Main Group Chemistry
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Lecture - 02
Periodic Properties, Periodic Trends and Classification of Main Group Compounds

In my last lecture I was discussing about the ionization energy or ionization enthalpy and how one can correlate their values by simply looking to the electronic configuration and the effective nuclear charge. So, here I made an attempt to compare the ionization energies or ionization enthalpies of potassium and aluminum.

Let us continue discussing more about these periodic properties; that means, this ionization energy gives lot of information about nature of the bond type, whether it is ionic or covalent and by knowing this chemical and physical properties of the substances can be predicted very easily and ionization energy refers to the loss of an electron from the gaseous atom or an ion.

I will repeat again ionization energy or ionization enthalpy refers to the loss of an electron from the gaseous atom or an ion ionization energy decreases down a group increases along a period one can compare chart size ratio in this case that means, the ionization energy decreases down a group and increases along a period that is very important one should remember this one and the electronegativity refers to the tendency of an atom in a molecule to attract electron to itself. I repeat again the electronegativity refers to the tendency of an atom in a molecule to attract electron to itself the most widely used scale is devised by Linus Pauling and it is also called Linus Pauling method and it is based on essentially the bond energies.

The most electronegative elements are in the top right of the periodic table with fluorine being the most electronegative with a maximum value of 4.0 on the Pauling scale. So, among all the elements present in the periodic table the fluorine is the most electronegative element with a value of 4.0 and the next one is oxygen having 3.5 and next we get chlorine about 3.1 and nitrogen comes very close to it 3.04 and continues, and of course, electronegativity is a very useful general parameter for predicting the general chemical behavior of an element and it gives a very good indication of bond types just by simply looking into the electronegativity of 2 atoms that are combined to make a bond we can simply predict the nature of that chemical bond.

2 elements with a large electronegativity difference will tend to form ionic compounds for example, halides with group 1 and 2 elements form ionic salts for example, Nacl and smaller electronegativity differences are enough when one of the elements is a highly electropositive metal again group 1 or group 2 element I am considering 2 elements with similar or intermediate electronegativities that is 2.5 approximately will tend to form covalent bonds example CH bond in case of methane.

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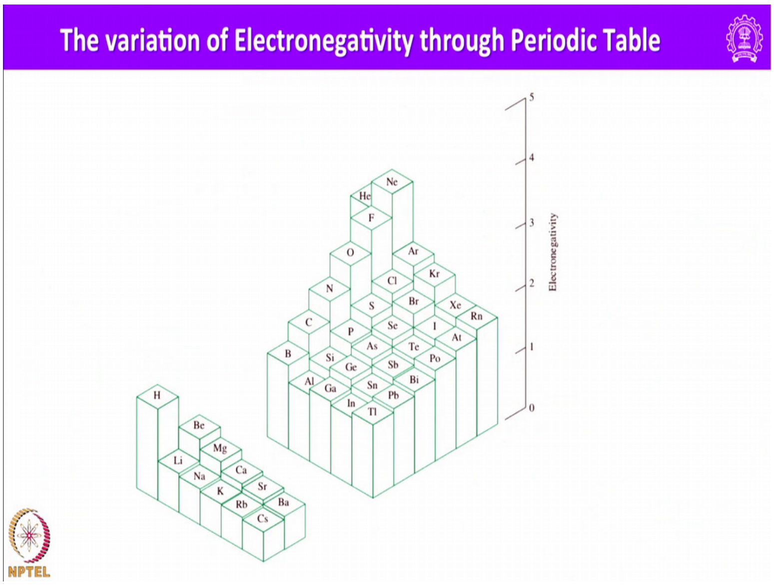

Let us look into the variation of electronegativity through periodic table, this very nicely shows the trends in the electronegativity you can see here the upper right corner elements in the periodic table shows very high electronegativity and of course, neon shows maximum and then helium comes we can ignore because we can never use them to make any compounds and if you leave those 2 the most electronegative element is fluorine, then oxygen comes and then as I mentioned chlorine comes and nitrogen comes out again argon has little higher value compared to chlorine again argon it is very inert.

So, we can ignore we have to consider only these remaining elements and we can see the trends these trends gives lot of information as I said and whereas, in case of alkali metals hydrogen shows maximum of 2.1 and then we have beryllium and then magnesium and of course, cesium has the least electronegativity value among all elements in the periodic table.

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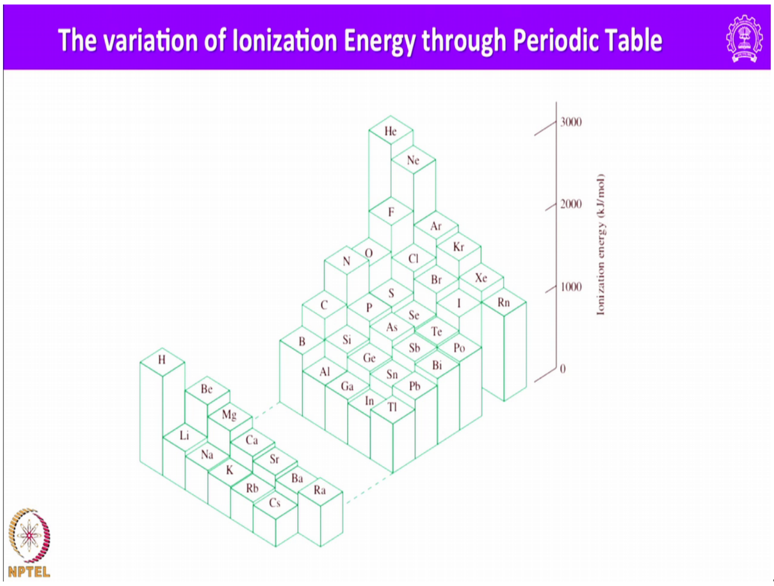

Similarly we can also look into the variation in the ionization energy through all the elements in the periodic table, here ionization energy refers to the first ionization energy and again here it is it follows almost the same trend we observed in case of electronegativity not much significant difference is there.

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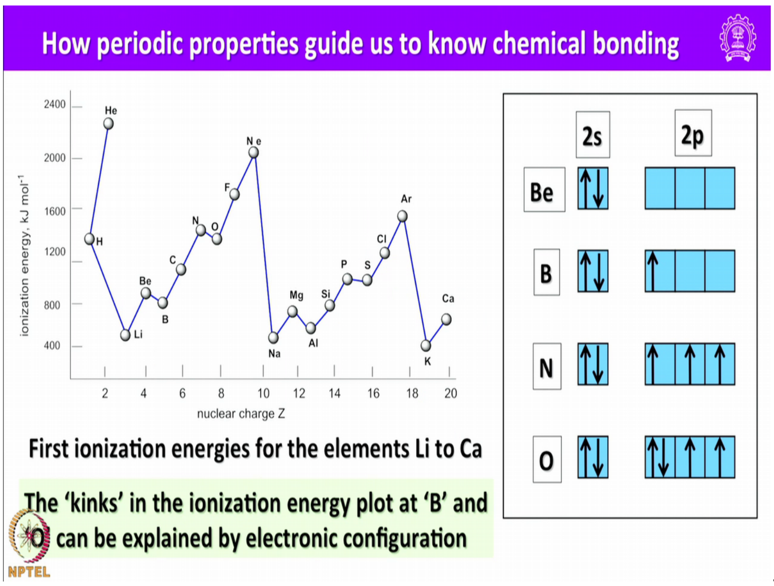

I have given a plot here to just get a idea about the relative ionization energies of first row elements you can see in case of helium it is very high and then it steadily drops and then lithium has the lowest value and then when you go to beryllium it increases here of course, here the nuclear charge is also increasing interestingly in case of boron despite increase in nuclear charge atomic number it drops here and the same type of kink we can also see in case of aluminium and another place where we observe this anomaly is in case of oxygen and sulphur. We can explain again based on their electronic configuration simply just by looking into the electronic configuration of beryllium 2 electrons are there here and it is a completely filled valence shell.

So, this large an electron from this one requires little higher energy as a result ionization energy of beryllium is first ionization energy is very high. In case of boron essentially although there is an increase in the atomic number essentially I had to remove the electron from the p orbital which is little far from the nucleus, as a result it is first ionization energy drops and there is a study increases there what is surprising is the lower ionization energy of oxygen compared to nitrogen despite it is being more electronegative.

The reason is very simple we can simply compare the electronic configuration of nitrogen and oxygen, we have a half filled electronic configuration in case of nitrogen whereas, in case of oxygen we have s 2 p 4 that means, one more than half filled electronic configuration is there; that means, by losing one electron oxygen can attain half filled electronic configuration status to add some stability.

As a result what happens the removal of one electron from oxygen is much more easier compared to removal of an electron from the half filled electronic configuration of nitrogen and same explanation one can give between phosphorus and sulphur and the trends you can see it can be nicely explained again by looking into the electronic configuration without any problem.

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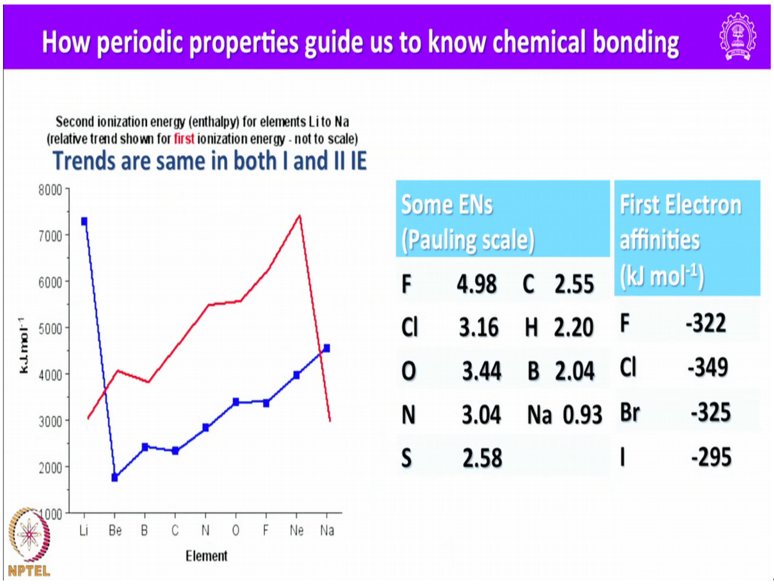

I have again plotted I have shown for comparison the first and second ionization energies again the trends are very similar again in case of oxygen and nitrogen now the secondary energy of oxygen is very high compared to nitrogen it is expected because oxygen being much more having more effective nuclear charge that is anticipated here and here electronegativity values I have given on Pauling scale main group elements here and in case of fluorine it is 4 whereas, in case of chlorine it is 3.16, in case of oxygen it is it is 3.44 and in case of nitrogen it is 3.04 and carbon has 2.55 value, it is more higher than that of hydrogen 2.20 and also first electron attachment enthalpy also I have given for halogens for fluorine it is minus 322 and in case of chlorine it is 349 and bromine it is 325 and iodine in is minus 295.

So, what is interesting is why if fluorine has no electron affinity compared to chlorine despite being the most electronegative element in the periodic table of course, the if we just look into the size of fluorine atom it is very small when it takes another electron to complete it is octet the inter electron repulsion will destabilize f ions as a result it can readily lose an electron in contrast chlorine being a bigger in atomic size what happens it can accommodate comfortably electron taken to make it a chloride anion. So, that is the reason that chlorine shows more electron affinity compared to fluorine.

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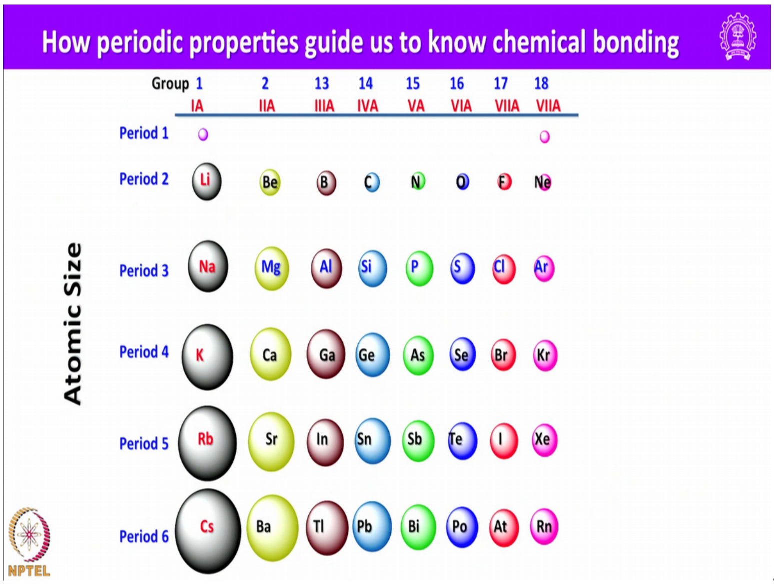

This chart shows the relative atomic size of all the elements in the periodic table you can see clearly in a group the atomic size increases and along a period atomic size decreases that you can see; that means, in any given group the last element will be having higher size and in the if you consider any period first element will be larger in size and that is going to be always alkali metal and then the next one is alkaline earth metal and always the last ones being inert gas or inert gas elements.

They are much smaller in size and these trends one should remember what one should remember is the electronic configuration and then the relative atomic size and once you know the relative atomic size and electronic configuration understanding their ionization, energy electronegativity, electron affinity would be very easy and hence the prediction of their physical and chemical properties would be very much easier and also one can make comparison of main group compounds no matter which atoms you are considering.

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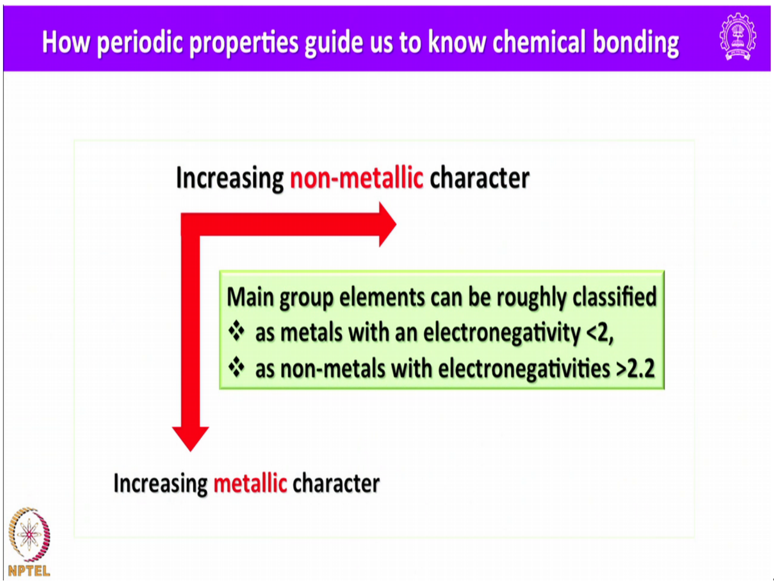

When we look into the periodic table we have some metals and we have some nonmetals and then in a period the non metallic character increases and similarly in a group metallic property increases; that means, the main group elements can be roughly classified as metals with an electronegativity less than 2 and as non metals with electronegativity greater than 2.2. Those which have electronegativity value more than 2.2 are essentially nonmetals all are in the right side of the periodic table and in case of metals the alkali metals or alkali earth metals and some of the heavier elements in each group are essentially having metallic properties.

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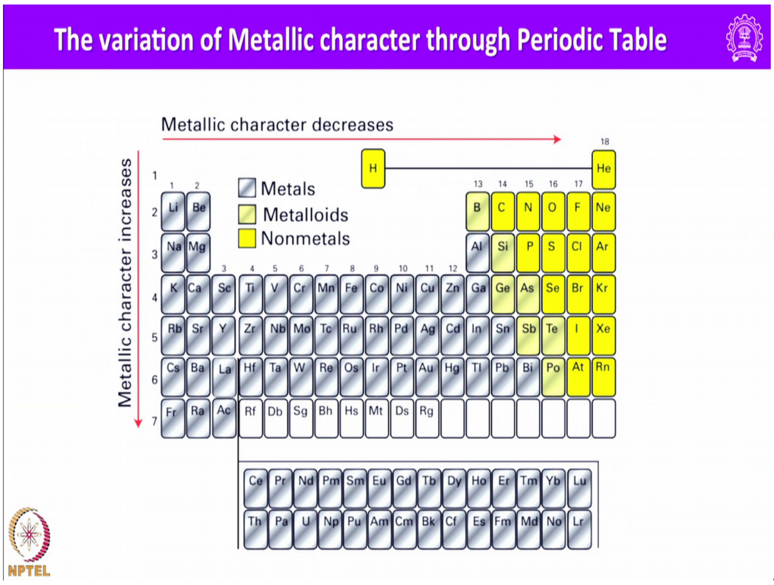

And this chart shown here represents the variation the metallic character throughout the periodic table you can see those elements which are marked in gray are essentially having metallic properties and those with grayish yellow are essentially called as metalloids and those which are marked in yellow color are essentially nonmetals. So, you can see clearly the right portion of most of the nonmetals are situated and in between elements such as boron and silicon are metalloids and of course, this metalloid property is also extended in case of germanium arsenic and also antimony.

The change in the properties can be nicely understood just by looking at the first long period starting from sodium to argon sodium and magnesium are both electropositive metals having 1 and 2 electrons in their valence shell. The next element is aluminum is a metal, but shows several characteristics of nonmetals in forming many covalent compounds.

When you go to the group 14 silicon; that means, we have carbon the next one is silicon is a metalloid being a semiconductor and has compounds which show characteristics of both metal and nonmetal compounds, and group 15 phosphorus onwards are truly nonmetals phosphorus exists in several elemental forms all of which contain covalent pp bonds. Phosphorus is a true nonmetal and rest of the elements are having some variable metallic properties and of course, in case of phosphorus all allotropes have covalent pp bond whether you consider white phosphorus red phosphorus or black phosphorus of course, we can learn more details when we go to group 15 elements.

In case of group 16 and 17 sulphur and chlorine are truly nonmetals sulfur exists as mainly covalent se 8 rings also in other several forms sulfur is known to exist and show allotropes and chlorine forms diatomic covalently bonded molecules. Argon exists as a monatomic gas under ambient conditions and does not participate in chemical bonding going to it is filled valence shell and very high ionization energy.

And going down in any of the main groups elements become more metallic in character that I had already told you, this is paralleled by a decrease in electronegativity because electronegativity is decreasing non metallic property is decreasing and metallic property is increasing and p block is the only part of the periodic table to contain nonmetallic elements I showed you in one of the previous slides if you see the nonmetals they are always in the right side of the periodic table and of course, when you talk about metals are very good conductors of heat and electricity and in solid metals the electrons are extensively delocalized over the whole material it appears as if we have a flow of electrons on the surface of the metal and because of this one all these metallic properties comes into picture.

Nonmetallic elements are insulators and have delocalizing bonding instead being formed from localized covalent bonds. In the center of p block there are so called metalloid elements such as boron and silicon the true metalloids of course, I showed you other few elements which also show metalloid properties. However, these boron and silicon which show intermediate electronegativity values and also show relatively low electrical conductivity compared to metals, but increases with temperature.

The main group elements and their chemical compounds cover a wide range of bonding types from ionic through polymeric to molecular, the general features of the chemistry of main group elements and their selected compounds can be understood analyzed and rationalized by using the variation in electronegativity of the elements as a very useful qualitative tool so; that means, if you look into now the main group elements we have a total of 42 elements with a vast number of chemical compounds and that is the reason students often think that energy in chemistry is highly complicated and it is very difficult lot of things are there to remember.

However if you find a method to classify all the compounds of main group elements into some class and if we do systematic study understanding of the chemistry of main group elements would be rather easier keeping this in mind in my lecture series I have classified all main group element compounds into simply 3 categories another 4th category also comes that I will elaborate later. These 3 categories are essentially the interaction of all main group elements with hydrogen or hydrogen sources to form hydrides and then reacting all main group elements with oxygen to form oxides and then reacting all main group elements with halogens to form halides or in particular fluorides which illustrate the general features very well.

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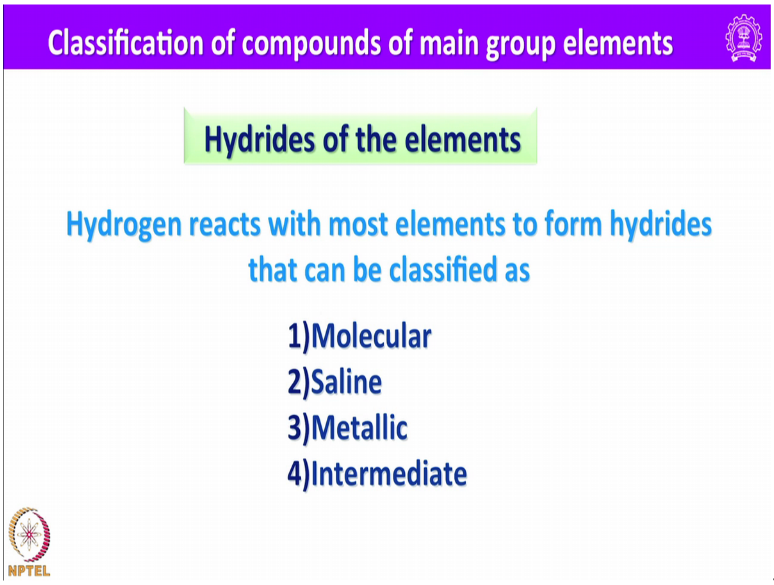

Once if we do this kind of classification understanding their properties comparing with a neighboring groups and within the group will be very easy and hence we can understand and remember all these properties without much complications.

Let us look into the first type of compounds that is hydrides of the elements the hydrogen reacts with most of the elements to form hydrides and again these hydrides can be classified as molecular hydrides, saline or ionic hydrides, metallic hydrides and also intermediate hydrides.

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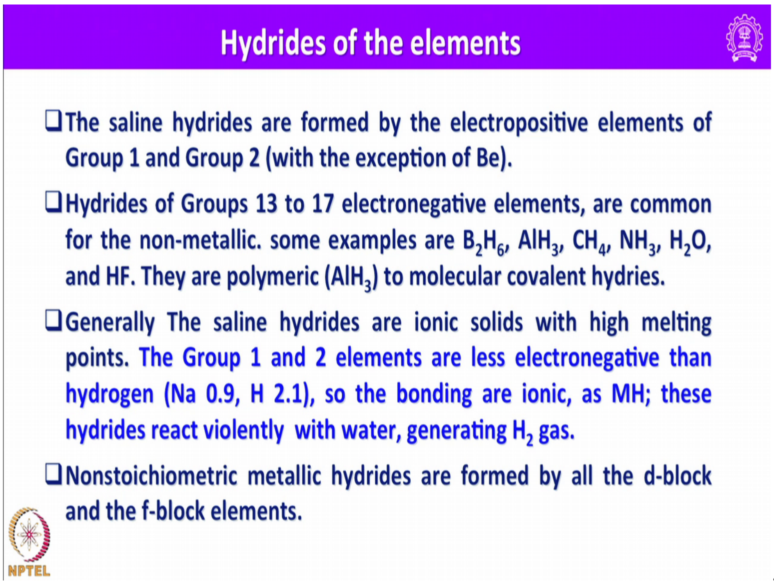

What are those classes the saline hydrides are formed by the electropositive elements of group 1 and group 2 the elements with an exception of beryllium in case of beryllium when it forms hydride it has some covalent character, other than that more of them are highly ionic. Hydrides of group 13 to 17 that is electronegative elements are essentially covalent in nature and for example, if we look into diborane B2H6, aluminum hydride ALH3, methane CH4, NH3, H2O and HF they are all. They are all covalent species and whereas, aluminium hydride is polymeric and rest of them are having covenant or polar covalent bonds.

Generally saline hydrides are ionic solids with high melting points the group 1 and 2 elements are less electronegative than hydrogen for example, if you take sodium has 0.9 and hydrogen has 2.1. The bondings are essential ionic and the composition is simply MH these hydrides react violently with water generating hydrogen gas and Nonstoichiometric metallic hydrides are formed by d block as well as f block elements. They are also essentially called as interstitial hydrides because when metals are reacted with hydrogen this hydrogen goes and sits in the interstitial spaces to form not stoichiometric metallic hydrides.

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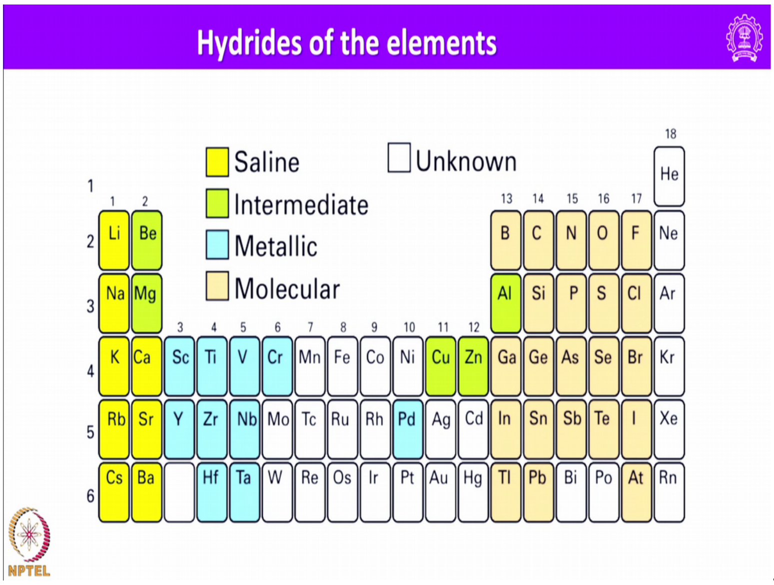

And here this chart shows the nature of the may hydrides of all the elements in the periodic table we can see some of the ionic ones are shown here saline and intermediate properties or ionic hydrides with covalent properties are shown in case of beryllium and magnesium and here they are truly metallic hydrides and of course, copper and zinc also shows intermediate properties whereas, the rest of the elements in the p block are essentially molecular or covalent hydrides.

So, for beryllium and boron the electronegative difference with hydrogen is very small beryllium hydride is covalent and boron hydrides are also form covalent compounds and as well as covalent clusters of course, we have a numerous examples of boron hydrides both neutral cationic and anionic all these boron hydrides we shall discuss when you go to group 13 in case of group 14 the hydrides are covalent molecular species a typical of having methane type structure.

Similarly group 15, 16 and 17 elements hydrides are all covalent molecular species and the acidity of these hydrides in aqueous solution increases on moving from left to the right of the period table as the electron unity difference between h and element increases the H-X bond especially in case of halides become more polarized and it will be like delta plus on H and delta minus on X. So, this has influence on the physical properties such as boiling points and other things again we shall learn more about those things when we go to the respective groups.

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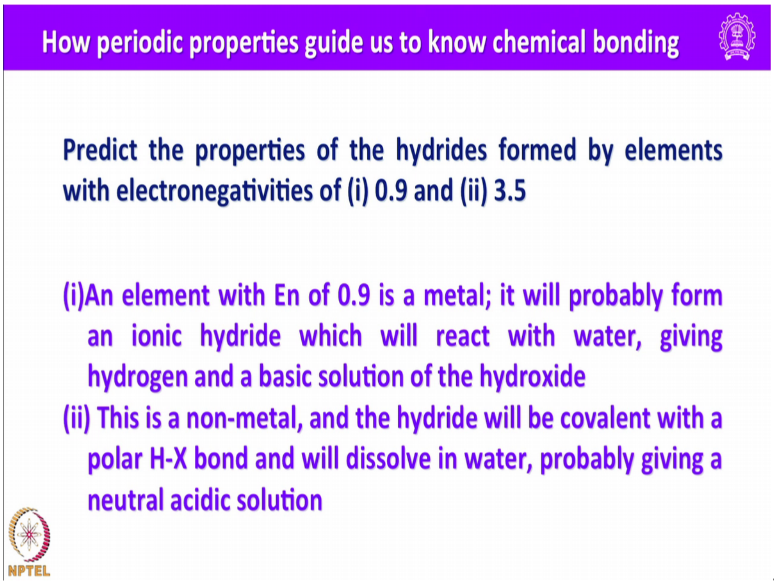

So, now a small question is there predict the properties of the hydrides formed by elements with electronegativities 0.9 and 3.5 and of course, the electronegative at hydrogen is around 2.1 and it has to combine with 2 elements given here with atomic with electronegativity 0. 9 and 3.5 and of course, if you look into the first one it has to be a metal of course, it is sodium it will probably form ionic hydride which will readily react with water giving hydrogen and a basic solution of the hydroxide that is sodium hydroxide. In case of second one 3.5 it is a nonmetal and the hydride will be a covalent with a polar bond where H will carry plus charge and the other element with 3.5 essentially here chlorine it is it will carry cl minus it is 3.0, it will carry a negative charge. These compounds of higher electronegativity will dissolve in water probably giving a neutral acidic solution.

So, let us look into the oxides of the element and generally metals form basic oxides.

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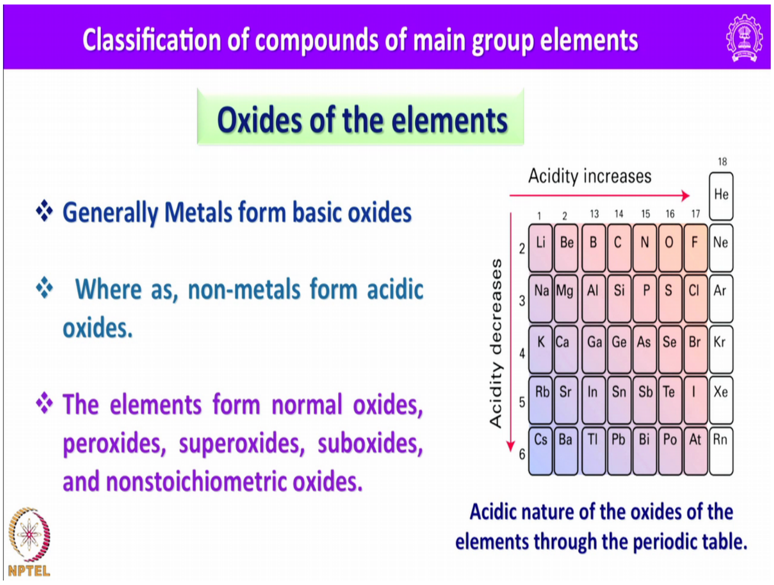

Whereas nonmetals form acidic oxides; that means, when you take a alkali metal or alkaline earth metal oxide and react with water they give the corresponding hydroxides whereas, nonmetal are acidic and when they react with water they form the corresponding acids. The elements form normal oxides, peroxides, superoxides, sub oxides and also non stoichiometric oxides as well, again how the acid properties are increasing or decreasing are shown in this chart here and acid properties are increasing in a period and decreasing in a group, group wise it decreases and period wise it increases these trends also very easy to remember if you remember just representative examples from s block as well as p block.

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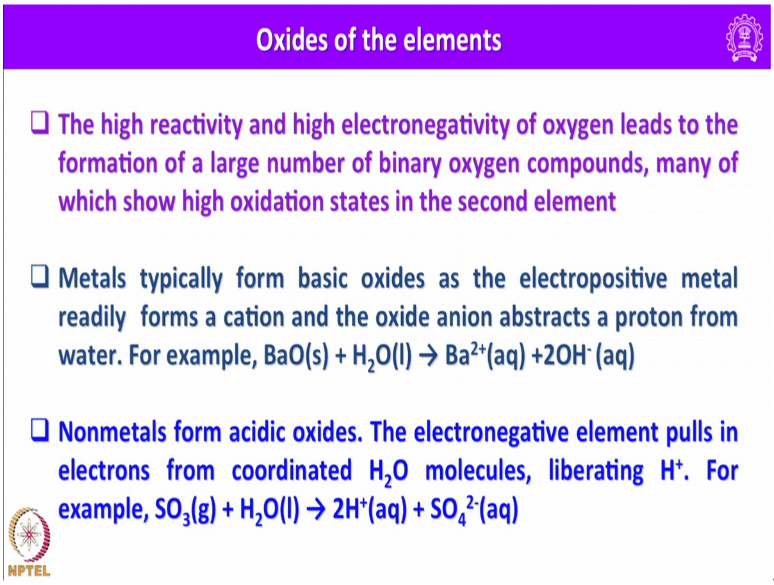

The high reactivity and high electronegativity of oxygen leads to the formation of a large number of binary oxygen compounds and many of them show high oxide state in the second element.

So; that means, oxygen the second most electronegativity element in the periodic table and for the same reason most of the elements do form very stable oxides and metals typically form basic oxides as the electropositive metal readily forms a cation and the oxide anion abstract a proton to form water a example is shown here barium oxide reacts with water to give barium hydroxide and in contrast nonmetals form acidic oxides the electronegative element pulls the electrons from the coordinated water molecule liberating H plus for example, SO3 when it reacts with water it forms sulfuric acid H2SO4. For main group oxides there is a similar trend from ionic oxides for the bottom left elements through polymeric oxides in the center to molecular covalent oxides for the elements of higher electronegativity on the right side of the p block so; that means, now you can see the trends simply by looking into the electronegativity and the electronic configuration of these elements.

For example if you take sodium oxide or calcium oxide which are basic oxides with water they give alkali solutions.

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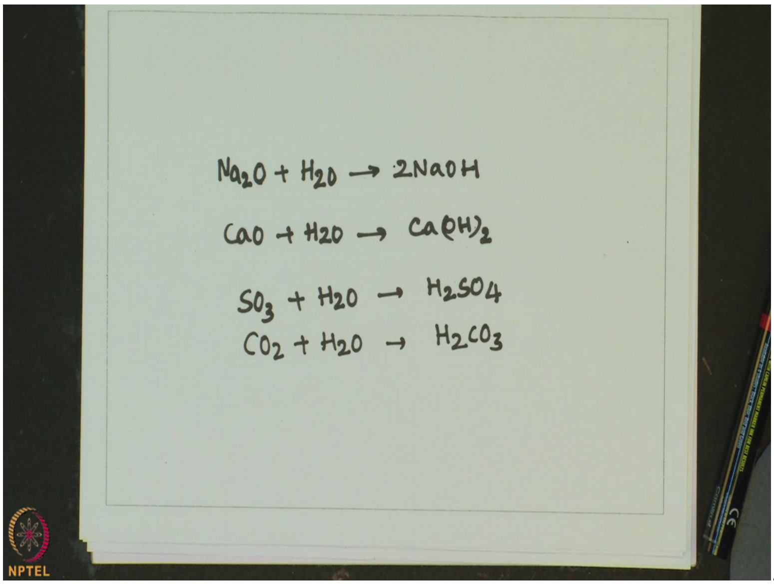

I will show you here, this indicates metal oxides alkali metal and alkaline earth metal oxides are basic in nature in contrast if you simply take SO3 and water it forms H2SO4; that means, main group p block oxides are essentially acidic are s block elements are essentially basic in nature. If you look into group 13 oxides such as B2O3 and AL2O3 or are polymeric and AL2O3 is also amphoteric in nature. In case of group 14 the oxides of the lightest element carbon such as CO and CO2 or molecular oxides, there is another one called carbon suboxide I will discuss about that one again later. In contrast SIO2 called silica is a polymeric oxide and CO2 is an acidic oxide again since it dissolves in water giving an acidic solution example one can also write in the same way CO2 plus H2O gives H2CO3.

In group 15 and 16 the oxides of nitrogen all are molecular covalent species many of which are acidic while those of sulfur are both acidic oxides are again you consider, SO2 or SO3 both are acidic in nature similarly group 17 and for xenon in group 18 the oxides are essentially molecular specie.

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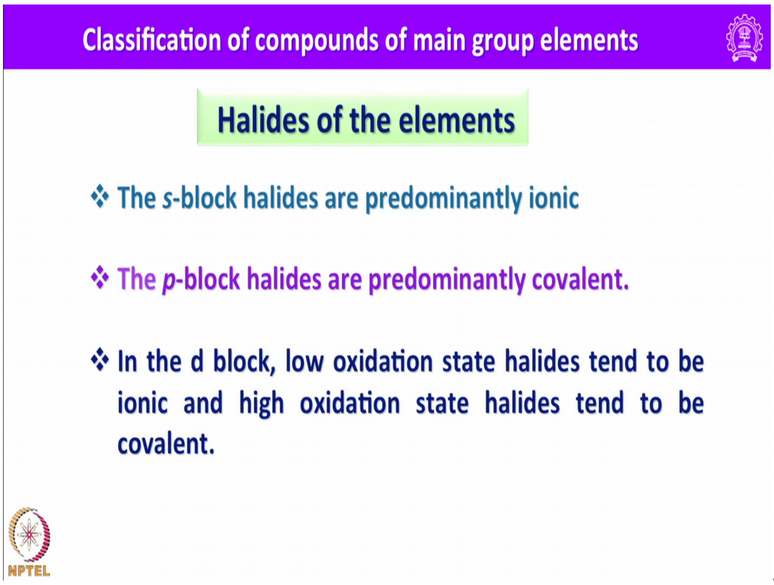

Let us just look into the last one in the series halides of these elements s block halides are predominantly ionic say $NaCl$ $CaCl_2$ etcetera, the p block halides are predominantly covalent. In the d block the lower oxide state halides tend to be ionic and high oxide state halides tend to be covenant similar to hydrides the properties of the chlorides follow a broadly similar pattern with chlorides of metals being ionic and of non metals being covalent molecules for the group 1 and group 2 metals except beryllium which has covalent character the chlorides are ionic solids which form neutral solutions in water.

The chlorides of small highly polarizing metal ions such as beryllium, aluminum, gallium and some other elements are polymeric in the solid state. The majority of the chlorides of group 14 and 15 elements and BCl_3 all our molecular covalent species, the chlorides of p block elements and beryllium generally give acid solutions in water because they react with it rather than simply dissolving and again CCl_4 unlike $SiCl_4$ does not react with water to give an acidic solution and this is purely kinetic effect I would also discuss the difference in their reactivity when I go to group 14 and some of the chlorides of the elements are listed here.

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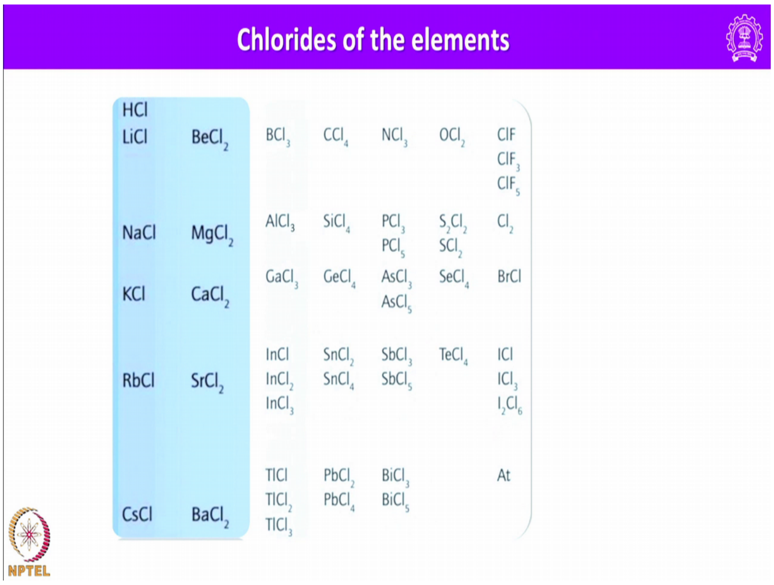

You can see alkali metals and alkaline earth metals will follow a mono chloride and dichloride species and whereas, in case of a group 13 you can see the lighter will form trihalides whereas, the heavier ones you can see in plus 2 as well as plus 1 state; that means, here in case of thallium chloride is stable in fact, thallium trichloride is oxidized in nature.

Some of these of course, here the inert pair effect start coming into the picture I again I will elaborate what is inert pair effect when you go to p block chemistry and similarly in most of the p block elements when you go for heavier elements essentially higher halides are oxidizing in nature and they show 2 or 3 different type of halides especially lead shows plus 2 and plus 4 and plus 2 is stable whereas, plus 4 is oxidizing same thing is true in case of tin as well as antimony SbCl 3 stable, SbCl 5 is unstable because the inter pair effect dominates same things too in case of BiCl 3 and BiCl 4; that means, overall now we looked into the 3 different type of compounds we come across among main group elements that is hydrides, oxides and then halides.

The one more type of compound is essentially interaction of this most of these main group elements with carbon or organic fragments they are called argon element compounds those aspects I will be discussing as and when we come across this type of compounds and in my next lecture I will be elaborating little bit more before I go to the chemistry of hydrogen and then I will start group wise chemistry of main group elements and I hope you have learnt something about the classification and periodic trends and periodic properties and new terms such as ionization energy, ionization enthalpy and also electronic configuration with this I will stop here I wish you very happy reading and thank you very much.