Main Group Chemistry
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Lecture - 03
Classification of Main Group Compounds

Welcome to my lecture series on the chemistry of main group elements. In my previous lecture I was discussing about the classification of main group compounds and I had mentioned that all compounds of main group elements can be simply classified into three categories; main group hydrides, main group oxides and main group halides.

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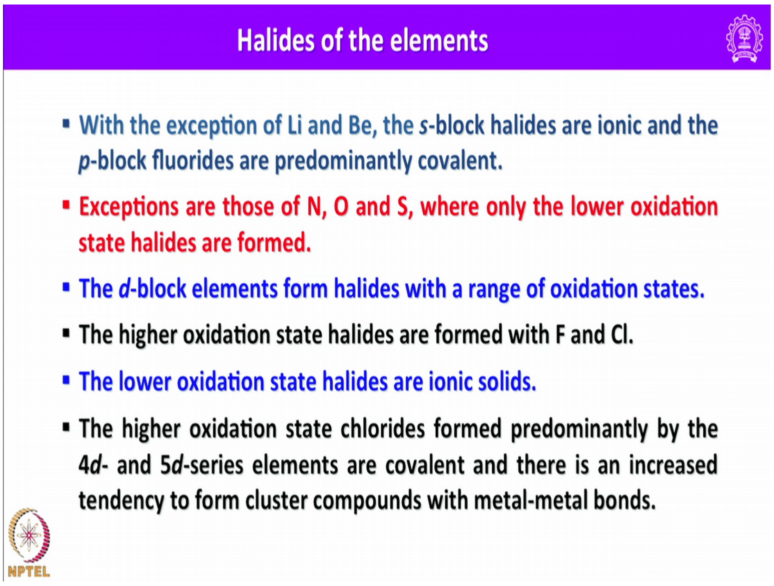

Halides of the elements

- With the exception of Li and Be, the *s*-block halides are ionic and the *p*-block fluorides are predominantly covalent.
- Exceptions are those of N, O and S, where only the lower oxidation state halides are formed.
- The *d*-block elements form halides with a range of oxidation states.
- The higher oxidation state halides are formed with F and Cl.
- The lower oxidation state halides are ionic solids.
- The higher oxidation state chlorides formed predominantly by the 4*d*- and 5*d*-series elements are covalent and there is an increased tendency to form cluster compounds with metal-metal bonds.

So, I had stopped while discussing about main group halides, so let me continue from where I had stopped. The halides of main group elements are an important class of compounds and with the exception of lithium and beryllium the s-block halides are essentially ionic in nature and the p-block fluorides are predominantly covalent and of course exceptions are always there and here exceptions are those of nitrogen, oxygen and sulphur where only the lower oxide state halides are formed.

And in case of d-block elements they form halides with a range of oxidation states, the higher oxidation state halides are formed especially with fluorine and chlorine I had already mentioned that, fluorine is capable of stabilizing any element in the periodic table in it is highest possible oxidation state. And the lower oxidation state halides of main group elements are essentially ionic solids, the higher oxidation state chlorides formed predominantly by the 4 d and 5 d series elements and which are covalent and there is an increased tendency to form cluster compounds with metal bonds.

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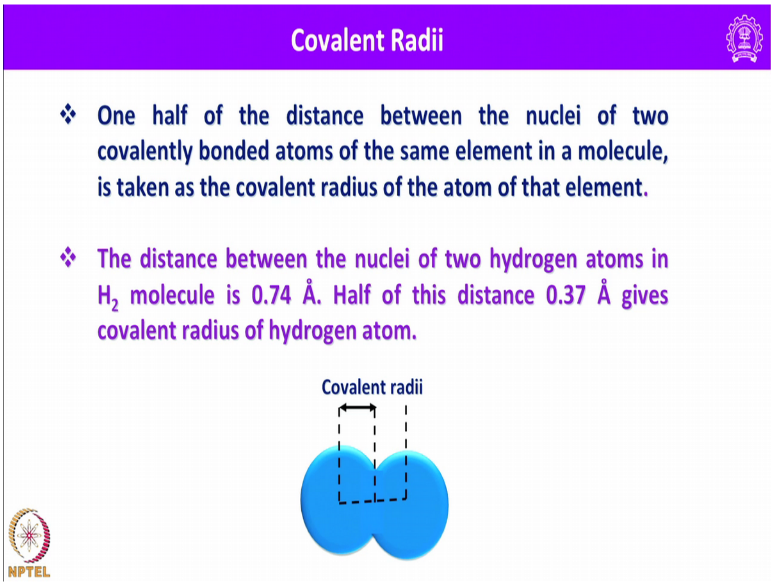

Covalent Radii

- One half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule, is taken as the covalent radius of the atom of that element.
- The distance between the nuclei of two hydrogen atoms in H_2 molecule is 0.74 Å. Half of this distance 0.37 Å gives covalent radius of hydrogen atom.

So, our interest is only focused towards the main group halides, so let us not worry too much about the transition metal chemistry and let us look into some important periodic properties and also some entities we come across while discussing the classification and periodic trends. The important term we come across is covalent radii, what is covalent radius is? One half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule is taken as the covalent radius of the atom of that element, essentially in a neutral homo diatomic species the distance between the two nuclei is essentially the covalent diameter and half of that one will give you the covalent radius of individual atoms.

The distance between the nuclei of two hydrogen atom in H 2 molecule is 0.74 angstrom unit, half of this distance that is 0.37 angstrom unit gives the covalent radius of hydrogen atom and you can see here how to determine the covalent radius for example you take a diatomic molecules shown like that and the distance between the two nuclei I will give you some information about the covalent diameter and now this half the distance is what we call it as covalent radius.

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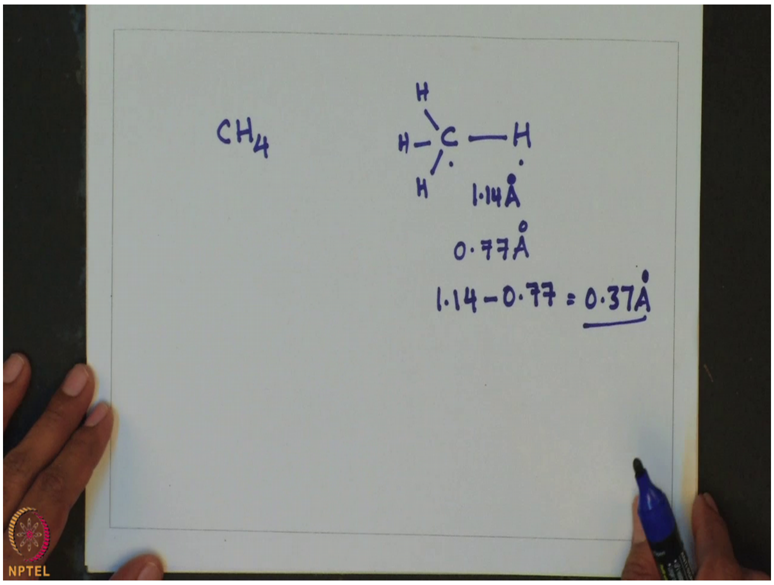

So one can calculate the covalent radii of other elements from the inter nuclear distance of the elements whose covalent radii are known, for example; You consider methane, I can simply write in this fashion and the inter nuclear distance between these two carbon and hydrogen is one 1.14 angstrom units, so in this we know the inter nuclear distance of carbon and hydrogen is 1.14 angstrom unit.

And also we know the covalent radius of carbon that is 0.77 angstrom unit, from this one we should be able to tell, what is the covalent radius of hydrogen atom so that means simply subtract 0.77 from 1.14 that essentially gives you 0.37 angstrom unit this is essentially the covalent radius of hydrogen. So this is how the covalent radius of unknown atom can be calculated just by measuring inter nuclear distance and knowing the covalent radius of one of the atoms.

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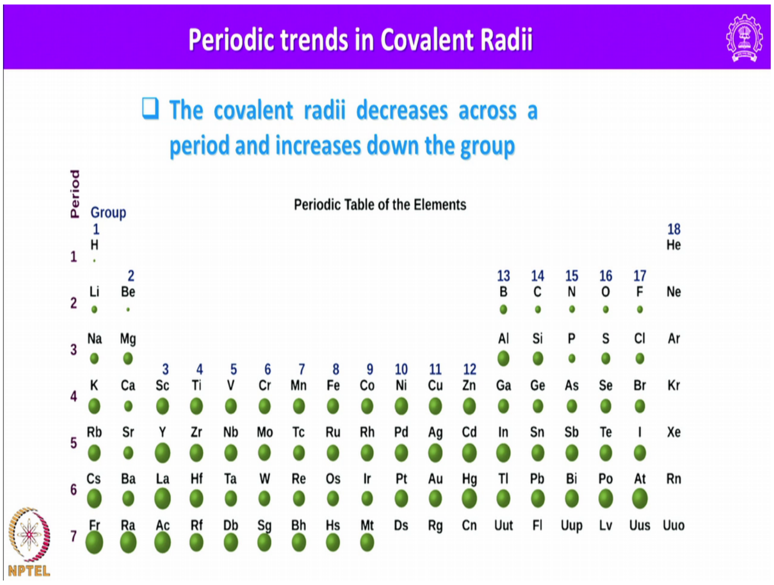

Periodic trends in Covalent Radii

- ☐ The covalent radii decreases across a period and increases down the group

Periodic Table of the Elements

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

So, this periodic table what I have displayed here shows the trend in covalent radii for example; if you see here the covalent radius is increasing down a group and decreasing across a period of course the reason we already discussed so let me not elaborate more on this one. What one should remember is the covalent radii decreases across a period and increases down a group.

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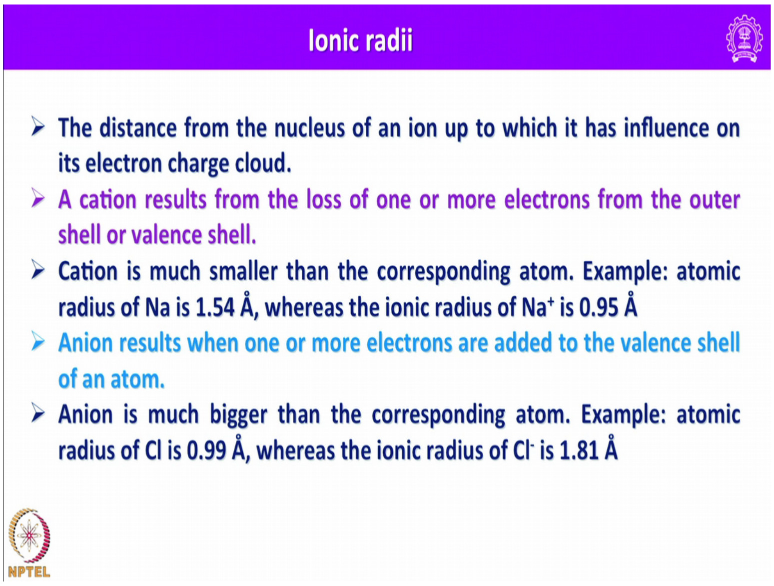

Ionic radii

- ➢ The distance from the nucleus of an ion up to which it has influence on its electron charge cloud.
- ➢ A cation results from the loss of one or more electrons from the outer shell or valence shell.
- ➢ Cation is much smaller than the corresponding atom. Example: atomic radius of Na is 1.54 Å, whereas the ionic radius of Na^+ is 0.95 Å
- ➢ Anion results when one or more electrons are added to the valence shell of an atom.
- ➢ Anion is much bigger than the corresponding atom. Example: atomic radius of Cl is 0.99 Å, whereas the ionic radius of Cl^- is 1.81 Å

And let us look into the ionic radius, the distance from the nucleus of an ion up to which it has influence on it is electron charge cloud is essentially termed as ionic radius, I repeat again that distance from the nucleus of an ion up to which it has influence on it is electron charge cloud or electron density is essentially termed as ionic radius and a cat ion results from the loss of one or more electron from the outer shell or valence shell and cat ion is much smaller than the corresponding atom.

For example; if you consider the atomic radius of sodium that is 1.54 angstrom unit, whereas the ionic radius of sodium plus ion is 0.95 angstrom unit and when we talk about anion that results when one or more electrons are added to the valence shell of an atom anion is much bigger than the corresponding atom you can see clearly in case of chlorine, the atomic radius of chlorine is 0.99 angstrom units whereas the ionic radius of chloride ion is 1.81 angstrom unit, so this gives you about the relative sizes of ionic radii versus atomic radius and also between ionic radii and covalent radii while considering the both for the cat ion and as well as anions.

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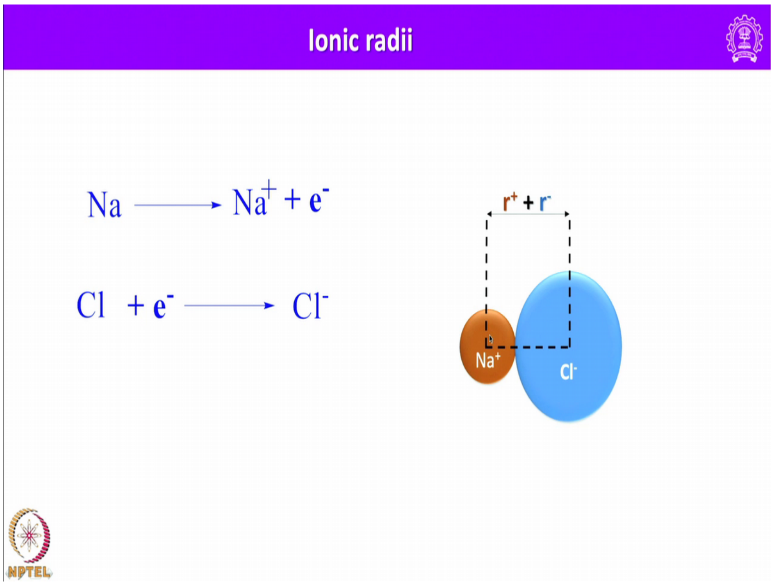

Ionic radii

$$Na \longrightarrow Na^+ + e^-$$

$$Cl + e^- \longrightarrow Cl^-$$

So, let us look into the sodium for example; sodium when you remove an electron that generates a cat ion and similarly chlorine on addition of an electron it generates an anion and I have shown in this cartoon here N a plus is there and it interacts with much larger chloride ion to form N a C l and this N a C l this inter nuclear distance is shown here. And this inter nuclear distance will give you the total sum of the ionic radii of sodium ion as well as chloride ion.

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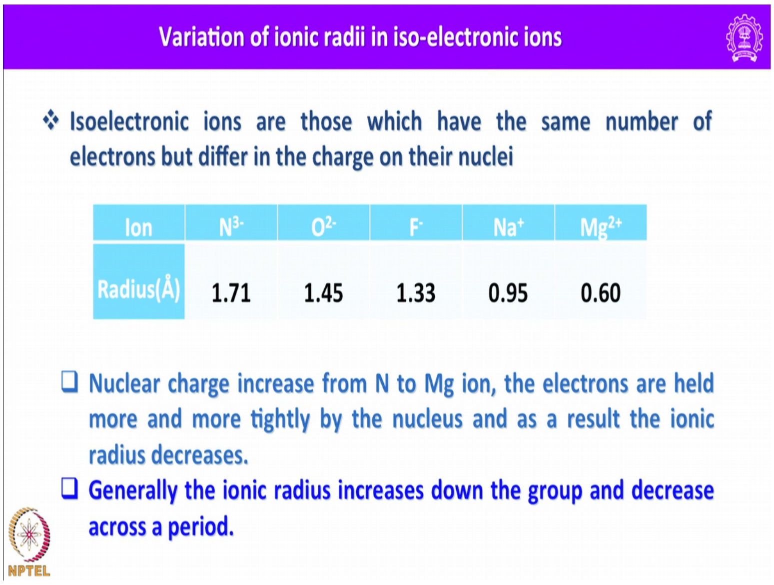

Variation of ionic radii in iso-electronic ions

- Isoelectronic ions are those which have the same number of electrons but differ in the charge on their nuclei

Ion	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}
Radius(Å)	1.71	1.45	1.33	0.95	0.60

- ☐ Nuclear charge increase from N to Mg ion, the electrons are held more and more tightly by the nucleus and as a result the ionic radius decreases.
- ☐ Generally the ionic radius increases down the group and decrease across a period.

So, another term I am going to introduce is isoelectronic species, so what is isoelectronic species? And how the ionic radii vary among isoelectronic is isoelectronic species can be seen here, so isoelectronic ions are those which have the same number of electrons, but differ in the charge on their nuclei. Let us look into this series of isoelectronic species I have given here, let us look into these series here nitride anion is given N 3 minus and oxide is there O 2 minus and fluoride F minus and N a plus and Mg 2 plus if you just look into the nuclear charge know now, nuclear charge essentially 12 in case of magnesium, 11 in case of sodium and 9 in case of fluorine 8 in case of oxygen and 7 in case of nitrogen.

Now, basically out of 2 valence electrons from magnesium 2 have been eliminated to form magnesium 2 plus and the 1 valence electronics taken from sodium to generate N a plus and then similarly 1 electron is added in case of fluorine and 2 electron in case of oxygen and 3 electron in case of nitrogen to generate this isoelectronic series in this isoelectronic series if you just look into it the number of electrons is confined to number 10 in all this compounds we have total 10 electrons are there, that means they have the neon electronic configuration. And here look into their ionic radii now in case of nitrate anion it is 1.71, in case of oxide it is 1.45 in case of fluoride it is 1.33 and in case of sodium cat ion it is 0.95 and in case of divalent magnesium it is 0.60.

And now the question is why this ionic radius is decreasing in this order? So that information comes if we just look into the effective nuclear charge, the nuclear charge increases from sodium to magnesium ion, the electrons are held more and more tightly by the nucleus and as a result the ionic radii decreases, generally the ionic radius increases down the group and decreases across a period that we saw in the previous slide. And so another term we should be familiar while discussing chemistry is Van der Waals interactions and Van der Waals radius.

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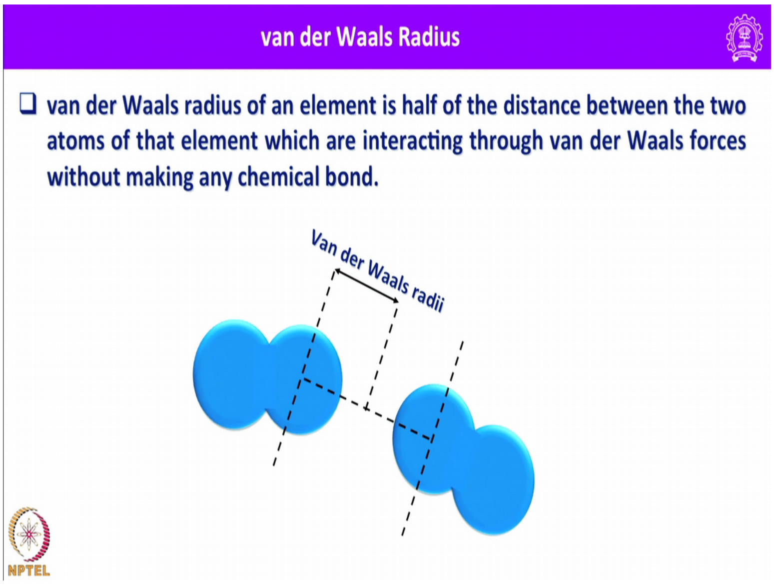

van der Waals Radius

- van der Waals radius of an element is half of the distance between the two atoms of that element which are interacting through van der Waals forces without making any chemical bond.

So what is Van der Waals radius? So Van der Waals radius of an element is half of the distance between the two atoms of that element which are interacting through Van der Waals forces without making a formal chemical bond, I repeat again Van der Waals radius of in element is half of the distance between the atoms of that element which are interacting through Van der Waals forces without making any formal chemical bond.

So, how to visualise that one? Let us look into this cartoon here let us assume there is a diatomic molecule is there and the another diatomic molecule is in it is close vicinity and now whatever the dotted line that shows the distance between the two nucleus through Van der Waals interaction and now this distance half the distance is essentially called as Van der Waals radius, Van der Waals forces or the weak forces which contribute to intra molecular bonding between the molecules.

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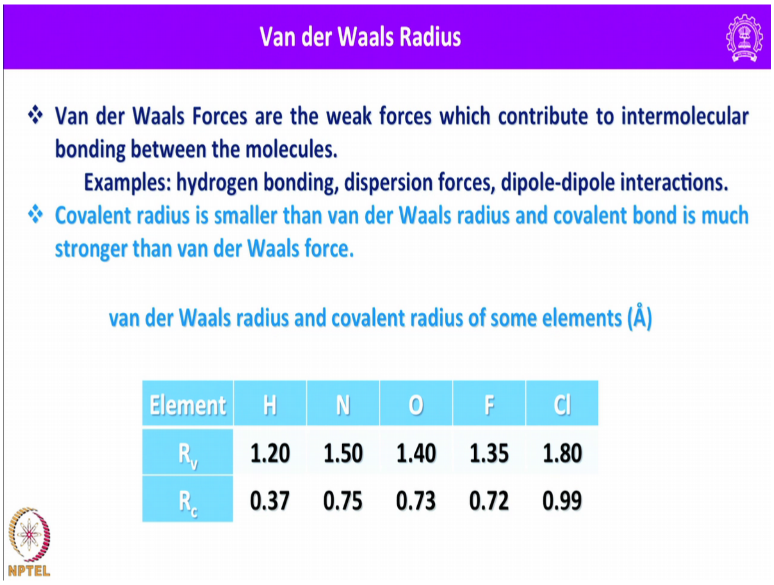

Van der Waals Radius

- Van der Waals Forces are the weak forces which contribute to intermolecular bonding between the molecules.
  Examples: hydrogen bonding, dispersion forces, dipole-dipole interactions.
- Covalent radius is smaller than van der Waals radius and covalent bond is much stronger than van der Waals force.

van der Waals radius and covalent radius of some elements (Å)

Element	H	N	O	F	Cl
R_v	1.20	1.50	1.40	1.35	1.80
R_c	0.37	0.75	0.73	0.72	0.99

Example; hydrogen bonding, dispersion forces, dipole interactions, London forces etcetera and covalent radius is smaller than Van der Waals radius and covalent bond is much stronger than Van der Waals forces. Van der Waals radius and covalent radii of some elements I have given here for better understanding for example; hydrogen, nitrogen, oxygen, fluorine and chlorine both covalent radii and Van der Waals radii are given here, you can see the covalent radii is about 0.37, 0.75, 0.73, 0.72 and 0.99 respectively in case of those element shown there and if you just look into the Van der Waals radii that is almost three to four times more in case of hydrogen and at least it is them it is the double the what measures as covalent radius, so that means essentially Van der Waals radii or much larger compared to covalent radius.

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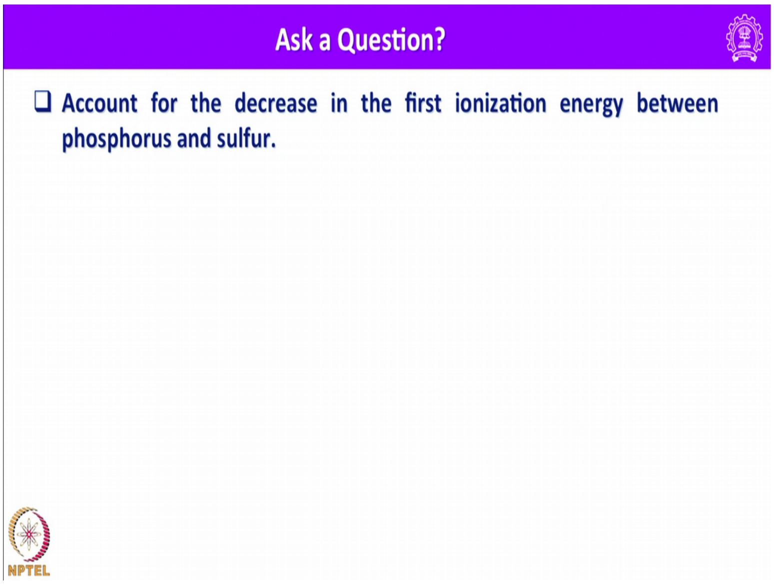

Ask a Question?

- ☐ Account for the decrease in the first ionization energy between phosphorus and sulfur.

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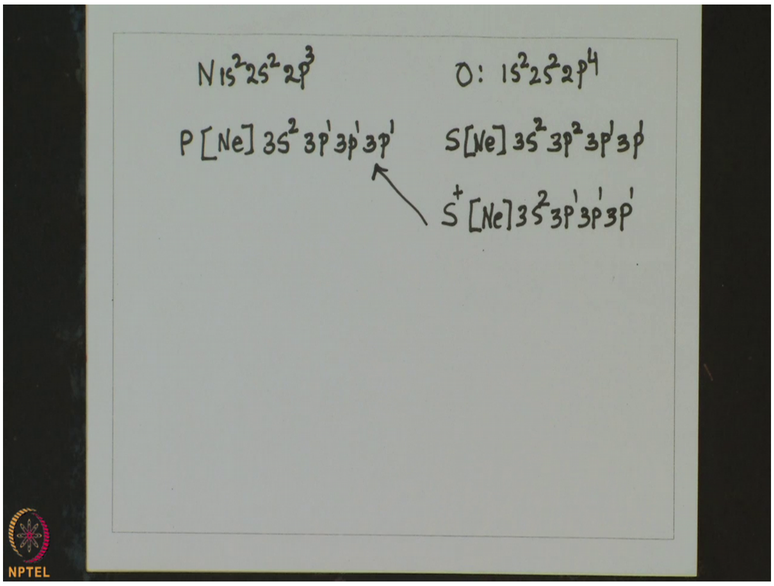

N $1s^2 2s^2 2p^3$　　O: $1s^2 2s^2 2p^4$

P [Ne] $3s^2 3p^1 3p^1 3p^1$　　S [Ne] $3s^2 3p^2 3p^1 3p^1$

S^+ [Ne] $3s^2 3p^1 3p^1 3p^1$

Let us look in to some questions here account for the decrease in the first ionization energy between phosphorus and sulphur. So, the question is account for the decrease in the first ionization energy between phosphorus and sulphur, let us look into it first what we should do is; first we should write the electronic configuration for both phosphorus as well as sulphur, instead of writing 3 p 3 for simplification and better understanding I am writing 3 p 1, 3 p 1, 3 p 1.

Similarly let me write for sulphur as well. So, if you just look into the electronic configuration of phosphorus and sulphur this is very similar to the case of nitrogen and oxygen, in case of nitrogen what we have is 2 s 2, 2 p 3 and in case of oxygen what we have is 1 s 2, 2 s 2, 2 p 4.

So that means in p orbital we have 3 electrons in case of phosphorus whereas 4 electrons in case of sulphur, so that means in case of sulphur we have one extra electron and that is paired up in one of the p orbital and here the intra electronic repulsion between these two electrons is considerably more compared to the situation in phosphorus as a result what happens by losing one electron sulphur readily attains half filled electronic configuration, that means I can write s plus.

So this is similar to what we come across in case of phosphorus, so because of this one what happens it is very easy to remove the electron from sulphur to make it s plus whereas, in case of phosphorus or in case of nitrogen since we have half filled electronic configuration little more energy has to be spent in order to remove that first electron in the form of first ionization energy. So this will give some idea about the relative ionization energy of various elements in the periodic table.

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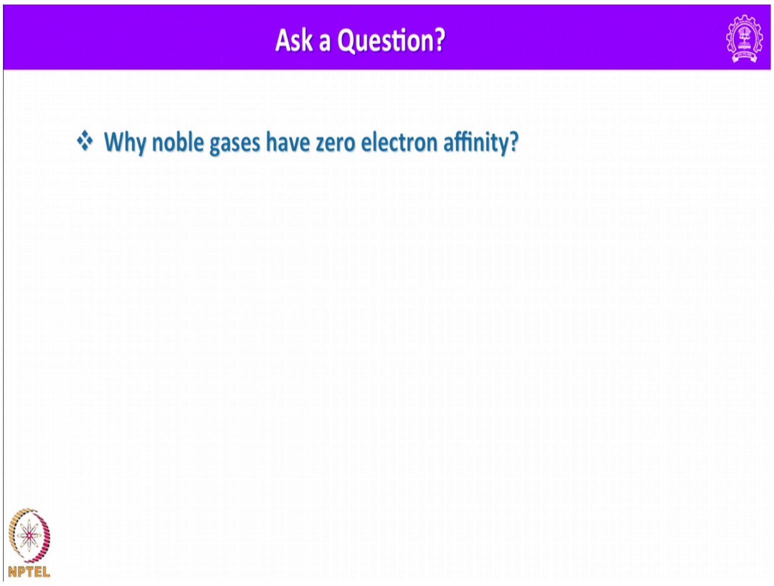

Ask a Question?

- Why noble gases have zero electron affinity?

Let us look into another question very interesting question, why noble gases have 0 electron affinity? So this is because all noble gases have completely filled valence shell, that means all the noble gases have s 2 p 6 electronic configuration and because of this s

2 p 6 configuration all electrons are held firmly and as a result it is very difficult to ionize the electrons to generate cationic species and since most of the elements have a tendency to attain the next inert gas configuration, because that is relatively more stable and electrons are much more firmly held by the nucleus, since noble gases do not have any vacant orbital in their valence shell and they have a completed electronic configuration of s 2 p 6 they have no tendency to add another electron as a result noble gases have 0 electron affinity.

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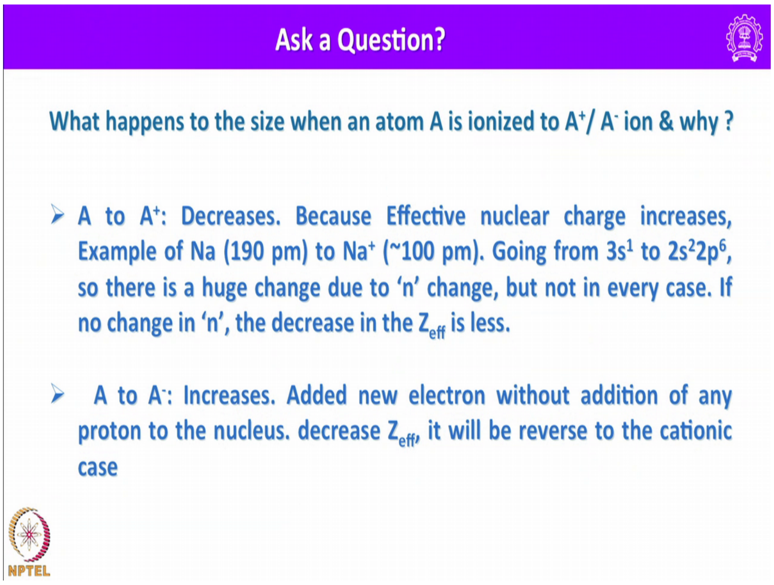

Ask a Question?

What happens to the size when an atom A is ionized to A^+/ A^- ion & why ?

- A to A^+: Decreases. Because Effective nuclear charge increases, Example of Na (190 pm) to Na^+ (~100 pm). Going from $3s^1$ to $2s^2 2p^6$, so there is a huge change due to 'n' change, but not in every case. If no change in 'n', the decrease in the Z_{eff} is less.
- A to A^-: Increases. Added new electron without addition of any proton to the nucleus. decrease Z_{eff}, it will be reverse to the cationic case

So, let us look into another interesting question, what happens to the size when an atom A is ionized to A plus or A minus and why? This already we discussed. When we add an electron a anion is generated and when we remove an electron a cat ion is generated, so in general this when you consider the radius A to A plus it should decrease, because the effective nuclear charge increases now remaining electrons are held more firmly by nucleus for example; we consider the case of sodium where sodium atom has 190 Pico metre as it is covalent atomic radius, whereas N a plus has 100 Pico metre, so that indicates the decrease in the atomic radius of sodium to become ionic radii of 100 Pico metre.

So that means, going from 3 s 1 to 2 s 2 p 6 electronic configuration, there is a huge due to n change but not in every case if no change in n the decrease in the Z effective is always less. So, similarly let us consider the case of A going to A minus, so here it is anticipated that ionic radius increases added new electron without addition of any proton to the nucleus will make the nucleus less effective in holding that extra electron that means, the decrease in effective nuclear charge is responsible for increasing the ionic radius of any given atom when an electron is added to it.

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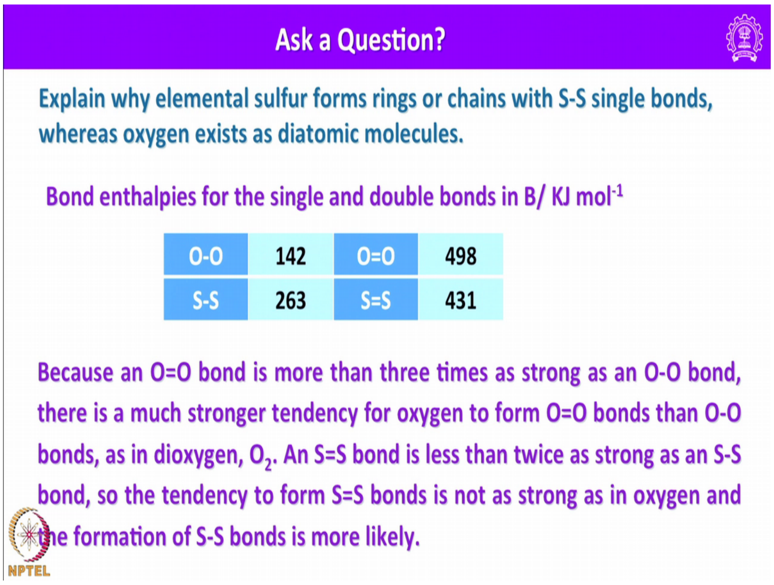

Ask a Question?

Explain why elemental sulfur forms rings or chains with S-S single bonds, whereas oxygen exists as diatomic molecules.

Bond enthalpies for the single and double bonds in B/ KJ mol^{-1}

O-O	142	O=O	498
S-S	263	S=S	431

Because an O=O bond is more than three times as strong as an O-O bond, there is a much stronger tendency for oxygen to form O=O bonds than O-O bonds, as in dioxygen, O_2. An S=S bond is less than twice as strong as an S-S bond, so the tendency to form S=S bonds is not as strong as in oxygen and the formation of S-S bonds is more likely.

So, let us look into another question explain why elemental sulphur forms rings or chains with S-S single bond? We know that sulphur exist as s 8 and higher ring form whereas, oxygen exists as a diatomic molecule, so let us look into the bond enthalpies for the single and double bonds in both the cases for example; in case of oxygen it is 142 kilojoules per mol whereas, in case of oxygen double bonds it is 498 kilojoules per mol and in the same way we shall look into S-S bond enthalpy that is 263 kilojoules per mol whereas, the S-S double bond is 431 kilojoules per mol.

So you can see the difference because O-O double bond is more than three times as strong as a O-O single bond oxygen has a tendency to form O-O double bond whereas, in case of sulphur if you just look into this S-S single bond enthalpy it is 263 when it has made S-S double bond, the bond enthalpy should have been at least twice the sum of the S-S single bond enthalpies that should have been at least 526 and so instead what we see is 431 kilojoules per mol.

So that means, by making a S-S double bond sulphur is not going to gain any extra stability, instead by making two single bonds it can have extra stability as a result sulphur exists in the form of S 8 ring whereas, oxygen exists in the form of a diatomic molecule. So, let us re look into some important properties of atoms, in an atom nucleus is surrounded by electrons in various shells depending on the atomic number, the nuclear charge experienced by the electrons is not uniform and it decreases as electrons are added to the higher shells.

So, as a result the magnitude of the influence of the nucleus on electrons decreases with the increase in the size of the atoms as added electrons are farther from the nucleus, that means this is due to the shielding or screening of nuclear charge by inner or core electrons that means, there should be a way to calculate or estimate the effective nuclear charge by each and every electron around the nucleus. That means we have to have some method of measuring the effective nuclear charge of an atom for this one Slater has formulated a new method through some rules to find out the effective nuclear charge so let us discuss the slater rules and how to determine effective nuclear charge for various atoms or various electrons in their different orbitals in my next lecture.

Thank you very much.