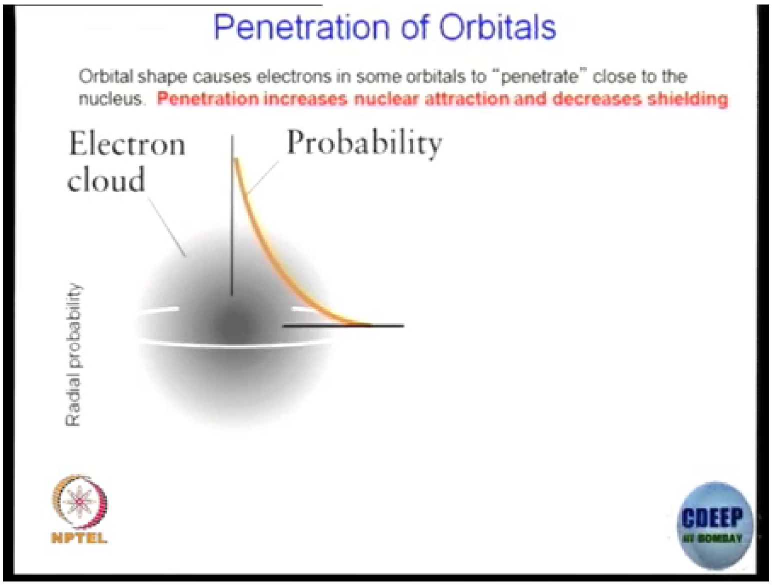

Penetration of Orbitals

Orbital shape causes electrons in some orbitals to "penetrate" close to the nucleus. Penetration increases nuclear attraction and decreases shielding

Yes, now this is a something you know these electron how the electrons are distributed outside the nucleus or you know this is probability of finding electron as you know like to call them; can be you know more clearly be taught in physical chemistry course. Here I will give you just a brief idea, may not be exactly clear idea, but you know it is something which will give you an idea to go forward.

Now, how are the orbital sets? Of course, we have learned that; so steps are different, but then if you want to see the electron distribution of course my physical chemistry colleague will perhaps kill me if I try to define like that.

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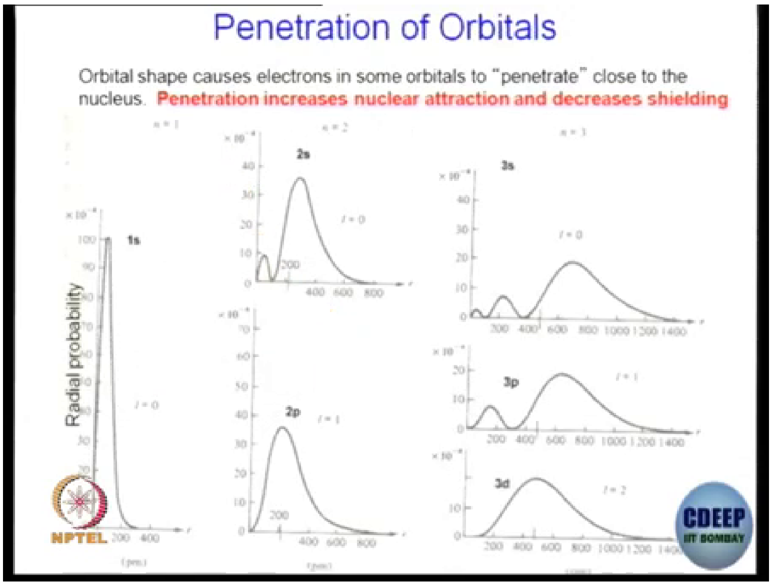

Penetration of Orbitals

Orbital shape causes electrons in some orbitals to "penetrate" close to the nucleus. Penetration increases nuclear attraction and decreases shielding

But let me do it anyway, you are going to learn better in physical chemistry course. So, if this is the 1s electron we are talking about; then 1s electron is distributed with respect to the nucleus, if the nucleus is at the center would like to think like that. The probability of finding the 1s electron is going to be like this. So, the probability of finding length 1s electron towards nucleus is quite high.

If you look at 2s electron, probability at finding 2s electron at the nucleus is not that much of course, there is a node at this distance; after that there is a probability of finding this 2s electron is quite high. If you look at 3s electron, it is you know one more node added and you can see this if you compare 2s versus 2p; you can further see of course, 2s as some component very close to the nucleus; over here 2p does not have really that much component very close to the nucleus.

So, the penetration is actually meaning that how much these orbitals are contributing towards or you know how much close they are towards the nucleus. So, as you can see 1s is very close to the nucleus and thereby the penetration of 1s is going to be the maximum and it can neutralize the positive charge most efficiently right. As you can see for the other for example, 3d; 3d is distributed or the maximum probability of finding 3d electrons are really far from the nucleus. Therefore, the neutralization ability of 3d electrons are going to be kind of least out of all these orbitals shown in here.

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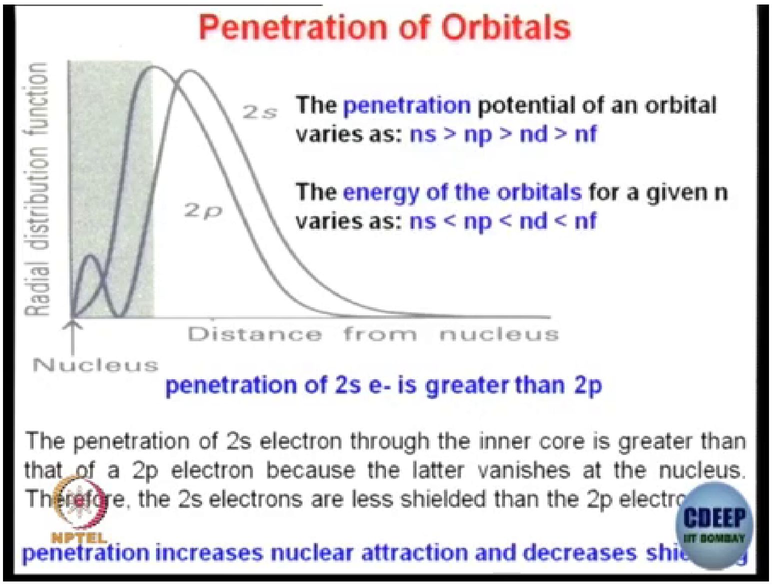

Penetration of Orbitals

The penetration potential of an orbital varies as: ns > np > nd > nf

The energy of the orbitals for a given n varies as: ns < np < nd < nf

penetration of 2s e- is greater than 2p

The penetration of 2s electron through the inner core is greater than that of a 2p electron because the latter vanishes at the nucleus. Therefore, the 2s electrons are less shielded than the 2p electro

penetration increases nuclear attraction and decreases shi

Now, if you compare directly 2s versus 2p; you over a you kind of you know overlap these 2s and 2p electron and then this is what the distribution curve you see. As you can see penetration of 2s electron is greater than 2p electron right because you have a very good component of 2s very close towards this nucleus.

So, the penetration; that means, the you know the positive component is getting neutralized by these electrons at the orbitals; the penetration of the 2s electron through the inner cell or inner core is greater than that of 2p electron because the latter vanishes at the nucleus. So, the 2p electron vanishes at the nucleus whereas, 2s electron are still there. Therefore, the 2s electrons are less shielded than 2p electrons ok; 2s electrons are basically penetrating much more compared to 2p electrons.

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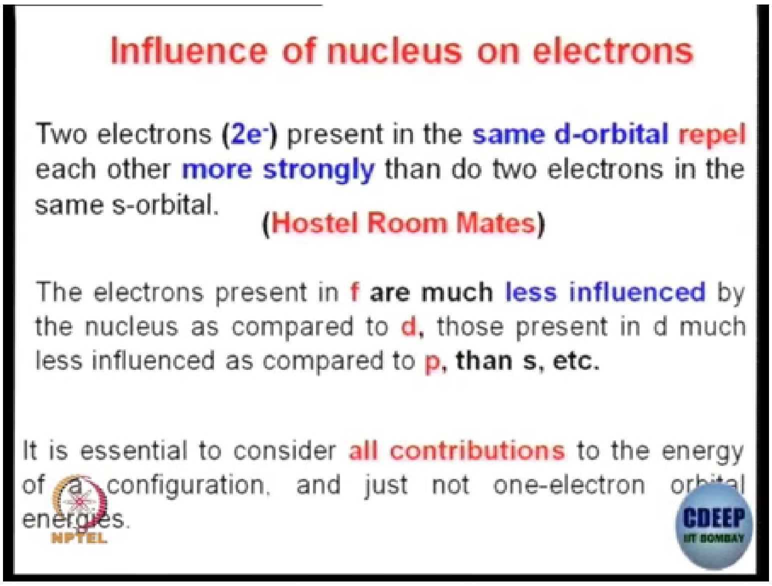

Influence of nucleus on electrons

Two electrons (**$2e^-$**) present in the **same d-orbital repel** each other **more strongly** than do two electrons in the same s-orbital.

(Hostel Room Mates)

The electrons present in **f are much less influenced** by the nucleus as compared to **d**, those present in d much less influenced as compared to **p**, **than s, etc.**

It is essential to consider **all contributions** to the energy of a configuration, and just not one-electron orbital energies.

Now, another thing you really need to understand very simply is you know the d electrons repeal each other much more compared to p or s electron; how is that? Shown you know it is like involvement right how much involve you are in a particular thing.

Well, let me give you an example of your hostel rooms right; in your hostel if you have let us say you know 3 people in a room; it is possible or 2 people in a room or 3, 4 people; 4 people in a room. Now, if out of this 4 people; 1 or 2 of them are involved in something; it could be music, it could be studying, it could be sports, it could be anything outside you know; outside the normal thing you would like to do.

So, if they are too much involved there it is less likely that they will have much more time to interact with the third or the fourth; you know roommates right. So, the if the first and second person in your hostel room are involved in something deeply; they are less likely that they will disturb you right. But on the other hand, third student or third mate and the fourth one are not being involved in anything that way. So, it is more likely that these two guys third and fourth guy will be having you know more number of fights or more number of disagreement right.

So, this is what we are trying to see in d electrons; what is happening is d electrons are not really involved with the nucleus, d electrons are kind of not capable of neutralizing or engaging with the nucleus. And therefore, the d electrons will be repelling each other very strongly or will have more conflict. On the other hand, if you look at comparatively let us say s electron; they are much more penetrating, they are much more involved with the nucleus and therefore, the s orbital having two electrons will repel less compared to d orbital having two electron.

So, what I am trying to say is two electrons if it is in d orbitals, those two electrons will repel each other more strongly compared to two electrons in the s orbital because s orbital is more engaged with the more engaged with the nucleus right. So, two electrons present in the same d orbital repel each other more strongly than do two electrons in the same s orbitals. So, that is what I am trying to say its hostel roommate; the electrons present in f are; obviously, much less influenced by the nucleus as compared to d.

So, electrons in the s orbital; it is much more involved with the nucleus, the p orbital its little bit less involved with the nucleus; d orbital electrons are less further less involved, f electrons are even I kind of least involved with the nucleus and therefore, the repulsion among the f electrons will be much more among each other will be much more compared to any two electrons in any other orbitals right.

So, you when you are trying to calculate in a or trying to understand any effect or any effect by these different electrons; you have to; you have to essentially think of a bigger picture. You have to; you have to think how much penetrating they are you have to think how much repulsion they we will be having with each other and so on; we will come to that.

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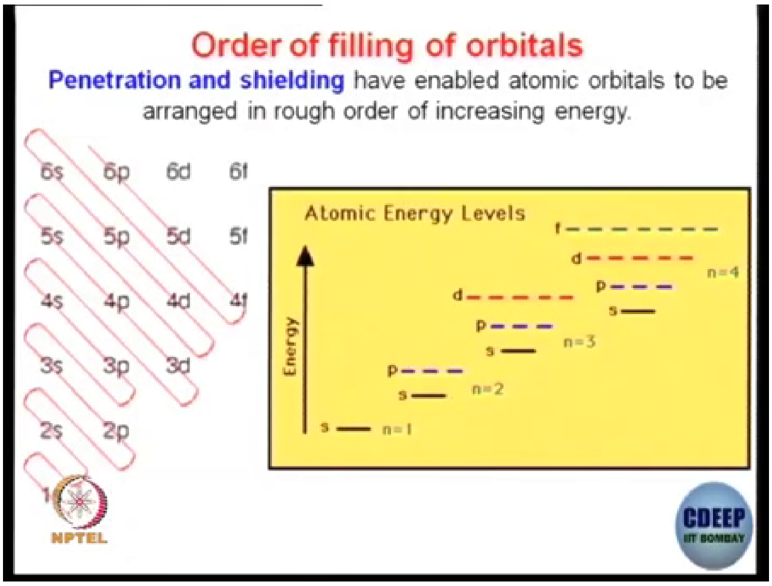

Order of filling of orbitals

Penetration and shielding have enabled atomic orbitals to be arranged in rough order of increasing energy.

So, now I will discuss order of filling of orbitals; you have studied quite long back I guess that order of feeling should be 1s should be fill out first and then 2s, then 2p, 3s, 3p; not 3d; then after 3p should be 4s, then 3d. And this is where I think we need to understand little bit better why after 3s; 3p gets filled, but after 3p not really 3d is getting filled, but 4s is getting filled.

Technically speaking, 4s is having more energy compared to 3d because the principle cell is of a higher number right. 3s, since it is the electron in 3s should be more or more stabilized means less or energy compared to 3p. So, 3s should be fill out first, then 3p; after 3p then it should be 3d, then 4s, but in reality what we see that 4s is fill out before 3d. Of course, first thing we need to understand that 4s and 3d are having very similar energy. If anything we would like to think that 3d is having lower energy compared to 4s.

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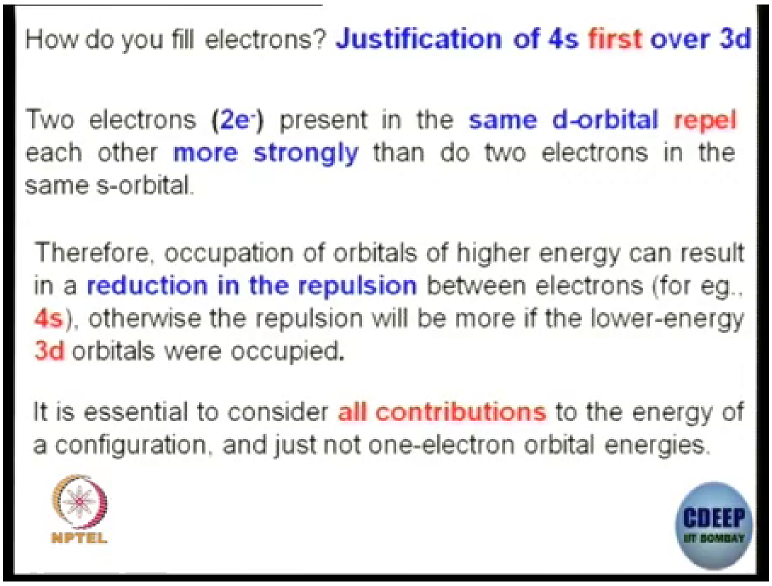

How do you fill electrons? **Justification of 4s first over 3d**

Two electrons (**$2e^-$**) present in the **same d-orbital repel** each other **more strongly** than do two electrons in the same s-orbital.

Therefore, occupation of orbitals of higher energy can result in a **reduction in the repulsion** between electrons (for eg., **4s**), otherwise the repulsion will be more if the lower-energy **3d** orbitals were occupied.

It is essential to consider **all contributions** to the energy of a configuration, and just not one-electron orbital energies.

But for that w we must think of something which is which we try to discuss just briefly like 5 minutes back we are discussing. So, the d electrons are less penetrating right; d compared to let us say s electron. So, compared to 3d electron; 4s electron is going to be more penetrating right and therefore, repulsion of electrons in 4s orbital will be less compared to repulsion in the 3d electron right.

So, 4s and 3d first of all they are having very little difference in energy; since the repulsion in 4s is going to be much less compared to 3d; what will happen that, 4s is going to get preferably filled out compared to 3d. So, this is an exception and this is how it can be perhaps explained. Therefore, occupation of orbitals of higher energy can result in a reduction in the repulsion.

So, in this case if you occupy the electrons in the 4s orbital; it is going to repel less consequently what we see is 4s electron is getting; 4s orbital is getting filled out preferentially over the 3d. Once again I think this is kind of becoming a disclaimer; you have to really consider all other contribution; not only you know numerically we should not be seeing that 1s, 2s, 2p, 3s, 3p, 3d; instead we should be looking at their relative energy and the consequences that is going to have if you fill out these orbitals; let us say 4s versus 3d. In this case, once again the repulsion among the electrons determines which one is going to be preferentially fill out.

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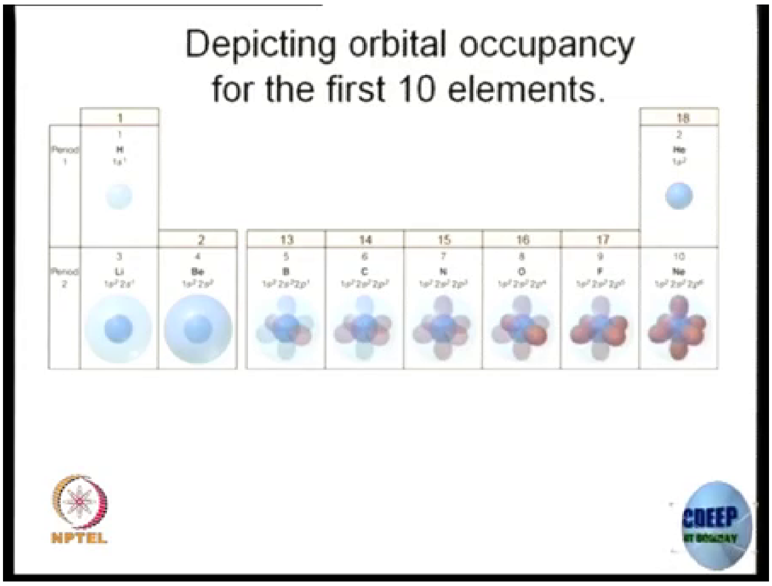

Depicting orbital occupancy for the first 10 elements.

Now, let me show you some other data which I think I like it very much, where it is clearly showing how kind of electrons are getting filled out. 1s you have one electronyl filled out for hydrogen let us say 1s 1, 1s 2 2 electrons filled out compared this one; you are seeing the dark are all of the same size; 1s electron getting filled out.

Now, over here for the lithium you have 1s 2 and 2s 1; so the 1s orbital is this one, 2s orbital is this one. So, it is you know overall you see the distribution of electrons kind of you know not. So, accurate picture once again, but this is something you can visualize to basically understand for 1s 2, 2s 2; you see that 1s of course is very dark, 2s orbital also becoming very dark.

If you see the borons that is 1s 1, 2s 2 and 2p 1; now one of the p orbital is getting occupied by electrons electron and then from 2p 1, if you see 2p 2, 2p electrons are getting occupied, then 2p 3, 2p 4; you are saying the p electron clouds are getting more and more deeper. And therefore, the overall if you see neon that is 1s 2, 2s 2, 2p 6; this should be something like this.

This is again this is an approximate picture; this is just to give you a feeling how perhaps the electrons are distributed with respect to the nucleus; in reality this picture perhaps you know in reality this does not exist.

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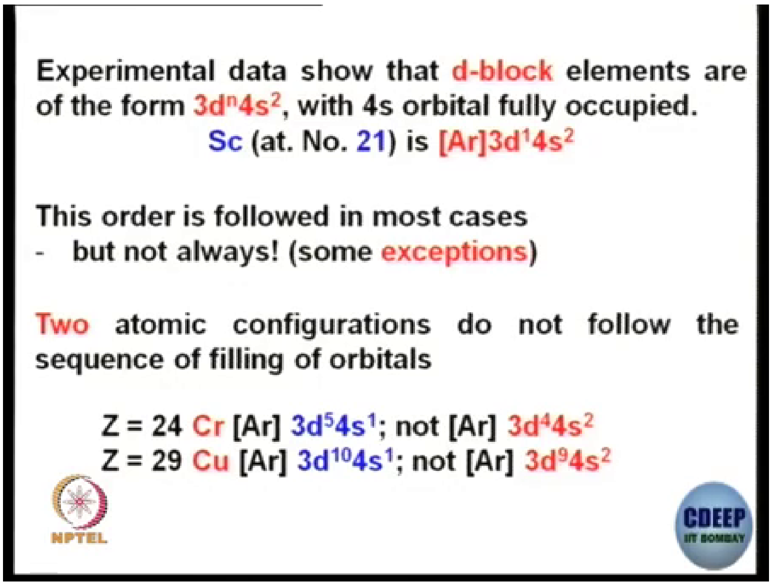

Experimental data show that d-block elements are of the form $3d^n4s^2$, with 4s orbital fully occupied.

Sc (at. No. 21) is $[Ar]3d^14s^2$

This order is followed in most cases

- but not always! (some exceptions)

Two atomic configurations do not follow the sequence of filling of orbitals

Z = 24 Cr $[Ar]\ 3d^54s^1$; not $[Ar]\ 3d^44s^2$
Z = 29 Cu $[Ar]\ 3d^{10}4s^1$; not $[Ar]\ 3d^94s^2$

I think I have discussed this; now of course, what we find that experimental data show that d block elements are of the form 3d n 4s 2; that means, 4s electrons are getting filled out preferentially compared to 3d electrons with 4s orbital fully occupied. For example, scandium atomic number which is 21; the electronic configuration for scandium would be this is the argon configuration and then 3d 1 4s 2.

So, it should be 4s filled out first two of them and then 3d 1. If atomic number scandium titanium let us say if you have; then it would be 3d 2 and 4s 2 and so on. This order is followed in almost all cases ok; that means, 4s 2 electrons will be distributed first or given first and then the remaining electron if any should be going to your 3d electrons.

Two atomic configuration actually kind of highlights this general principle; what are those cases? You might will know that is chromium and copper, what is happening in these cases? In this cases, it should be you know according to what we were discussing; it should be 3d 4, 4s 2 electronic configuration; of course, now this is going to be a half filled fulfill configuration or the zone where you can have 3d 5 electronic configuration to gain the further stability, if the electronic configuration will become now 3d 5 4s 1; not 3d 4 4s 2.

In case of copper, it is a similar situation where according to what we were discussing earlier the you know electron repulsion in the d orbital; it should be 3d 9 and 4s 2, but it is not; it should it is 3d 10 and 4s 1 because the d orbital; if gets one more electron, it becomes 3d 10 which is a full filled electron configuration.

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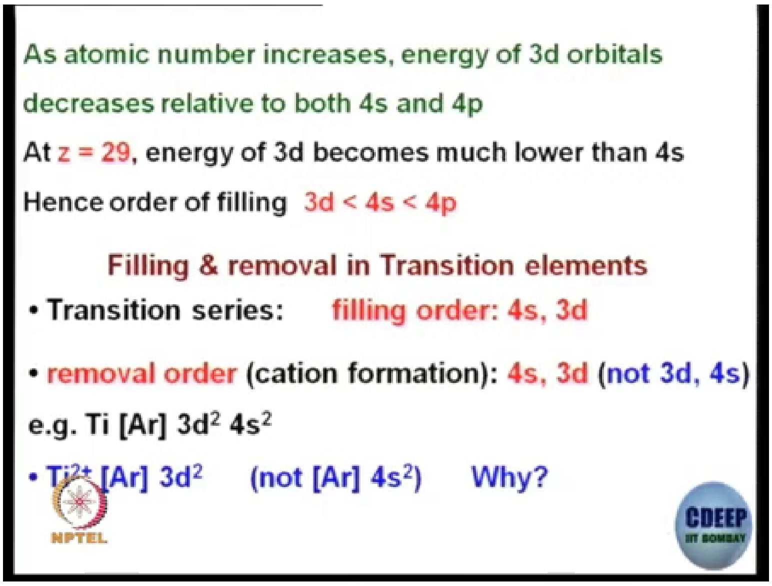

As atomic number increases, energy of 3d orbitals decreases relative to both 4s and 4p

At $z = 29$, energy of 3d becomes much lower than 4s

Hence order of filling 3d < 4s < 4p

Filling & removal in Transition elements

- Transition series: filling order: 4s, 3d
- removal order (cation formation): 4s, 3d (not 3d, 4s)

e.g. Ti [Ar] $3d^2\ 4s^2$

- Ti^{2+} [Ar] $3d^2$ (not [Ar] $4s^2$) Why?

So, the cases where you have half fill or fulfill electronic configuration attainment; then you are going to see the deviation from the standard 4s filling first and then 3d electron. As atomic number increases energy of 3d orbitals decreases related relative to both your 4s and 4p.

So, we are trying to say that 3d should be having comparable energy with 4s; 4s should be having lower energy compared to 4p that is fine, since the d electron electrons can repel each other strongly compared to 4s electron; this repulsion energy or the destabilization energy preferentially allows 4s electron to be filled out first, but once d electrons getting filled out more and more; what happens is d orbitals is no longer having a higher energy compared to 4s; the energy of d orbital 3d orbital decreases compared to 4s.

So, in that case the filling order should be as expected or normal; 3d should be fill out first and then 4s and then 4p. Now, another thing to understand see overall what we tried to say is 4s should be filling out first, then 3d, but removal what will be the removal order? So, this is what we now need to understand; for transition metal series your filling ordered should be 4s and 3d, removal order should be again 4s and 3d ok.

This is what I think its little bit contradictory; I think you would expect since 3d is filling out later on ok. So, the removal time 3d electrons should go first right, but that is not the case; 4s fills out first, 4s gives out first ok. How is that possible or what is the explanation? Let us say take the examples of titanium. So, it is 3d 2 4s 2 fine; 4s filled out first and then 3d filled out.

When titanium 2 plus we are thinking, then it should be according to the filling order 3d orbital electron should go out right; that is not happening what we are seeing is in reality 4s electron is going out, not the 3d electron. How can you explain this? This is one of the small topic we need to discuss.

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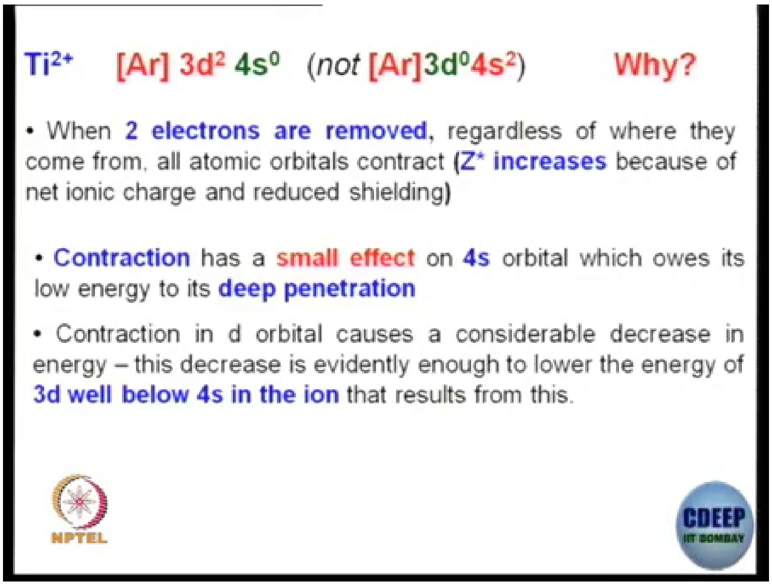

Ti^{2+} [Ar] $3d^2$ $4s^0$ (*not* [Ar]$3d^0 4s^2$) Why?

- When **2 electrons are removed**, regardless of where they come from, all atomic orbitals contract (**Z^* increases** because of net ionic charge and reduced shielding)
- **Contraction** has a **small effect** on **4s** orbital which owes its low energy to its **deep penetration**
- Contraction in d orbital causes a considerable decrease in energy – this decrease is evidently enough to lower the energy of **3d well below 4s in the ion** that results from this.

So, now once again I think you have to see the clear picture before and after electronic electron removal. During filling out what is the consequences we have understood; that d electron repel each other strongly therefore, d electron should not be filled out first, that is the filling time; so the 4s electron fills out first. Forces 4s electron fills out first because 4s electron is kind of more stabilized compared to the 3d electron right.

Now, once you are trying to remove; let us say you have removed two electron titanium 2 plus right. Now you have to see the overall stability, 4s electron is having lower energy or s electron in general is having lower energy mainly due to the fact that it is more penetrating ok; it is more penetrating therefore, it is getting more stabilized.

Now, when you remove two electron either from 4s; irrespective of 4s or 3d overall what is happening is your attraction of the nucleus towards the electrons is going to be much more right; electrons are less right. So, the atomic number remains same, the attraction of nucleus towards the outer sphere electron or towards all the electrons is going to be much more compared to the normal or neutral situation.

Since the Z star; that means, effective nuclear charge is going to increase dramatically; this will give you know give the stability ok; this will reduce the shielding of the electron. So, there will be some sort of contraction right; contraction has a small effect in 4s because 4s is already very close to the nucleus. Comparatively, the stabilization or the contraction will cause the stabilization to 3d are much more compared to your 4s.

So, what is happening here is after removing two electrons; the effect of contraction is going to be much more filled at 3d compared to your 4s because 4 is; 4s is already lower in energy and the lower energy is the reason why they are going to be they were filling out first. Now during removal since 4s is already kind of neutralized or 4s is already having lower energy; the removal effect is going to be felt much more at that d orbital.

So, d orbital energy will be much more stabilized and removal of the electrons will be much more easier from the 4s compared to your 3d. 3d energy is going to be stabilized 3d electrons are going to be stabilized compared much more compared to 4s. So, the stabilization will lead to the removal of electrons from the 4s; not from 3d.

So, that is what we tried to summarize in here; contraction in d orbital causes a considerable decrease in energy, this decrease is evidently enough to lower the energy of 3d well below 4s in the ion that results from this. The removal of electron from 4s will be easier compared to 3d electron.