Main Group Chemistry
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Lecture - 04
Effective Nuclear Charge

Welcome to my lecture series on the chemistry of main group elements. In my last lecture I was discussing about the effective nuclear charge so let me continue from where I had stopped, I had just mentioned that the magnitude of the influence of the nucleus on electrons decreases with increasing the size of atoms as added electrons are further from the nucleus this is essentially due to the shielding or screening of nuclear charge by inner or core electrons that means, we should find a method to calculate or estimate the effective nuclear charge by each and every electron around the nucleus for this one as slater has suggested some rules.

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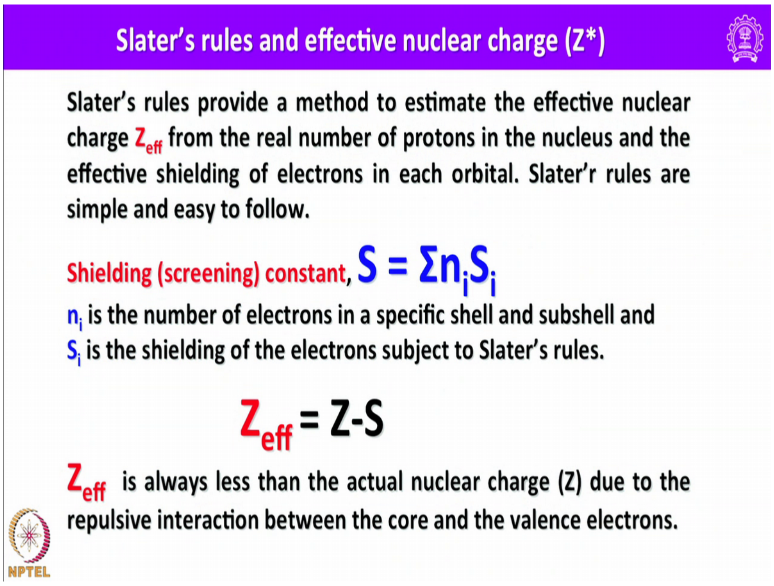

Slater's rules and effective nuclear charge (Z*)

Slater's rules provide a method to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital. Slater'r rules are simple and easy to follow.

Shielding (screening) constant, $S = \Sigma n_i S_i$

n_i is the number of electrons in a specific shell and subshell and
S_i is the shielding of the electrons subject to Slater's rules.

$$Z_{eff} = Z\text{-}S$$

Z_{eff} is always less than the actual nuclear charge (Z) due to the repulsive interaction between the core and the valence electrons.

Let us look into those things; Slater's rule and the effective nuclear charge how slater estimates is given here, so he provides a method to estimate the effective nuclear charge Z effective from the real number of protons in the nucleus that is equal into the atomic number and the effective shielding of electrons in each orbital, Slater's rules are simple and very easy to follow for example; you can look into the formula he has given the shielding or screening constant S is nothing but the sigma n i s i, where n i is the number of electrons in a specific shell and sub shell and s i is the shielding of electrons subject to Slater's rules. And then by knowing the screening constant and simply by subtracting the value of screening constant from the atomic number one can estimate the effective nuclear charge Z effective. So, Z effective is nothing but Z minus S and one should remember the effective nuclear charge Z effective is always less than the actual nuclear charge Z due to the repulsive interaction between the core and valence electrons.

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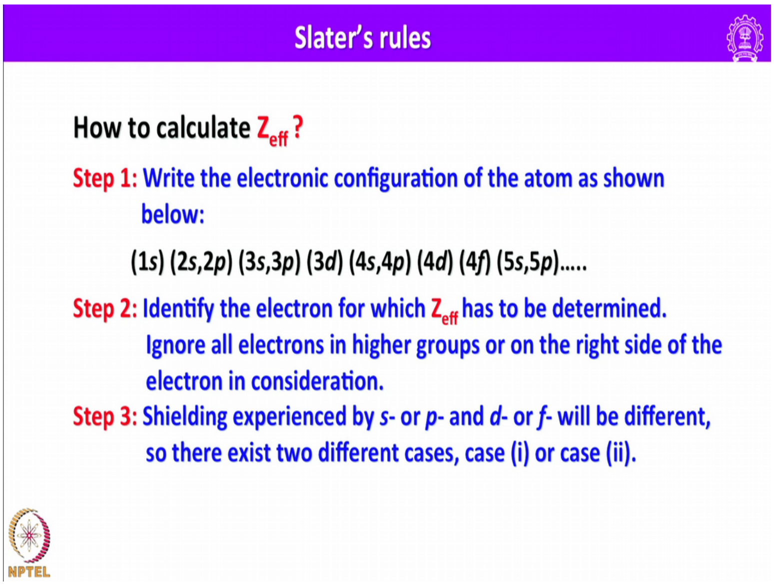

Slater's rules

How to calculate Z_{eff} ?

Step 1: Write the electronic configuration of the atom as shown below:

(1*s*) (2*s*,2*p*) (3*s*,3*p*) (3*d*) (4*s*,4*p*) (4*d*) (4*f*) (5*s*,5*p*)…..

Step 2: Identify the electron for which Z_{eff} has to be determined. Ignore all electrons in higher groups or on the right side of the electron in consideration.

Step 3: Shielding experienced by *s*- or *p*- and *d*- or *f*- will be different, so there exist two different cases, case (i) or case (ii).

So how to calculate effective nuclear charge, we have to follow simple three steps, first: one has to write down the electronic configuration of the atom as shown there you can see here 1 s, 2 s, 2 p, 3 s, 3 p, 3 d, 4 s, 4 p, 4 d something like this and also I have added some parenthesis at regular interval it has some significance, step 2: Is identify the electron for which Z effective has to be determined and ignore all electrons in higher groups or on the right side of the electron in consideration, because whatever electrons we have on the right side or not coming in between the nucleus and the electrons we are considering. And third step: Is shielding experienced by s or p and d or f will be very different.

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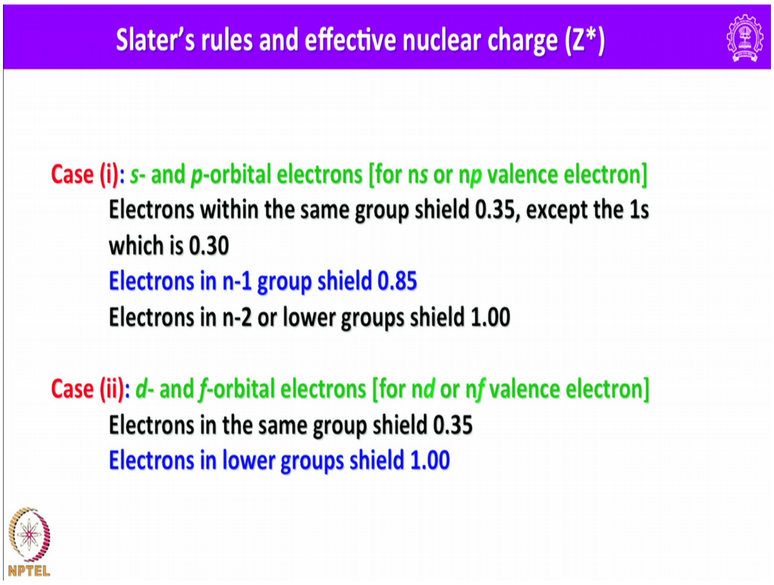

Slater's rules and effective nuclear charge (Z*)

Case (i): *s*- and *p*-orbital electrons [for *ns* or *np* valence electron]

Electrons within the same group shield 0.35, except the 1s which is 0.30

Electrons in n-1 group shield 0.85

Electrons in n-2 or lower groups shield 1.00

Case (ii): *d*- and *f*-orbital electrons [for *nd* or *nf* valence electron]

Electrons in the same group shield 0.35

Electrons in lower groups shield 1.00

So that means there exist two different cases we call them as case 1 and case 2; how to determine the shielding constant is given in case 1 for example; electrons within the same group shield to an extent of 0.35 except the 1 s electron in that one it is estimated to be 0.30 and electrons in n minus 1 group shield to an extent of 0.85 and electrons in n minus 2 group or lower groups shield to an extent of 1 that means all electrons should be together multiplied by 1 to get that screening constant, in case of case 2: we are considering for determining the screening constant for d and f electrons.

So, here electrons in the same group shield to an extent of 0.35 this is very similar to what we mentioned about s and p and electrons in lower groups shield to an extent of 1, so that is a difference between s and p and d and f, in case of s and p we are considering both n minus 1 group and n minus 2 group and the rest as separate units whereas, in case of d and f only we are considering 2 cases, one is; the shielding of the electrons within the same groups and the Shielding's in lower group no matter how many electrons are there simply they have to be multiplied by 1 to get the value.

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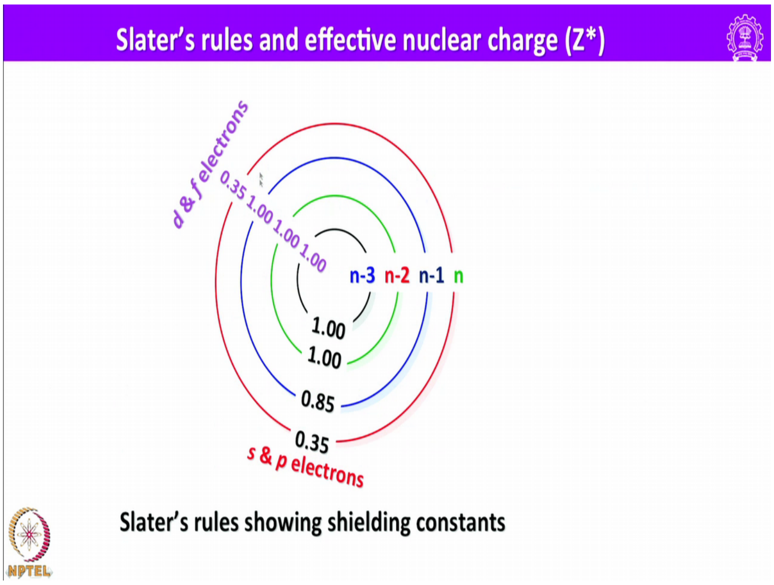

Slater's rules and effective nuclear charge (Z*)

Slater's rules showing shielding constants

So, this figure depicts very nicely a Slater's rules you can see here in case of d and f block; the electrons in the same group will contribute 0.35 and rest of the elements will be simply contributing 1 towards the screening where in case of s and p electrons; in the within the same group the shielding is to an extent of 0.35 and in case of the n minus 1 shell it is 0.85 and n minus 2 and lower it is 1.

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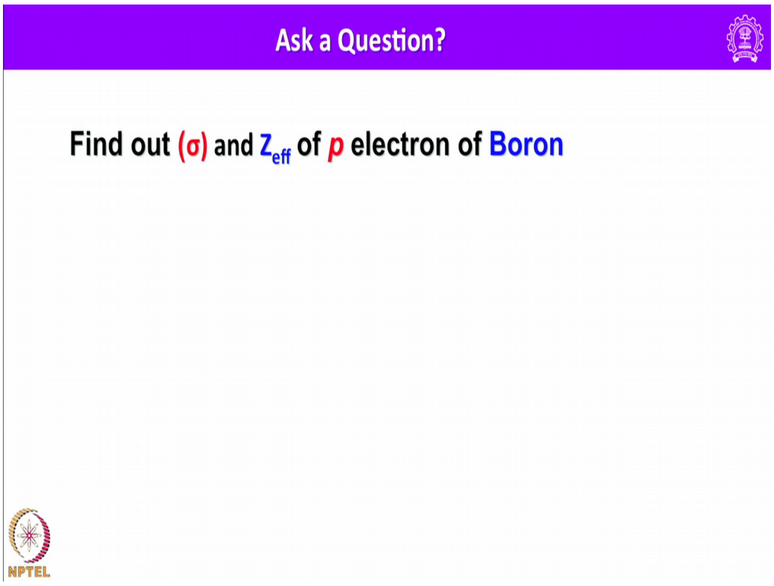

Ask a Question?

Find out (σ) and Z_{eff} of p electron of Boron

So, let us look into some examples; to examine authenticity of Slater's rules, the first one is find out screen constant and effective nuclear charge of p electron of boron, what we should do is first we should write the electronic configuration for boron atom, so electronic configuration of boron atom is 1 s 2, 2 s 2 and 2 p 1.

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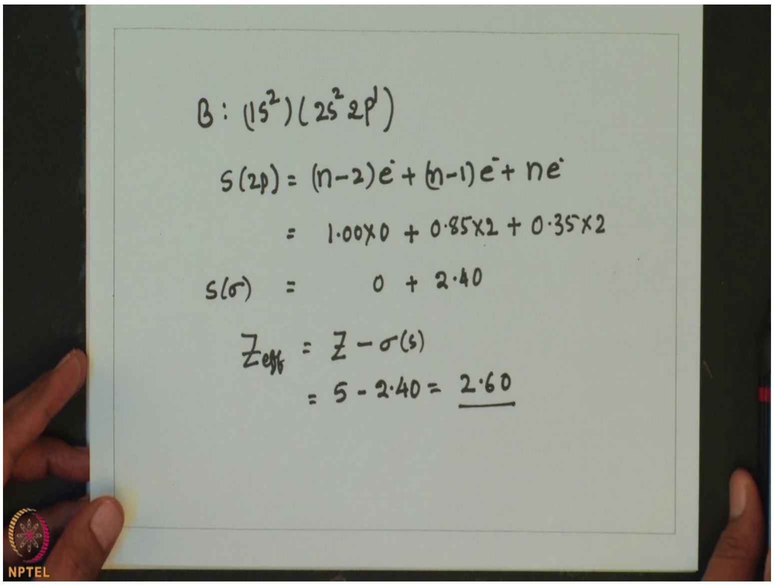

$$B : (1s^2)(2s^2 2p^1)$$

$$s(2p) = (n-2)e^- + (n-1)e^- + ne^-$$

$$= 1.00 \times 0 + 0.85 \times 2 + 0.35 \times 2$$

$$s(\sigma) = 0 + 2.40$$

$$Z_{eff} = Z - \sigma(s)$$

$$= 5 - 2.40 = \underline{2.60}$$

So, the consideration here is the p electron for which we have to calculate the effective nuclear charge as well as screening constant. Let us use this simple formula given by Slater s of 2 p is asked for this one, one should write first n minus 2 electrons and n minus 1 electrons and plus n electrons. So, here n minus 2 we do not have anything, 0 plus we have 2 electrons here 0.85 into 2 and then we have here only one electron is there. And in this case we have two electrons are there 0.35 into 2, so now this will come around 0 plus total will be 2.4, so now this is you can call it as s or sigma, so now Z effective equals Z the atomic number minus sigma or s, so here in case of boron atomic number is 5 minus 2.40 which will give you 2.60, so this is the effective nuclear charge for P electron of boron.

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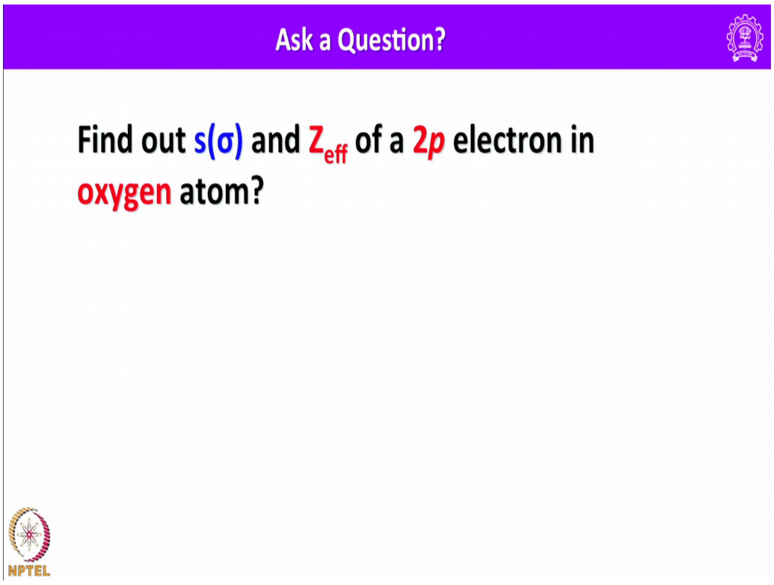

Ask a Question?

Find out s(σ) and Z_{eff} of a 2*p* electron in oxygen atom?

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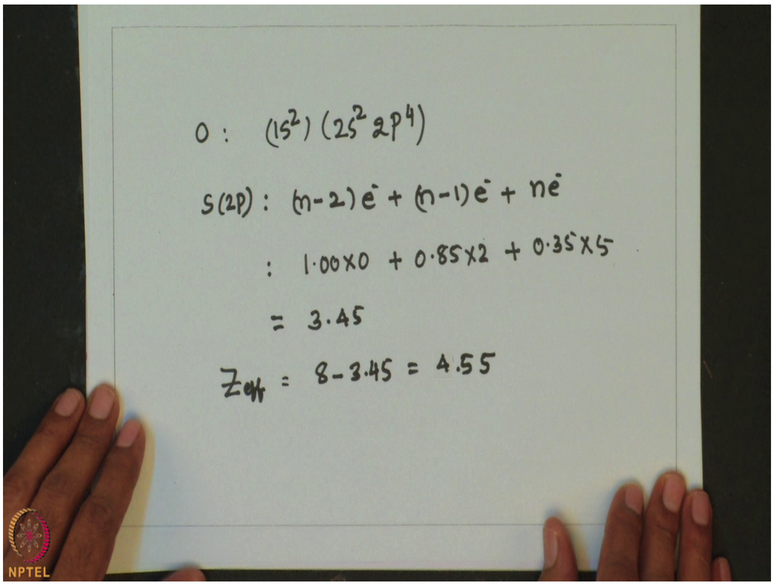

O : $(1s^2)\ (2s^2\ 2p^4)$

$s(2p)$: $(n-2)e^- + (n-1)e^- + ne^-$

: $1.00 \times 0 + 0.85 \times 2 + 0.35 \times 5$

$= 3.45$

Z_{eff} : $8 - 3.45 = 4.55$

So, let us look into the same values for 2 p electron in oxygen atom, find out screening constant or shielding constant and effective nuclear charge of a 2 p electron in oxygen atom for this again we have to do the same exercise, first we should write the electronic configuration of oxygen that is 1 s 2, 2 s 2 and 2 p 4, so here if you the same analogy we are calculating screening constant for 2 p electron, so to make you familiar I repeat again n minus 2 electron plus n minus 1 electron plus n electrons.

So, here we do not have any electrons n minus 2, so 1.00 into 0 plus here we have two electrons are there in n minus 1, so that is in 1 s 2, .85 into 2 plus we have about 5 electrons in the same group that is 0.35 into 5, so out of 6 electrons we are considering one of the p electron the remaining 5 electrons will be screening it so that is 0.35 into 5, so this will come around 3.45. So, now Z effective of 2 p electron of oxygen is 8 minus 3.45 that is equivalent to 4.55, so this is the effective nuclear charge for 2 p electron in oxygen atom, so this how one can calculate without any problem.

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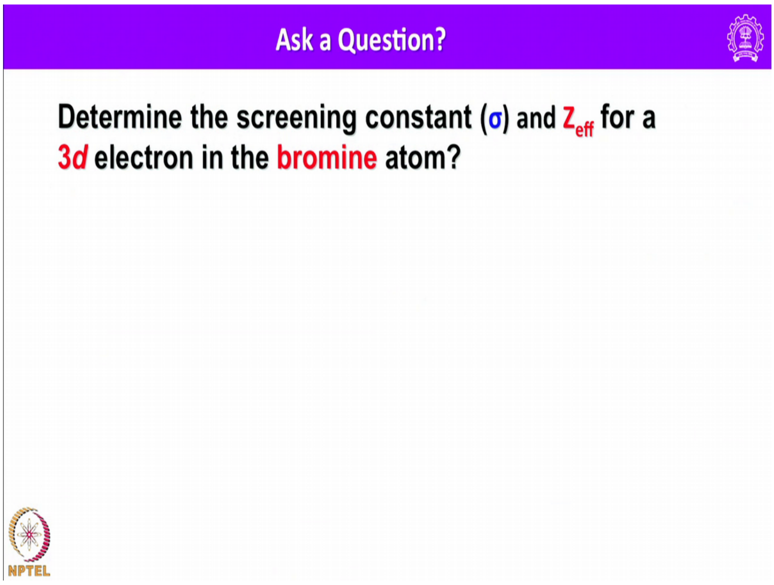

Ask a Question?

Determine the screening constant (σ) and Z_{eff} for a *3d* electron in the bromine atom?

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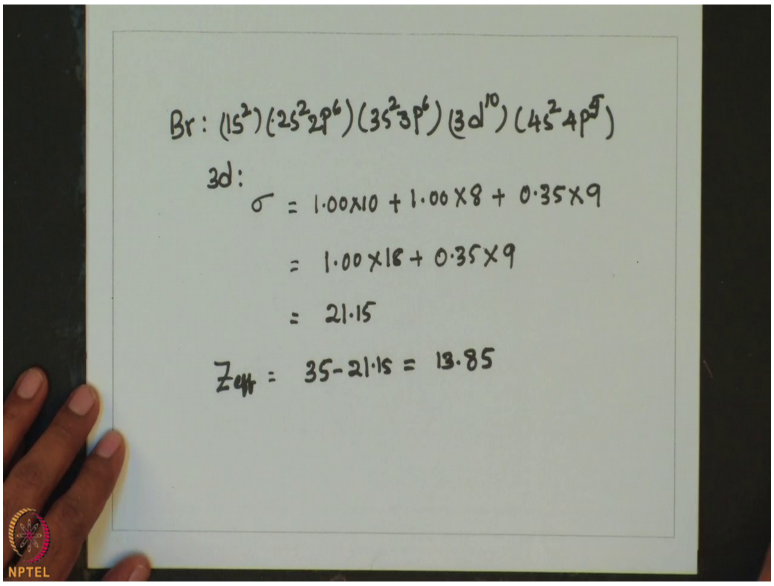

$Br: (1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^2 4p^5)$

3d:

$\sigma = 1.00 \times 10 + 1.00 \times 8 + 0.35 \times 9$

$= 1.00 \times 18 + 0.35 \times 9$

$= 21.15$

$Z_{eff} = 35 - 21.15 = 13.85$

Let us look into one more example here. Determine the screening constant and effective nuclear charge for a 3 d electron in the bromine atom same exercise one has to do it. Let us write the electronic configuration of bromine 1 s 2, 2 s 2, 2 p 6, 3 s 2, 3 p 6, 3 d 10, 4 s 2, 4 p 5. Since the electron in consideration is from 3 d, we have to find out the 3 d electron screen constant for that one sigma equals 1.00 into 10 plus 1.00 into 8 plus 0.35 into 9.

So, here 4 s 2, 4 p 5 or on the right side of d orbital so they should be ignored as they are not contributing towards the screening constant. So we have to consider only here 1 s 2, 2 s 2, 2 p 6, 3 s 2, 3 p 6 and within the group this 9 electrons that is what I have written here, so this is for this 9 electrons one electron we are considering and then it is total 18.

I have simplified by writing 10 and 8 essentially one can also write this has 1.00 into 18, so 18 will account for this 8 plus 8 16 plus 2 18 and plus .35 into 9. So, this comes around 21.15 so Z effective for 3 d electron in case of bromine is bromine atomic number is 35 minus 21.15 will give a value of 13.85. So this is essentially the effective nuclear charge of d electron in case of bromine, so this is how one can calculate the effective nuclear charge using simple and easy to follow Slater's rules.

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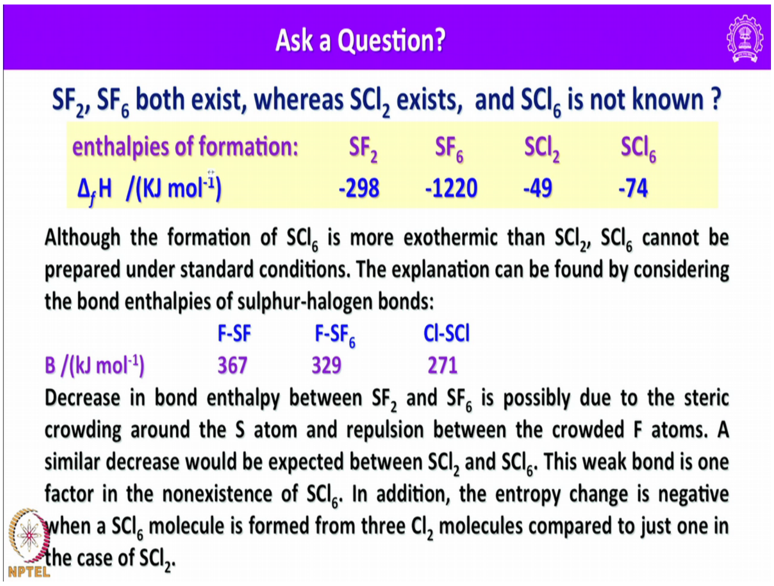

Ask a Question?

SF_2, SF_6 both exist, whereas SCl_2 exists, and SCl_6 is not known ?

enthalpies of formation:	SF_2	SF_6	SCl_2	SCl_6
$\Delta_f H$ /(KJ mol^{-1})	-298	-1220	-49	-74

Although the formation of SCl_6 is more exothermic than SCl_2, SCl_6 cannot be prepared under standard conditions. The explanation can be found by considering the bond enthalpies of sulphur-halogen bonds:

	F-SF	F-SF_6	Cl-SCl
B /(kJ mol^{-1})	367	329	271

Decrease in bond enthalpy between SF_2 and SF_6 is possibly due to the steric crowding around the S atom and repulsion between the crowded F atoms. A similar decrease would be expected between SCl_2 and SCl_6. This weak bond is one factor in the nonexistence of SCl_6. In addition, the entropy change is negative when a SCl_6 molecule is formed from three Cl_2 molecules compared to just one in the case of SCl_2.

So, let us look into another question here it is a very interesting question S F 2, S F 6 sulphur di fluoride and sulphur hexafluoride both exist whereas, sulphur dichloride exist and sulphur hexafluoride is not known. Let us look into the enthalpy of formation of these four molecules the values are given in kilojoules per mol in case of S F 2 it is minus 298 kilojoules per mol, whereas in case of S F 6 minus 1220 kilojoules per mol, where is in case of sulphur dichloride is minus 49 and in case of sulphur hexafluoride is minus 74 of course in both the cases compared to S F 2, S F 6 is exothermic similarly in case of S C l 2, S C l 6 formation is exothermic, but it does not give satisfactory answer for not existence of S C l 6.

So, let us look into somewhere information. So, all though the formation of S C l 6 is more exothermic just by looking to the values of S C l 2 to S C l 6 that is 49 and 74, S C l cannot be sulphur hexafluoride cannot be prepare under normal conditions. The explanation can be found simply by considering bond enthalpies of sulphur hydrogen bond in the series given here, just focus your attention here the bond enthalpy.

In case of S F 2 is 367 kilojoules per mol and bond enthalpy in case of S F 6 is very less that is 329 kilojoules per mol and in case of S C l 2 it is 271 kilojoules per mol, that means how to explain the decrease in the bond enthalpy between S F 2 and S F 6 of course; one can explain using the steric crowding of 6 florin atoms which are loaded with 8 electron each which generates enormous repulsion between the crowded F atoms.

So, a similar decrease is anticipated in case of S C l 6 comparative S C l 2, this weak bond is one factor that is makes to preparation S C l 6 or sulphur hexafluoride preparation but difficult. In addition one can also considered entropy change entropy change in both the cases are negative for example; one sulphur is interacting with 3 molecules of chlorine gas to generate 1 S C l 6, that means the entropies very negative and so that means exercise the steric crowding and the entropy effect to goes against the formation of S C l 6 there is a reason S C l 6 is not known, however in case of S F 6 because of the enthalpy of formation is little larger so S F 6 can be made easily, but and normal or compactuses at ambient condition S F 6 is stable but higher temperature it decomposes to form lower halides or lower fluorides.

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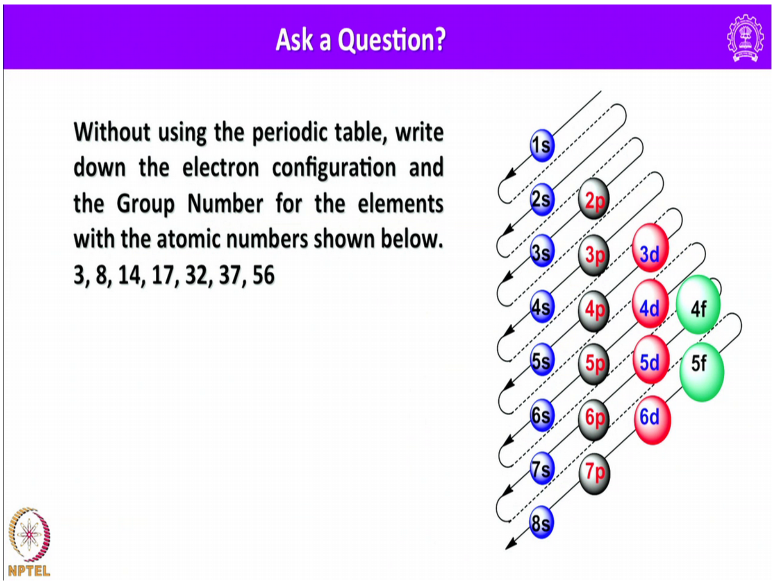

Ask a Question?

Without using the periodic table, write down the electron configuration and the Group Number for the elements with the atomic numbers shown below.
3, 8, 14, 17, 32, 37, 56

So, there is another question? Without using the periodic table write down the electronic configuration and the group number for the elements with the atomic number shown below. So, how to do that one? For this one it appears like it is very complicated, but once if we are familiar with electronic configuration and also if we are familiar with (Refer Time:16:53) principle it is not at all difficult to write the electronic configuration for any value, for example; let us look into this (Refer Time:17:05) principle that gives the relative energy of the all the orbitals if you follow this sequence, that is shown the writing the electronic configuration for any atomic number would be very easy ok.

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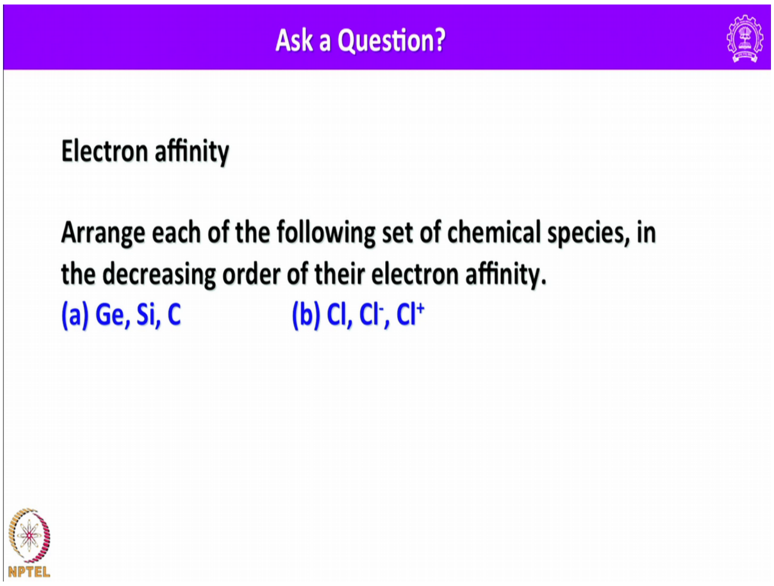

Ask a Question?

Electron affinity

Arrange each of the following set of chemical species, in the decreasing order of their electron affinity.

(a) Ge, Si, C (b) Cl, Cl^-, Cl^+

So, let us look into the electron affinity the question here is given for two sets of chemicals species arrange each of the following set of chemicals species in the decreasing order of their electron affinity. So, just we have to see the two groups, in one group essentially germanium, silicon and carbon are given all this three elements belongs to group 14 in the same order for examples; carbons, silicon and germanium are written in the decreasing order of their atomic number and in case b; it is chlorine, chloride ion and chloride anion and chloride cation is given.

So, let us try to make an attempt to write the decreasing order of their electron affinity it is very simple, we have to look into the effective nuclear charge and what to do happen to the electron negativity of removal or addition of electron one should follow simply that one in case of a it is very straight forward.

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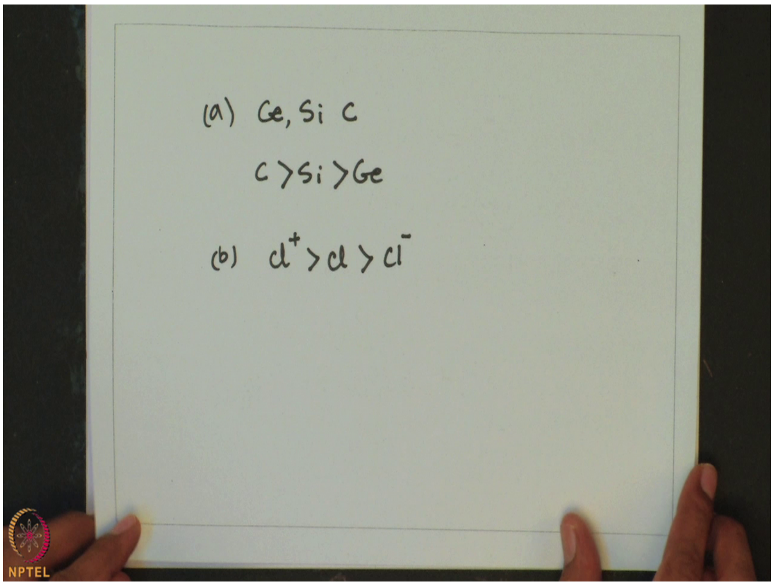

(a) Ge, Si C

$C > Si > Ge$

(b) $Cl^+ > Cl > Cl^-$

A given elements are germanium, silicon and carbon simply we can follow the same sequence as this one. So, here electron negativities decreasing down the group, so electron affinity also decreasing down the group this is the answer, in case of b it should be other way round c l plus has more electron affinity compared to c l and that in term compare to c l minus, so this is the decreasing order of the write on affinity for both the set of chemical species given here.

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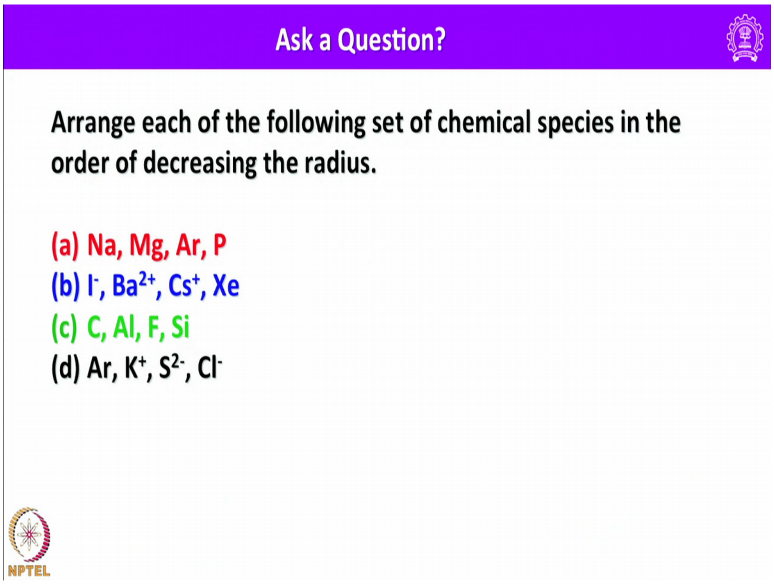

Ask a Question?

Arrange each of the following set of chemical species in the order of decreasing the radius.

(a) Na, Mg, Ar, P
(b) I^-, Ba^{2+}, Cs^+, Xe
(c) C, Al, F, Si
(d) Ar, K^+, S^{2-}, Cl^-

Let us look into one more question here. So, arrange each of the following set of chemical species in the order of decreasing the radius, let us considered the first row at a time one row at a time in the first set; we have sodium, magnesium, argon and phosphorus, in the second one; we have iodide B a 2 plus C s plus and xenon, in the third series; we have carbon aluminium, florine and silicon and in the last one we have argon k plus S 2 minus and C l minus ions let us start one at a time. So, first we have to identify the elements present in that series and we have to write down the atomic number and by looking to the atomic number and there relative positions in the periodic table we should be able to write it without any problem.

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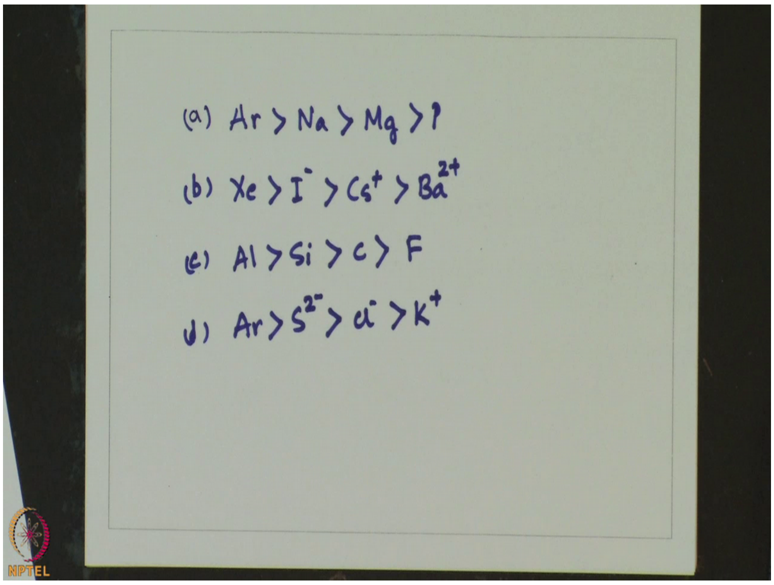

(a) Ar > Na > Mg > P

(b) $Xe > I^- > Cs^+ > Ba^{2+}$

(c) Al > Si > C > F

(d) $Ar > S^{2-} > Cl^- > K^+$

For the first one the answer is, so this is the order similarly for the second one the order is; xenon then I minus and C s plus and then barium 2 plus, in series c; it is aluminium, silicon, carbon and then florin in the last series it is argon then S 2 minus sulphide ion and then chloride ion and then k plus. So, here we had discussed in the previous lecture and also my first lecture about the relative variations in the radius, atomic radii and covalent radii and all those things by simply identifying the position of these elements in the periodic table and by adding remove one of electron to generate the species shown one should be able to write in this sequence without any problem again.

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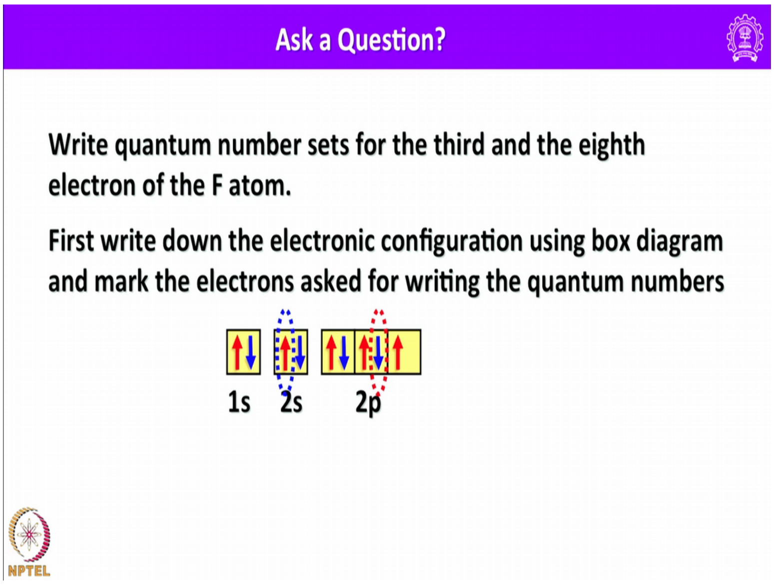

Ask a Question?

Write quantum number sets for the third and the eighth electron of the F atom.

First write down the electronic configuration using box diagram and mark the electrons asked for writing the quantum numbers

So, first right down the electronic configuration using box diagram and mark the electron asked for writing the quantum number, so here the question asked is to write quantum number sets for the third and the eighth electron of the chlorine atom, that means that means first we have to write the electronic configuration and we have to identify is the electron for which we have to write all the quantum numbers. So, it is convenient to write in the form of box, so label them 1 s, 2 s and 2 p. And then you feel it so now we have about 9 electrons are there, in 9 electrons we have identify the third electron third electron is from the 2 s and the ninth electron is from the 2 p series.

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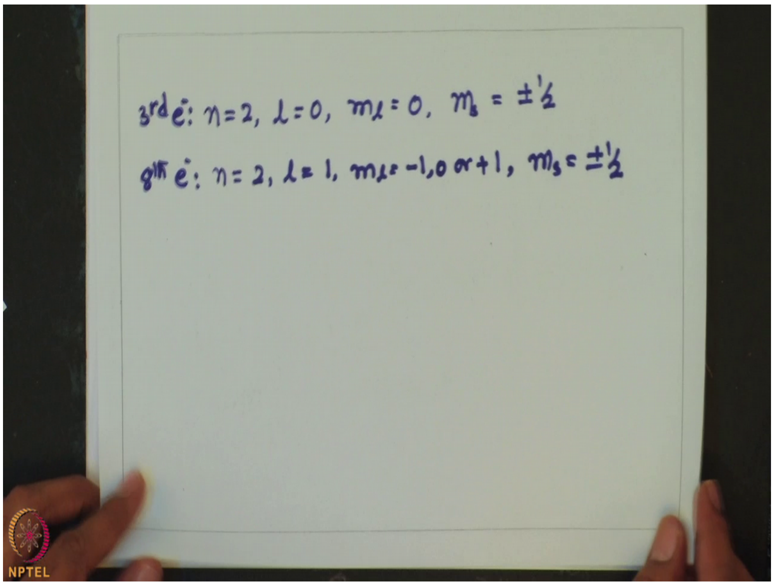

3rd $\bar{e}$: $n=2$, $l=0$, $m_l=0$, $m_s=\pm\frac{1}{2}$

8th $\bar{e}$: $n=2$, $l=1$, $m_l=-1, 0$ or $+1$, $m_s=\pm\frac{1}{2}$

So, for this one we have to right now, so third electron is in the 2 s orbital it is quantum numbers are n equal 2, l equals 0, m l equals 0 and m s equals plus or minus half. So, similarly quantum number for the eighth electron is can be written here; again n equals this is for the third electron, this for the eighth electron n equals 2, l equals 1, m l equals minus 1 0 or plus 1 and m s equals plus or minus half, so this is how one can write all the quantum numbers for any electron in an atom.

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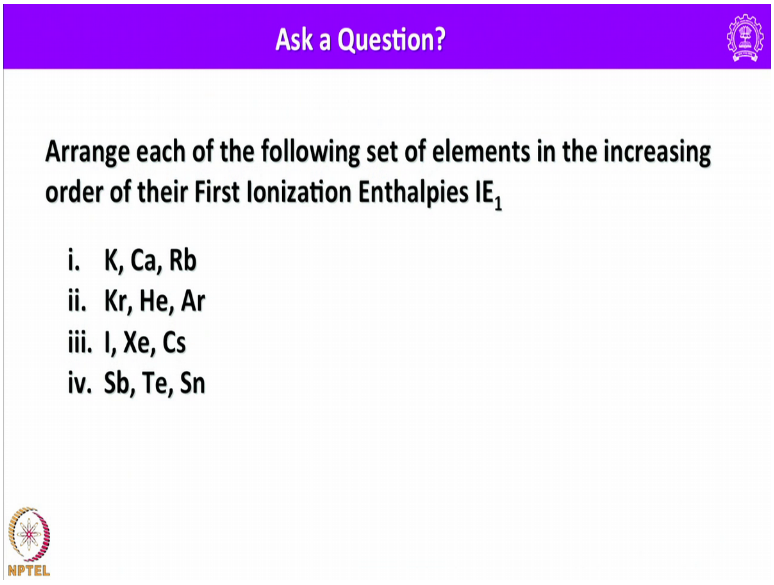

Ask a Question?

Arrange each of the following set of elements in the increasing order of their First Ionization Enthalpies IE_1

i. K, Ca, Rb
ii. Kr, He, Ar
iii. I, Xe, Cs
iv. Sb, Te, Sn

So, now another question is there arrange each of the following set of elements in the increasing order of the first ionization enthalpies I E 1. So, I repeat again arrange each of the following set of elements in the increasing order of their first ionization enthalpy, so we have 4 sets, in the first set we have potassium, calcium, rubidium. Next we have krypton, helium and argon and third one we have a iodine xenon and caesium in the last series we have antimony, tellurium and tin.

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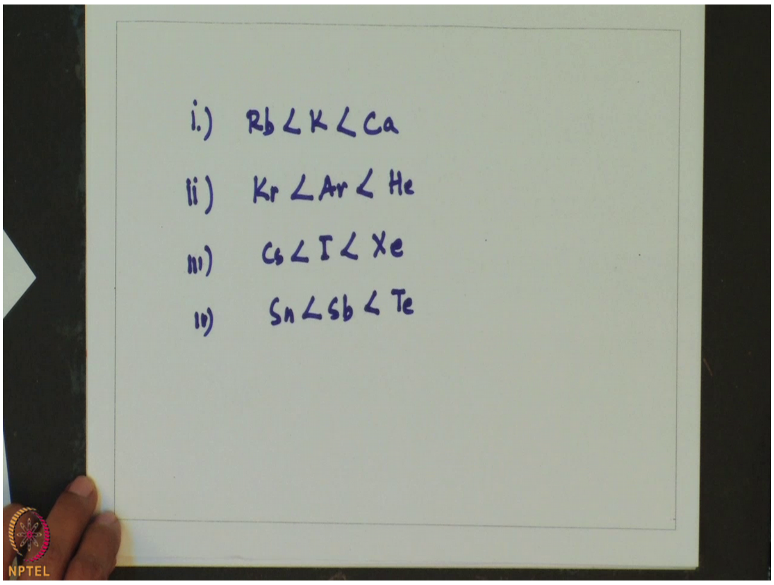

i.) $\mathrm{Rb} < \mathrm{K} < \mathrm{Ca}$
ii) $\mathrm{Kr} < \mathrm{Ar} < \mathrm{He}$
iii) $\mathrm{Cs} < \mathrm{I} < \mathrm{Xe}$
iv) $\mathrm{Sn} < \mathrm{Sb} < \mathrm{Te}$

Again we have to identify their position in the periodic table, whether they belongs to this same group or in a same period or from different groups once of identifying and knowing there atomic number there we should be able to write taking clue from the periodic trance, first one answer is; rubidium. Similarly for the second one, it is krypton, argon and helium, third one, C m is less than iodine is less than xenon and the last one, tin is less than antimony is less than tellurium. So, like this one should be able to answer any question and here I complete the classification of elements and their periodic trends and periodic properties.

In my next lecture I will be discussing about structure and bonding accepts where I will be introducing various bonding concepts to explain, how one can understand physical and chemical properties of molecules of main group elements and look into their chemical behaviour and chemical properties through structure and bonding concepts have a pleasant reading.

Thank you very much.