Concepts of Chemistry for Engineering
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Lecture No. 26
Polarizability

Welcome to this segment of BSC teaching, which is known as the polarizability. In this segment we will discuss about the periodic property known as polarizability. So, polarizability we can explain it as how we can distort the electron density present surrounding an atom. So, if we have an electron density that we can distort very easily in the presence of an external electric field and where the external electric field is coming, it is nothing but coming from the neighboring ions.

If it is such that this electron density present on an atom, we can easily distort we say we have a higher polarizability, and if we cannot we say it is lower polarizability and generally it is represented by this term alpha, α.

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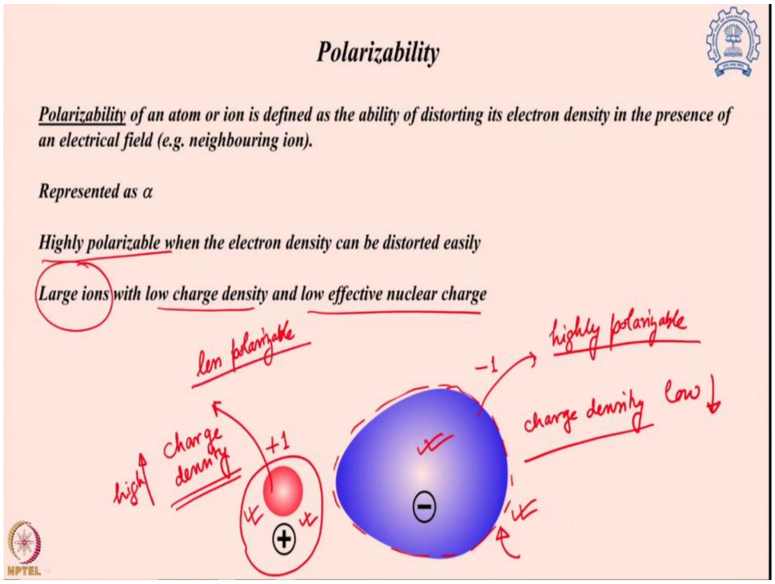

Polarizability

Polarizability of an atom or ion is defined as the ability of distorting its electron density in the presence of an electrical field (e.g. neighbouring ion).

Represented as α

Highly polarizable when the electron density can be distorted easily

Large ions with low charge density and low effective nuclear charge

So, over here I am showing you the example how we can define polarizability So, over here I am showing you two ions, one positive ion over here and one negative ion over here. Both these ions actually having one charge, red one having a + 1 charge and the blue one having - 1 charge, but this charge is distributed all over the atom electron density differently. In this red color, positively charged cation, it is a very small in size, so all the charge is confined in a very small space.

So, we can say over here the charge density which is nothing but showing you how much charge is there around the system at unit volume it is quite high because it is + 1 charge at a very small space. But at the same time, over here the charge density for this blue anion is pretty low; over there, it is quite high and over there, it is quite low. Although we have the same magnitude of charge and why it is so, because it depends on the electronic distribution around the system.

This anion is a large size anion where the electron density is quite well spread around it and that is why it is actually have a low charge density and not only that the presence of a strong electric field, for example, the presence of this red cation itself it actually distorts that electron density because this electron density around the anion is loosely held, they are not controlled very strongly from the nucleus.

So, that is why a low effective nuclear charge and the low charge density which is generally found in large ions is the main place where we can easily distort the electron density and that is why we can say these are the highly polarizable system. So, over here out of these two systems, I will call this one a highly polarizable system. And that is because the electron density of this system can be distorted very easily.

On the other hand, this system over here, we cannot distort it very easily because it is much more strongly controlled by the presence of the nuclei. So, we cannot play from outside with this electron density and distort that very easily. So, we will say this is less polarizable.

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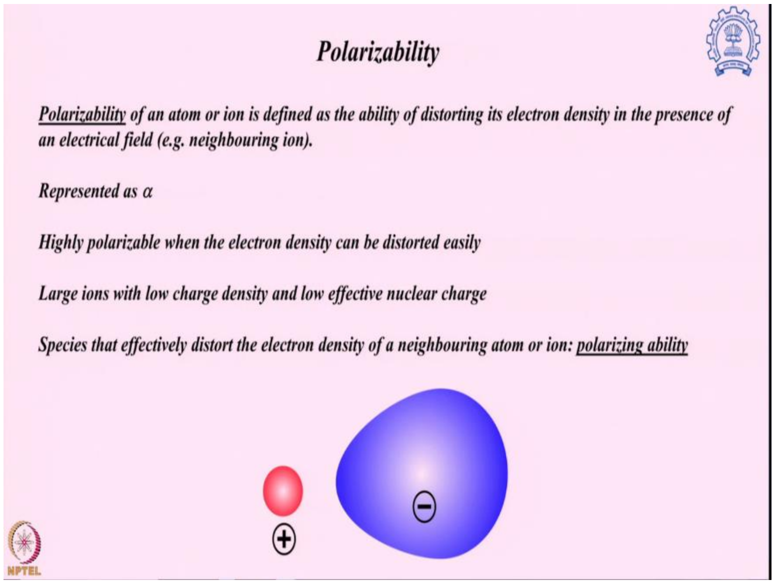

Polarizability

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Represented as α

Highly polarizable when the electron density can be distorted easily

Large ions with low charge density and low effective nuclear charge

Species that effectively distort the electron density of a neighbouring atom or ion: __polarizing ability__

Now, if we combine them together, we can say a good polarizable system or highly polarizable system is such those where the ions are in higher in size. So, they are larger in size, they have very low charge density and low effective nuclear charge so that the control over this electron density is actually pretty low from the nucleus. So, that is why in another electric field coming in the form of a neighboring ion can still control that electron density. So, not only the presence of electron density, but a very weak control from the nucleus itself is the main reason where we can see a highly polarizable system.

On the other hand, if I have a very small ion, very high charge density with a very high nuclear charge, that means, my electron density will be controlled very strongly I cannot distort that very easily, and that is going to show very low polarizability. In a different term, when we have a system and ion such a way that which actually cannot be distorted very easily that means less polarizable, but they can have polarizing ability, because they can use their large charge density to control the electron density of the other metals, the other ions, the other ligands present around.

So, that is known as the polarizing ability. The polarizing ability can be high, the polarizing ability can be high, when we have a less polarizable system. So, we can conclude over here that the high polarizable system is having less polarizing ability, whereas, the low polarizable systems having high polarizing ability.

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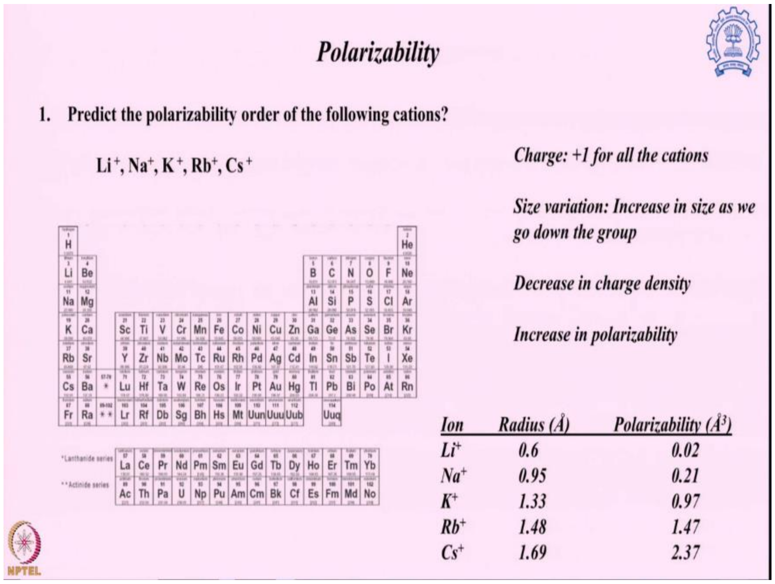

Polarizability

1. **Predict the polarizability order of the following cations?**

Li^+, Na^+, K^+, Rb^+, Cs^+

Charge: +1 for all the cations

Size variation: Increase in size as we go down the group

Decrease in charge density

Increase in polarizability

Ion	Radius (Å)	Polarizability (Å^3)
Li^+	0.6	0.02
Na^+	0.95	0.21
K^+	1.33	0.97
Rb^+	1.48	1.47
Cs^+	1.69	2.37

Now, to understand this fact, we are going to use a few problems to follow the polarizability system. To understand the polarizability better, we are going to go through some examples. So, the first problem in this particular set is we have a series of cations given over here, lithium, sodium, potassium, rubidium and cesium, each of them has + 1 charge, we try to understand what is the polarizability order among those cations.

So, as polarizability is a periodic character, we are going to show you the periodic table over here. And over here you can see the cations, all the things we are talking about is present in group 1. Now, what is happening over here, so, each of the cations have + 1 charge, so that is quite straightforward. Then, we look into the size of each of the cations because that is + 1 charge.

Now, we want to have idea where we have the lowest charge density because lowest charge density means there is less control over the electron density from the nucleus. And to have an idea, what is the lowest charge density, I need to have an idea about the charge. And about the volume. Charge you already know all of them are in + 1 charge, the difference now comes with respect to the volume.

And from a periodic table, we know if I go through this particular group from top to bottom, the size of the atoms or ions increases. So over there, from lithium to sodium to potassium to rubidium to cesium, if we take the cation size and look into the radii, we found that the size will increase as we go down.

And as it is shown over here, lithium + ion has a size of 0.6 angstrom. Sodium increases to 0.95, potassium is now more than double of lithium 1.33, it continued to increase even in rubidium to 1.5, cesium is 1.7. So, you can see almost three times increase as we go from lithium to cesium. And at the same time what is happening, we are not increasing the charge, charge is remaining the same, only we are increasing the radii. That means if we consider each of the ions as a sphere, the overall volume actually also increases.

So, as we know the volume is equal to $\frac{4}{3}\pi r^3$, if we consider a perfect sphere, r is the radii and the radii increase almost 3 times from lithium to cesium. So, almost 27 times increase in the volume is expected as we go from lithium to cesium. And that is going to affect the charge density, because the same amount of charge + 1 I am distributing over a huge amount of volume as I am increasing from lithium to cesium periodically.

And that is going to affect my polarizability, because as we know from the definition of the polarizability; low charge density, high volume is actually gives me a better or higher polarizability. So, we expect the polarizability will also follow the same trend as you go from the lithium to sodium to potassium to rubidium to cesium ions. And once it is measured, we found that is the case, so the polarizability is given in a volume factor, so that way it is $A^{\circ 3}$.

It starts from 0.2 unit for lithium is slowly increased by almost 10 times to sodium, it continues to increase almost 5 times to potassium then to almost 1.5 in the case of rubidium ion and cesium ion it is almost close to 2.4. So, you can see a huge increase in the polarizability as we move towards size.

So, if we are talking about the same amount of charge, we are only increasing the volume in a periodic property, the polarizability will also follow the same trend; increase the volume increase in the polarizability, because if we consider the same charge, the charge density is going to follow the same trend as the volume. So, that is the first question we discuss about the polarizability.

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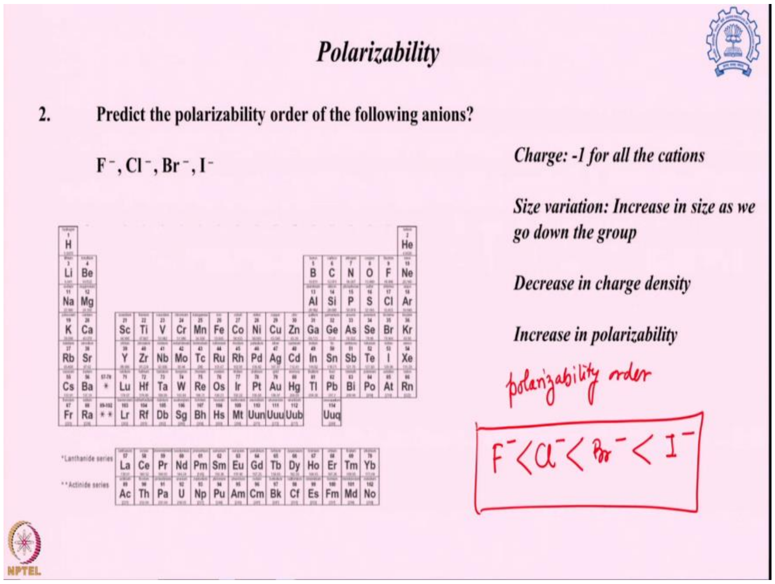

Polarizability

2. Predict the polarizability order of the following anions?

F^-, Cl^-, Br^-, I^-

Charge: -1 for all the cations

Size variation: Increase in size as we go down the group

Decrease in charge density

Increase in polarizability

polarizability order

$F^- < Cl^- < Br^- < I^-$

Let us take another question. Now, we have taken instead of a cation, an anion set, we have fluoride, we have chloride, bromide and iodide over here, which is nothing but, in this group, over here, group 17. So, all of them again have the same charge - 1 and again, we want to have an idea about the charge density. Because the charge is same, so, if we want to have an idea about the charge density, we need to know the volume and again very similar to this group 1, all the groups if you go about top to the bottom, you increase the volume and we increase the volume over here also from fluoride to chloride to bromide to iodide.

So, we are going to increase the volume and that is going to decrease the charge density as we go from the fluoride to the iodide. Why? Because charge density is nothing but amount of charge divided by the volume, the amount of charge is remaining same, volume is only increasing as we go down to the group, so, the charge density also decreases around it. And as we just know, the polarizability means nothing but increase.

So, as we know polarizability is directly connected to the charge density, as we decrease the charge density, there is an increase in polarizability. Because with a decrease in charge density, there is a more probability that I can distort the electron density with ease and this easiness of charge density distortion is known as the polarizability. So, if we have a very low charge density, that means control over this electron distribution from the nucleus is pretty low and that is going to reflect with higher polarizability.

So, even in this case, the polarizability order will be fluoride greater than chloride greater than bromide. So, with an increase in polarizability, we are going to see in a way iodide will showing you the highest polarizability is the largest ion then the bromide then the chloride then the fluoride. So, if I want to write down over here, the polarizability order, so iodide has the highest, then comes the bromide, then comes the chloride and at the end comes the fluoride. So, this is going to be the order of the polarizability of this system.

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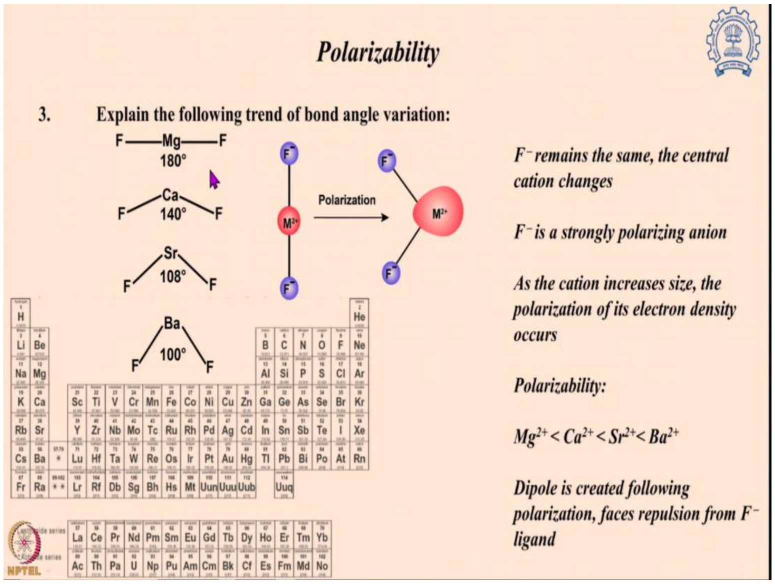

Polarizability

3. Explain the following trend of bond angle variation:

F^- remains the same, the central cation changes

F^- is a strongly polarizing anion

As the cation increases size, the polarization of its electron density occurs

Polarizability:

$Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$

Dipole is created following polarization, faces repulsion from F^- ligand

Now, go to a next question, this is a very interesting question, we talk about some metal fluorides and all these metals are coming over here from this group number 2; alkaline earth metals. We have taken magnesium, calcium, strontium and barium, it has a + 2 charge and that has two fluorides bound to it. Then, when we get a look into the bond angle of this fluoride metal fluoride, we found in magnesium fluoride, the bond angle is 180 degree which is actually expected for this kind of molecule, we were expecting a linear structure.

However, we go to magnesium to calcium we see a little bit bent structure from 180 degree it becomes 140, it bent further when you go to strontium almost 108 degree and this trend continues as we go from strontium to barium it becomes 100 degrees over here. The question is why? So, if we look into this, all these metal fluorides the common factor is fluoride is the same anion bonding to all the metals.

And then when it binds to that metal, we know fluoride itself is actually less polarizable, but it can be a strong polarizer. So, it is a strongly polarizing anion. So, it can polarize the electron density of the metal it is binding with. So, both of these fluorides present over there that can interact with the electron density present in the metals and try to distort or polarize them. So, now you have to find an idea about those four metal ions + 2 charge, which is going to be more polarizable, which is going to get polarized with respect to the fluoride atoms present there?

So, over there as you are seeing these periodic properties, again polarizability, they have all same charge + 2, all the metals are in + 2 charge over here. Then, we look into the volume magnesium to calcium to strontium to barium, I am going to increase the volume as we go down. And as we increase the volume with the same + 2 charge, I am going to decrease the charge density as I go magnesium to calcium to strontium to barium.

And that is going to give me an idea, because lower charge density means highly polarizable. So, the order of polarizability will be this following; barium will be the most polarizable system then strontium, then calcium and magnesium will be the least one. So, the fluoride, which is a strongly polarizing ion that can polarize each of the metal ions, but extend a polarizability will be different, the maximum polarizability you will find in the case of barium, then the strontium then the calcium, then the magnesium, and how it is connected with the bond angles.

Because when you have a huge electron density present with very low charge density, these fluoride ions are going to polarize them. When it polarizes, it has larger charge density on this side, less charge density on this side. And these fluoride atoms are going to face some serious repulsion with respect to this polarized electron density. So, this polarized electron density is going to repulse these fluorides and that is why they are moving from the original linear position.

So, when it is a magnesium, the charge density is quite high in the magnesium. So, there is not much interaction with the polarizability. So, magnesium is very less polarizable. So, that is means it is not get polarized, and it is not showing any interaction between the fluoride and magnesium charge density because it is not polarized anymore. But as we go to calcium, it starts polarizing and it starts moving the fluoride out of its origin linear position.

And that start from calcium and increases as we go down, because this electron density is going to get bigger and bigger. With the less charged density, the electron cloud the volume is going to increase as we go down. So, the fluoride is going to squeeze further and that is shown in the bond angle over there.

So, it is the fluoride which induces the polarizability and then the polarizable character of the metal ions come into the picture, higher polarized, highly polarizable barium is getting a huge impact on the position of the fluoride, which actually repositioned in such a way that we have a very narrow fluoride, barium fluoride bond angle of 100 degree which is almost 80-degree shift compared to the original linear magnesium fluoride.

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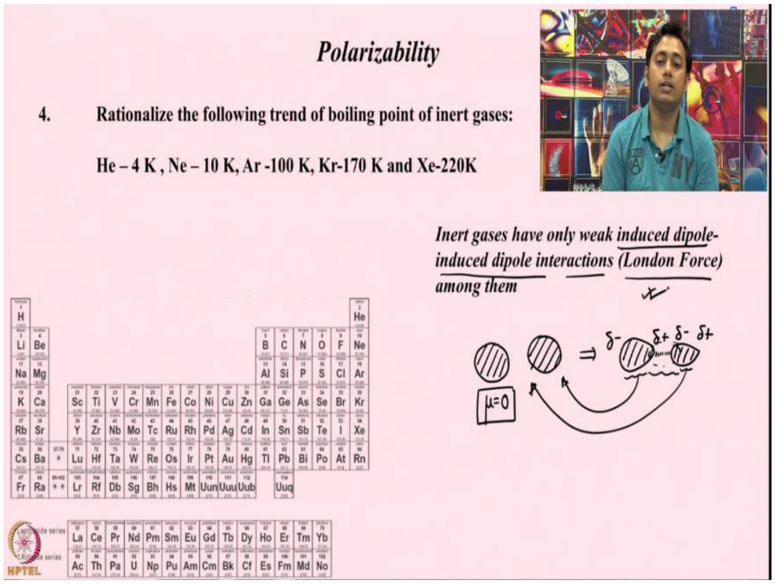

Polarizability

4. Rationalize the following trend of boiling point of inert gases:

He – 4 K , Ne – 10 K, Ar -100 K, Kr-170 K and Xe-220K

Inert gases have only weak induced dipole-induced dipole interactions (London Force) among them

Now, the last question of this segment, we have put five different inert gases over here from helium to neon to argon, krypton and xenon. And we are given the boiling point, from helium it is only 4 Kelvin, Neon 10 Kelvin, Argon 100 Kelvin, Krypton 170 Kelvin and Xenon 220 Kelvin. So, you can see it is slowly increasing; question is, can we rationalize it?

So, understand it, we have to understand the basic phenomena of boiling first. So, in the boiling when it happens, there is a liquid phase changes to a gaseous phase. Now, in the liquid phase, we have a better intermolecular interaction between the molecules; in gaseous phase the molecules are far apart, so, they have very minimal interaction happening there. So, in the liquid phase, there is good interaction, in gaseous phase it is not.

So, now, it depends how good the intermolecular interactions are, if that is a very good and very strong intermolecular interaction that is going to bring the molecules together, and that it will be very tough to get rid of this interaction so that I can move from the liquid to the gaseous state. So, if a system has a very strong interaction between the molecules, it will have higher boiling point. And if it has very less amount of intermolecular interaction, I am going to see a lower boiling point.

Now, these inert gases, does not have any dipole moment, does not have any charge to initiate some intermolecular interaction. However, they create a very unique phenomena called induced dipole induced dipole interaction. So, how that is actually coming into the picture. So over here, say we have inert gas molecule, which is spherical in nature, and have no particular dipole moment present over here, the dipole moment for this term is 0.

However, when it is coming near to another molecule, such for instantaneous motion, because the electrons are not static, so they are moving for instantaneous motion. For a particular instant, this electron density can actually get distorted a little bit. And that will create a dipole moment that can happen to the other molecule also. And that will create this dipole moment where we will have a dipolar interaction, but this is happening only for a very little instant, and then it goes back to its original position again.

But this very minute amount of dipole moment creation is good enough to create some interaction between those inert gas molecules. And those are known as induced dipole-induced dipole interaction or in other term London force, which is actually the main factor which actually bring the inert gases together.

So, now, better is this instantaneous dipole moment formation, higher will be the London force, higher will be the intermolecular interaction between the molecules and that will make sure that the inert gas would like to stay in the liquid form longer and that will reflect it in the higher boiling point. So, what we just need to know where we can get better induced dipole- induced dipole interaction. Now, induced dipole interaction happens better when we have a polarizable electron density.

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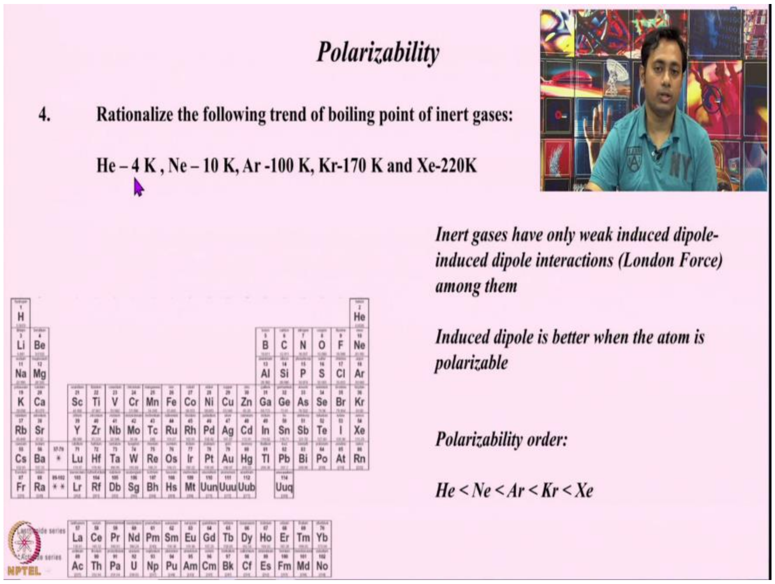

Polarizability

4. Rationalize the following trend of boiling point of inert gases:

He – 4 K , Ne – 10 K, Ar -100 K, Kr-170 K and Xe-220K

Inert gases have only weak induced dipole-induced dipole interactions (London Force) among them

Induced dipole is better when the atom is polarizable

Polarizability order:

He < Ne < Ar < Kr < Xe

So, when you have a polarizable electron density, it has much higher chance to create this induced dipole moment, because it is controlled pretty weakly by the original nucleus. And now, the polarizability order in this particular system is again coming from this particular group helium to neon to argon to krypton to xenon, as we go down, we increase the volume and that means it increased the polarizability order also in the same way.

So, the highest polarizability I am going to find xenon, then the krypton, then argon, then neon then helium. So, xenon has the higher polarizability. So, now, if we say what is the order of producing the induce dipole moment, it is going to be the same; higher the polarizability higher is the tendency to create the induced dipole moment. So, that is why we are going to create a very similar trend of polarizability order.

So, over here, higher the polarizability higher will be the tendency to create this induced dipole moment-induced dipole moment or London forces among them. So, xenon will have the most strongest interaction and that is why it is reflected the highest boiling point, on the other side helium, which is a much more smaller size atom, which will have the least amount of polarizability it will have the least amount of induced dipole moment and that is also shown in the boiling point which has the lowest boiling point among this particular series.

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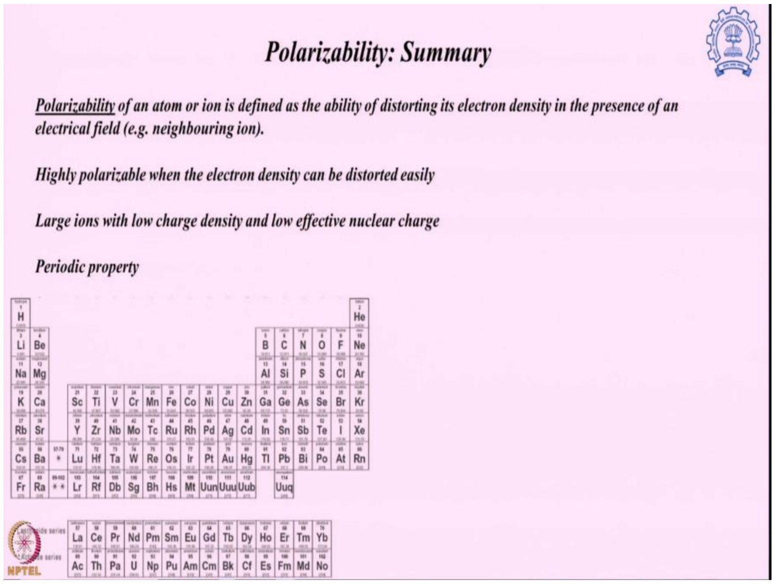

Polarizability: Summary

Polarizability of an atom or ion is defined as the ability of distorting its electron density in the presence of an electrical field (e.g. neighbouring ion).

Highly polarizable when the electron density can be distorted easily

Large ions with low charge density and low effective nuclear charge

Periodic property

So, if we want to summarize polarizability of an atom of an ion is actually nothing but how much we can distort the electron density. If it is very easy, we say it is highly polarizable and generally it is found with large ions with huge volume of electron but with very low charge density. And that is also important to know that if we have a system which is not very polarizable but it can polarize other things very easily.

For example, is small cation with very high charge density, it can distort electron density of the neighboring atom. So, it can be highly polarizing power, although it itself will be less polarizable. Same thing happens, the other side a system can be highly polarizable, when it has the very low charge density. However, it will also affect the neighbor also pretty weakly, so it will be less polarizing.

So, that is what happens in the polarizability which is a direct connection with respect to the electron density distortion with the effect of an external electric field generally given by the neighboring ions. Thank you.