Hello students, I am doctor Madhavi Zilba Naik and we will be

discussing today's module which is Lanthanide contraction.

Title of the unit is transition elements,

Module name is Lanthanide Contraction

Outline of the module:

In this module what we are going to learn is lanthanide contraction.

Cause of lanthanide contraction and consequences of Lanthanide Contraction.

Learning outcome: Students will be able to know

What is lanthanide contraction?

Understand the cause of lanthanide contractions, and justify the consequences of lanthanide contraction.

So before we start with the lanthanide contraction,

let us just briefly revise where basically this Lanthanides are present in the periodic table,

so this is your periodic table.

If you can see the square that is having a yellow colour so if you can

see that position in the periodic table, your lanthanides are basically

present there, which we normally write at the bottom of the table the way it is written.

So the lanthanide series which starts from lanthanum to lutetium, all these elements with the

atomic number starting from 57 to 71,are basically present at this position in the periodic table.

Now, going ahead and learning something about the electronic configuration.

So this is a table which highlights the lanthanides,

so the names of the lanthanides from lanthanum to lutetium

These are the symbols. This is the atomic number, the outer electronic configuration,

the electronic configuration when they are in the ionic form, that is when they lose 3 electrons with stable

Oxidation state of 3+ when they attain, what is the electronic configuration and the ionic radii of that

particular lanthanide in the ionic form, i.e the 3+ oxidation state.

So what is unique here to observe is that as you go down the group from

Lanthanum to Lutetium, the ionic radius has reduced.

There is a steady decrease in the ionic radius which we need to take into consideration.

So now actually defining what is lanthanide contraction?

So as you move from lanthanum to lutetium, there is a continuous decrease

in the size of lanthanide ions with increasing atomic number.

This decrease is known as lanthanide contraction which we have

already seen in the previous observation table.

In the pictorial form you can also see it that is represented

as you go from lanthanum to Lutetium, there is a steady decrease in the radii.

Lanthanum has the largest radius whereas Lutetium has the smallest Radius,

from Cerium 3+ to Lutetium 3 + , 14 electrons are added to the 4f orbitals.

That is after lanthanum, as you start from cerium, the filling of the 4f orbital

takes place lanthanides i.e is one electron is added as one atomic number increases.

Ionic radius decreases from 103 picometer to 85 picometer, overall the change is 18 picometers only.

Although this is a less difference but there is a steady decrease

as you can see if we directly see from lanthanum to lutetium..

Although change between the consecutive elements may not be very high,

but as you see across the series, it is quite considerable.

Now what is the cause of lanthanide Contraction?

Before understanding the cause of lanthanide contraction,

Let us understand the electrons, how they are present in different orbitals in the lanthanides.

so just a brief example of one Lanthanum which I have given here on the slide.

These are your all orbitals corresponding to respective principle quantum numbers as 12345 and 6.

and the maximum number of electrons that these orbitals contain for a lanthanum given here,

which are in the form of two electron in the first orbital, 8 electrons in the second orbital

8 in 3rd and then 18 in 4^{th}.

This is a fourth orbital which is a ***f*** orbital wherein the filling starts from cerium and

then you have 9 electrons in 5^{th} orbital and two electrons in the last outer 6s orbital.

So basically these electrons are continuously revolving around your positively charged nucleus.

So when you have this arrangement of electrons which are revolving around the nucleus.

Suddenly you are thinking about the lanthanide contraction.

So why is this lanthanide contraction happening and how this orbital arrangement is responsible for it? We will see.

What is the cause of lanthanide contraction?

The important cause of lanthanide contraction is imperfect shielding by the ***4f*** electrons,

as the atomic number increases, each succeeding element contains one

more electron in the ***4f*** orbital and one proton in the nucleus.

The ***4f*** electrons are ineffective in screening the outer electrons from the nucleus

causing imperfect shielding.

So as we have seen in the previous slide arrangement of the orbitals.

So for ***f*** orbital,the electrons which are present in the ***4 f*** orbitals are ineffective in screening

the outer electrons from the nucleus thereby causing imperfect shielding.

So basically let us understand first of all, what is shielding? and what is imperfect shading?

So when you have nucleus and you have

electrons in the different orbitals, consider this as your nucleus which is positively charged.

You have electrons may be in this is closer to the nucleus so I will see it as inner orbital.

Slightly away from the nucleus can be considered as an outer orbital.

So when you have electrons like this there are two forces that are acting over there.

So two electrons can have repulsion between the outer and the inner electrons causing repulsive force,

Or there could be an attraction between them, outer electron and with the positively charged nucleus.

Now when there is an attraction between the outer electron and the nucleus and wherein the inner

electrons are unable to stop this attraction or prevent the outer electron from

getting attracted to the nucleus when they are unable to do this, it is called as improper shielding.

Now in this case if you can see if such thing happens then the electrons will get

repelled and then they will go away.

This will be attributed towards a shielding, but when you have such kind of an

arrangement wherein the inner electron unable to shield the outer electrons get attracted to the nucleus,

that time it is called as imperfect shielding.

Here Inner orbitals are called to have a less shielding effect.

As a result of this imperfect shielding t here is a gradual increase in the nuclear attraction for the outer electrons and consequently gradual decrease in the size occurs.

Now ***4f*** electrons are in effective in screening or shielding why?

We are saying that lanthanides are getting contracted because the ***4f*** orbital which is present inside and outside there is ***5d*** and ***6s*** orbitals. Why the **4f** electrons are ineffective in shielding?

Because the there are two factors on which it depends.

First is the order of shielding effect of different orbitals

is as shown on the slide. **S** orbital Is having a higher shielding effect

then **p** then ***d*** and then ***f*** , it is dependent on the azimuthal quantum number.

As you can see the number of nodes also increases as you go from ***s*** to **d** and ***f***

Also, another important factor is the shape of the orbitals.

So shape of the **f** orbital is very much diffused.

There is one picture which displays the shapes of the ***f*** orbitals.

You can see that the shape of the ***f*** orbital is very much diffused,

which also makes it Inefficient to screening the outer electron from nuclear attraction.

So now we have seen the cause of lanthanide contraction as the

improper shielding of ***4f*** electrons, so now there is a lanthanide contraction,

So definitely there will be certain consequences of this lanthanide contraction.

So let us see the consequences of Lanthanide contraction.

The first consequence is there is a regular decrease in their ionic radii from lanthanum 3+ to lutetium 3+

So from lanthanum to lutetium there is gradual decrease in the ionic radii of these elements

Second, there is a slight increase in the electronegativity of the trivalent ions,

so definitely size is increasing that means the outer orbital electrons are

getting attracted towards the nucleus, thereby their electronegativity also increases.

Third there is a decrease in the basic strength of the oxides

and hydroxides of lanthanides with increasing atomic numbers, so thus lanthanum hydroxide

is the most basic while lutetium hydroxide is the least basic.

Now why that happens according to the Fajan's rule decrease in size of the

Cation increases the covalent character,thereby reducing the basic character of lanthanide hydroxide.

There is also regular decrease in their tendency to act as reducing agent with increasing atomic number.

Coming to the E^{o} value, There is a small but smooth increase

in the standard electrode potential values ranging from -2.5 Volts for - 2.25 Volts for Lutetium

So when they have M^{3+} ion get reduced by accepting 3 electrons,

you can see that there is a smooth increase in this electrode potential when you

move from Lanthanum to Lutetium.

Due to lanthanide contraction these elements occur together

in natural minerals and are also very difficult to separate,

which is another important consequence of lanthanide contraction.

Sixth the lanthanide contraction has a highly significant effect

on the relative properties of the elements which precede and follow the lanthanides in the periodic table.

So now what has happened because of the position of the lanthanide in the periodic table,

as we have seen earlier, the lanthanide contraction is having

an effect also on the elements which follow lanthanides in the periodic table i.e , the preceding elements.

So what is that effect on the preceding elements is that, there is close resemblance between the ***4d*** that is a second transition series and ***5d*** i.e third transition series.

we know that there are three transition series, 3d,4d and 5d but because of lanthanide contraction, there is a close resemblance between the ***4d*** and ***5d*** series elements.

Now when we say close resemblance meaning exactly what is happening?

So a close resemblance, example is that of Zirconium and Hafnium, Niobium and Tantalum of Molybdenum and tungsten.

These are basically the elements from 4d and the 5d series which have almost the similar atomic radius and this is the basic main important consequence of the lanthanide contraction.

Now where are these elements situated? how lanthanide contraction is affecting that , we will see in the next slide.

so this is your Periodic table and you have your lanthanides which are situated here.

OK,

so basically from here to here that is 57 to 71 Number . Actually the position is here and the following element which is 72. Now how that is affecting the atomic radius of the these preceding elements we shall see.

As for the periodic trend, your atomic radii increases as you go down the group. So if I consider this group which has a Scandium element as I go down the group.

Atomic radius increases. This is a Proper common trend of the periodic

table followed along this column or your group. Now when it comes to this group wherein

There is a titanium ,zirconium and hafnium, what we observe is that the atomic radius

of zirconium and hafnium is almost similar. There is no increase as such which

you can see in the previous element also in the first and second group

or even in the following groups. So why is this similarity in the sizes?

Because between this and this element, there is this entire lanthanide series,

and which shows lanthanide contraction, which means a gradual decrease in

size so that decrease in size is actually affecting the reduction

in the size of this half name, ultimately making Zirconium and

Hafnium of the same atomic radius. Similar observations are also

seen for the niobium tantalum, Molybdenum, tungsten and so.

So this is one of the important consequences lanthanide contractions.

Also, there is another effect on the ionization energy.

That is the ionization energy of ***5d*** transition series is higher

than 3d and 4d Transition series. So comparing with the 3d series and 4d series,

the ionization energy of 5d is higher again because there

is reduction in size. So definitely electrons are pulled

towards the nucleus and they by their ionization energy is higher so it

will take more energy to remove those.

Electrons, so these were the consequences of lanthanide contraction.
These are the references.