Main Group Chemistry
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Lecture – 20
Chemistry of Group 2 elements

I once again welcome you to MSB lecture series on main group chemistry let me begin my talk today on group 2 elements. Group 2 elements are known as alkaline earth elements this group consists of beryllium, magnesium, calcium, strontium, barium and radium and the electronic configuration of alkaline earth elements is NS 2 that is valence electrons; that means, we have 2 electrons in the valence shell as a result the group oxidation state is plus 2 and as expected being the first element beryllium differs from other elements owing to it is smaller size. In fact, beryllium resembles more of aluminum than magnesium and calcium and that is about diagonal relationship between beryllium and aluminum I will discuss those aspects later.

And atomic and ionic radii are smaller than those of group one elements of course, here one electron is added to the same shell and nuclear charge is also increased as a result one can expect the atomic and ionic radii of alkaline earth metals smaller than the corresponding group one elements. The alkaline earth metals are named after their oxides the alkaline earths whose names were berilia, magnesia, lime, strontia, and barita respectively for beryllium, magnesium, calcium, strontium and barium.

These oxides are basic when combined with water; that means, these oxides when they are reacted with water they give hydroxides the basic solution as a result they are called as basic oxides, earth in these elements is referred to earlier essentially for non metallic substances earlier the term earth was added since they were insoluble in water and resistant to heating.

And of course, these properties are shared by these oxides and hence they are called alkaline earth metals and they readily form m 2 plus ions since the group oxidate is plus 2 and as expected m 2 plus ions are smaller than m atomic and ionic radii increases down the group as the size increases. This is the periodic trend we are familiar with and ionization enthalpy decreases down the group, first ionization enthalpies are higher than those of the corresponding group one elements this is again following the same expected periodic trends.

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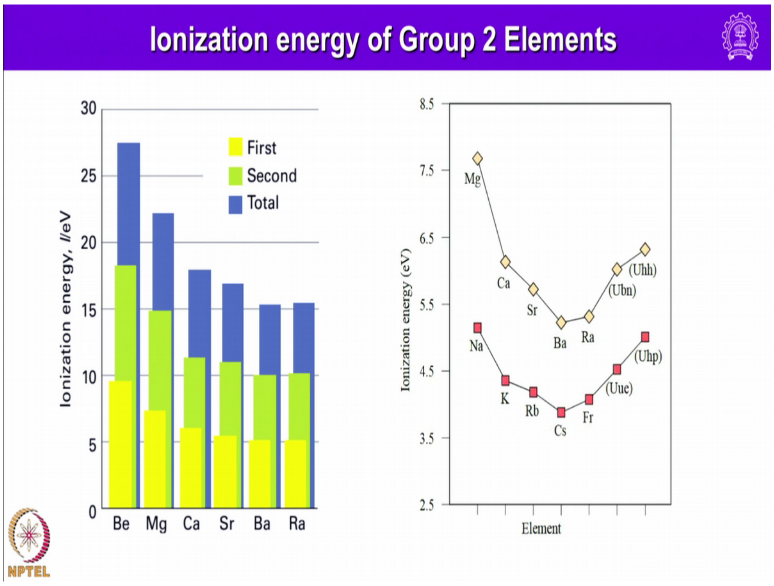

And second ionization enthalpies are higher than the first ionization enthalpies for all alkaline earth metals you can see here the ionization energy of group 2 elements are shown here. For example, you can see first ionization energy is much higher and the second ionization energy is shown here and overall the ionization energy of all alkaline earth metals are shown in this plot and you can see here the first ionization energy or ionization enthalpy or of all alkaline earth metals are much higher than those of alkali metals or group one elements I already mentioned why.

So, then hydration enthalpy, this hydration enthalpy decreases down the group due to the increase in the ionic size, as the ionic size increases down the group charge to size ratio also decreases as a result what happens hydration enthalpy that depends heavily on the charge to size ratio decreases due to the increase in the ionic size and decrease in the charge to size ratio as a result one can expect the trend in this fashion.

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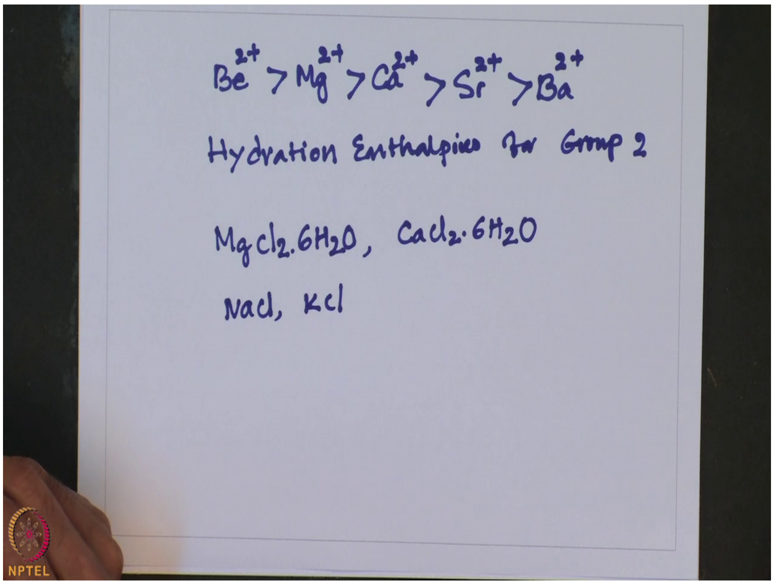

For group, due to the larger size group 2 elements are more extensively hydrated compared to group 1 elements for example, if you see a magnesium chloride is 6H2O; that means, it has 6 water molecules similarly calcium chloride can take up to 6 water molecules if we compare these things with sodium chloride or potassium chloride they do not form hydrates. So, that is the difference between group 1 and group 2 elements and similar to group 1 metals, group 2 metals are also silvery white in color, soft, but harder than group 1 elements. The hardness relatively more hardness compared to group 1 elements comes because of the availability of 2 electrons for metal bonding strong electropositive property is shown by group 2 elements and this trend increases down the group.

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Properties of Group 2 Elements

	Be	Mg	Ca	Sr	Ba	Ra
Metallic radius/pm	112	150	197	215	217	220
Ionic radius, $r(M^{2+})$/pm (coordination number)	27(4)	72(6)	100(6)	126(8)	142(8)	170(12)
First ionization energy, $I/(kJ\ mol^{-1})$	900	736	590	548	502	510
$E^{\ominus}(M^{2+}, M)/V$	-1.85	-2.38	-2.87	-2.89	-2.90	-2.92
Density, $\rho/(g\ cm^{-3})$	1.85	1.74	1.54	2.62	3.51	5.00
Melting point/°C	1280	650	850	768	714	700
$\Delta_{hyd}H^{\ominus}/(kJ\ mol^{-1})$	-2500	-1920	-1650	-1480	-1360	-
$\Delta_{sub}H^{\ominus}/(kJ\ mol^{-1})$	321	150	193	164	176	130

All these properties are displayed here whatever I said so, far. So, let us look into the properties of group 2 elements and the trends whatever I said can be clearly seen here in the metallic radius, metallic radius as expected it is increasing from beryllium to radium and ionic radius also should increase and it is increasing with beryllium showing 27 picometer. Whereas, radium showing 170 picometer and first ionization energy is decreasing as the valence electrons are moving farther from the nucleus ionization of those electrons would be rather easy that you can see here that is also reflected in the reduction potential here.

Reduction potential you can see here the trend and the density is given and melting point also decreases down the group and enthalpy also decreases and all these properties are according to the periodic trends one should expect by looking into the trends seen along rose and also down the group. Let me tell you little about alkaline earth metals and who discovered and as I mentioned all alkaline earth metals are silvery white in color.

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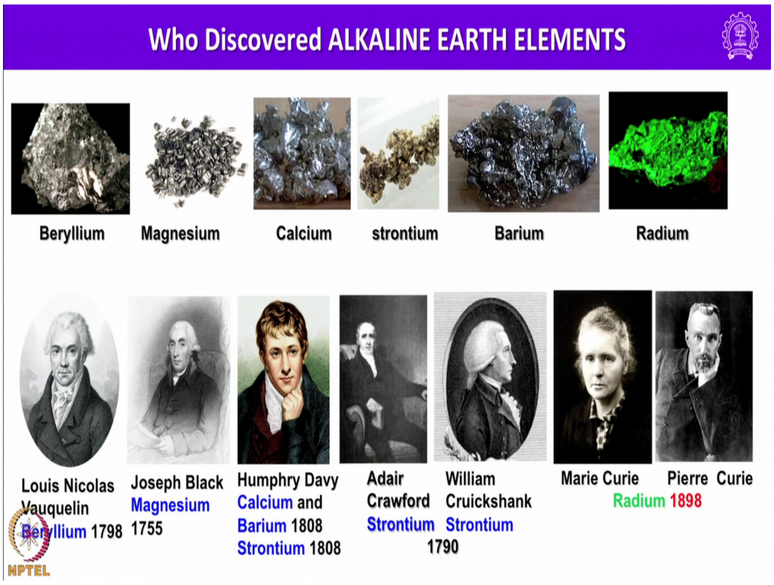

So, you can see here Beryllium, I have shown here Beryllium, Magnesium turnings I have shown Calcium, Strontium little gold color is there freshly sublimed one and Barium and Radium is radioactive. Beryllium was discovered by Louis Nicolas Vauquelin in 1798 and Magnesium was discovered by Joseph Black in 1755 and Humphry Davy.

In fact, her has contributed significantly to the understanding and growth of chemistry especially alkaline earth metals and alkali metals and alkaline earth metals. In fact, he is responsible for discovering and isolating in the pure form many elements that I will be discussing in the next slide and he is responsible for discovering calcium, barium and strontium. Strontium was collectively together discovered by Crawford and Cruickshank in 1790 and later it was isolated in it is pure form by Humphry Davy and Marie Curie and Pierre Curie they discovered radium in 1898.

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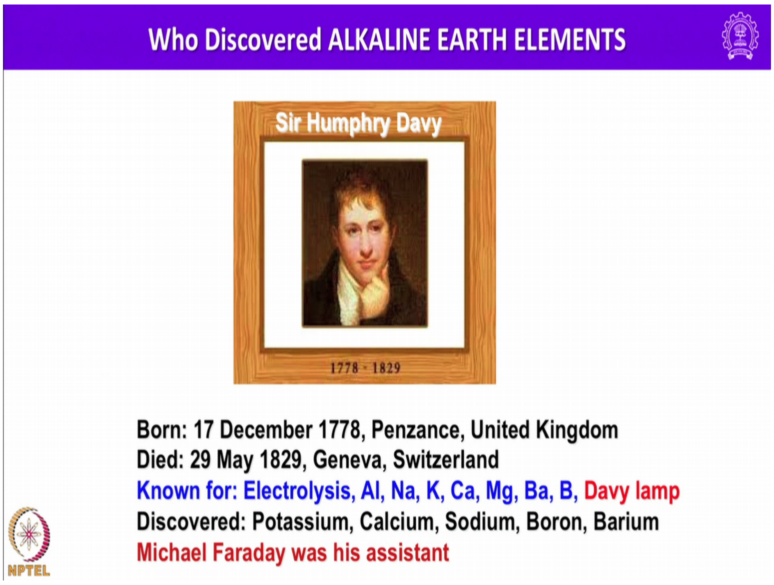

And of course, as I mentioned Humphry Davy s contribution is remarkable he just lived for 51 years and he is known for the electrolysis and also giving the method of isolation of and discovery of elements such as aluminum, sodium, potassium, calcium, magnesium, barium, boron and also he is well known for his safety lamp also known as Davy lamp for people who work in the mines.

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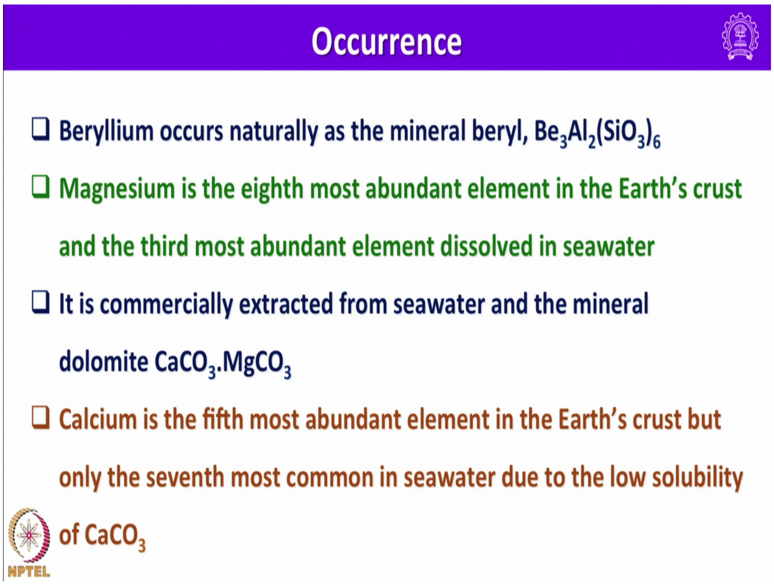

So, let us look into the occurrence of alkaline earth elements beryllium occurs naturally as the mineral beryl important ore of beryllium or important source of beryllium with composition Be3 Al2 SiO3 6 times and magnesium is the 8 th most abundant element in the Earth's crust and the third most abundant element dissolved in sea water it is commercially extracted from sea water and the mineral dolomite is nothing, but a combination of calcium carbonate and magnesium carbonate in 1 is to 1 ratio and calcium is the 5 th most abundant element in the earth s crust, but only the 7 th most common in sea water due to the low solubility of calcium carbonate.

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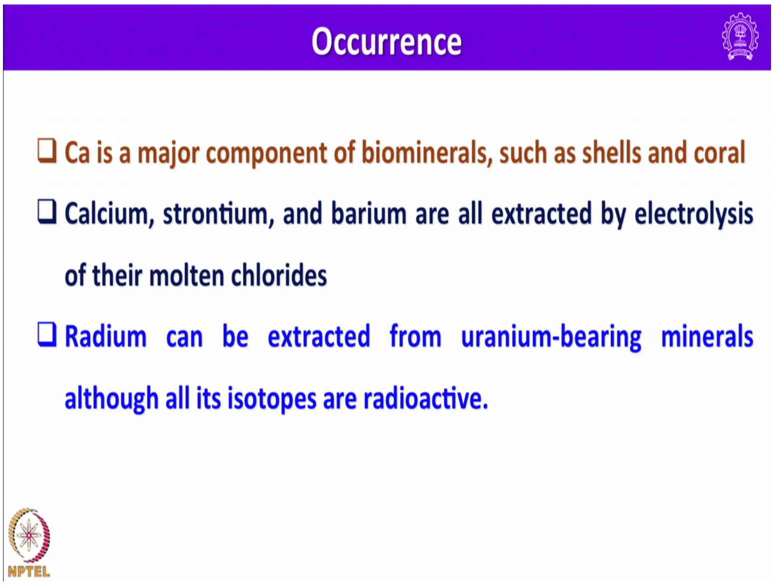

And of course, Calcium is a major component of bio minerals such as shells and coral and calcium, strontium, and barium all are extracted by electrolysis of their corresponding molten chlorides.

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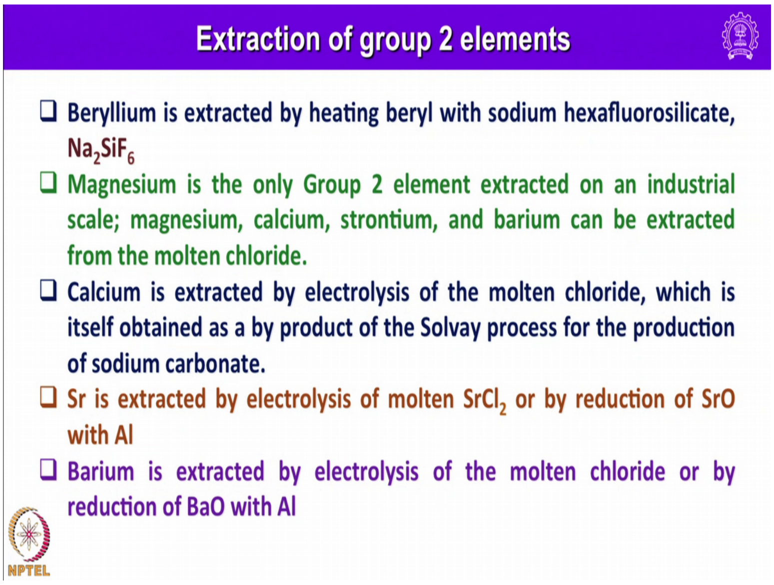

Radium can be extracted from uranium bearing minerals such as pitch blend all it is isotopes are radioactive and Beryllium is extracted by heating beryl with sodium hexafluorosilicate that is Na2 SiF6 and Magnesium is the only group 2 element extracted on an industrial scale and magnesium, calcium, strontium and barium can be extracted from the respective molten chlorides very similar to down s process employed in the extraction and isolation of sodium from sodium chloride.

Calcium is extracted by electrolysis of the molten chloride which is itself obtained as a byproduct of solvay process for the production of sodium carbonate and strontium is extracted by electrolysis of molten strontium chloride or by reduction of strontium oxide using aluminum very similar to thermite process and barium is extracted by electrolysis of the molten chloride or by reduction of barium oxide with aluminum; that means, essentially we have 2 methods at our disposal to extract strontium either from molten halides or from the corresponding oxides.

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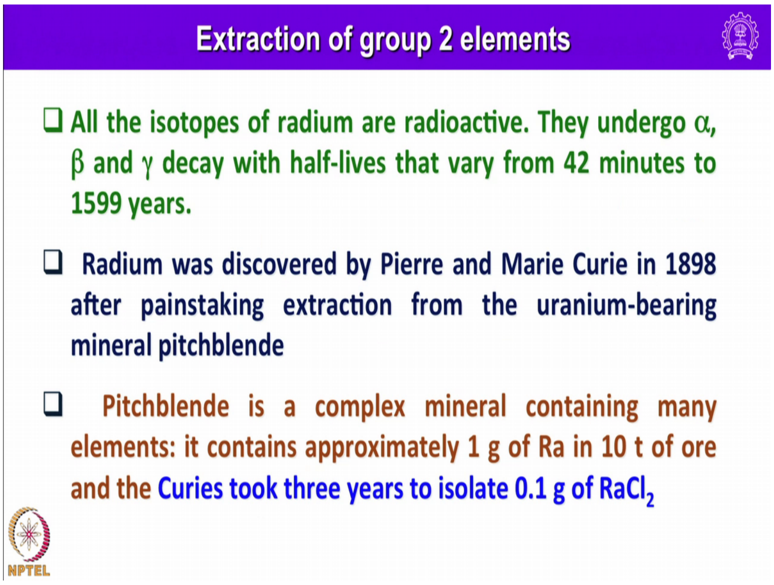

So, when it comes to radium all isotopes of radium are radioactive they undergo alpha, beta and gamma decay with half life that vary anywhere between 42 minutes to 1599 years for some of their radioactive isotopes and radium was discovered by Pierre Curie and Marie Curie in 1898 after painstaking extraction from the uranium ore Pitchblende and in fact, Pitchblende is a complex mineral containing many elements it is a besides uranium it is a source of many trace elements and also some of the radioactive isotopes of some of the heavier elements and it contains approximately 1 gram of radium in 10 tons of ore and in fact, Curies together took nearly 3 years to isolate 0.1 gram of radium chloride from pitchblende. So, let me the extraction method of beryllium starting from Beryl.

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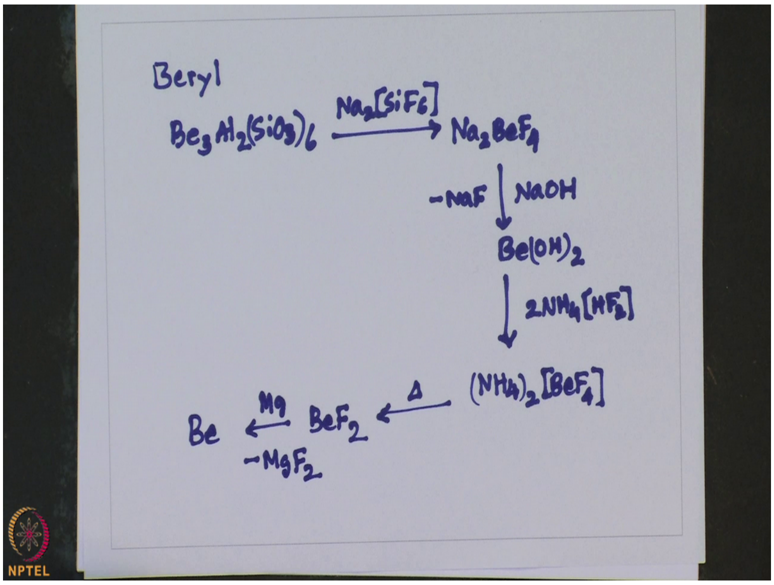

So, as I said beryl is nothing, but Be3 Al2 SiO3 6 times so, first it has to be treated with hexafluorosilicate sodium hexafluorosilicate. So, it gives Na2 Be F4. So, it acts as a (Refer Time:13:36) agent and then this is stated with sodium hydroxide leads to the formation of sodium fluoride and Be OH will be separated beryllium hydroxide and on treatment of beryllium hydroxide with this salt gives beryllium tetra fluoride this one on heating gives beryllium fluoride.

So, this beryllium fluoride on reduction with magnesium gives pure beryllium through the formation of magnesium fluoride. So, this is the method used for the extraction of beryllium starting from beryl. So, let me give the extraction method in used in the case of magnesium as I said in case of magnesium one can use molten magnesium chloride, molten magnesium chloride and; that means, preparation of magnesium chloride involves the treatment of magnesium hydroxide.

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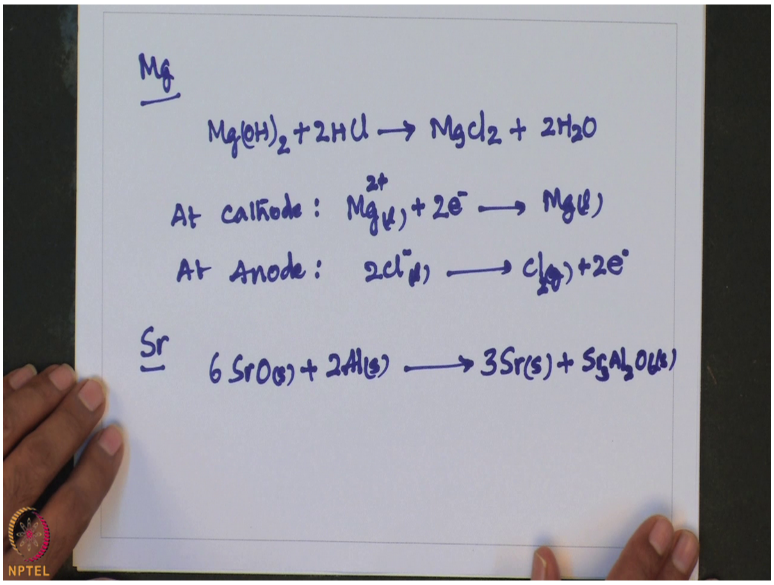

With Hcl essentially a neutralization process giving the salt and water so, in molten electrolysis at cathode, at Anode (Refer Time: 16:10) of chloride takes place and this is for magnesium the similar method in case of strontium and barium as well in case if we have oxide one can use aluminum of course, here to initiate the formation of aluminum oxide that is highly exothermic first reaction needs. So, this method one can conveniently use in case of barium as well.

So, other method of molten will be similar to this reaction now let us look into the flame test we are familiar with flame test in case of alkali metals, similarly in case of alkaline earth metals calcium imparts brick red color whereas, strontium imparts crimson red and barium imparts characteristic apple green color to the flame and with this let me begin the discussion about the chemical reactivity of group 2 elements of course, when we are looking to the reactivity we follow this sequence.

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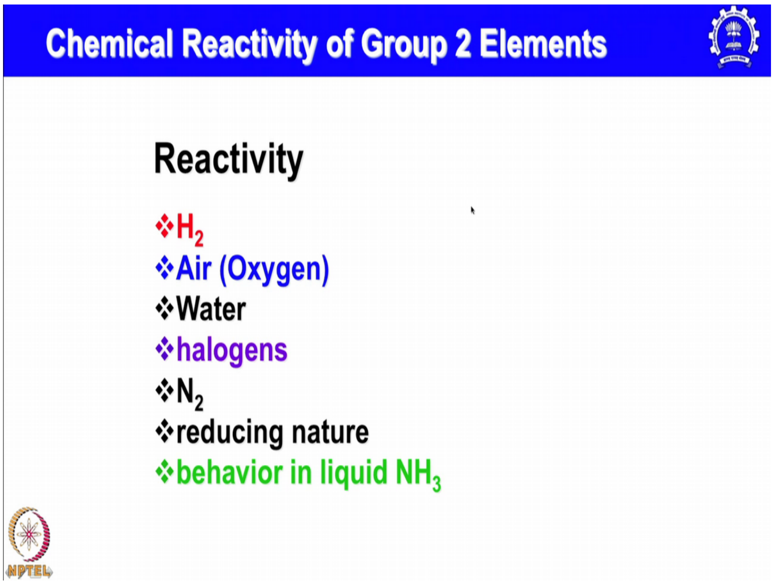

Let us look into first reaction with hydrogen to form hydrides and then with oxygen to form oxides and maybe with other chalcogens to form the corresponding chalcogenides and the interaction with water and then halogens and nitrogen and other reagents and then it is reducing nature and also behavior of alkaline earth metals in liquid ammonia.

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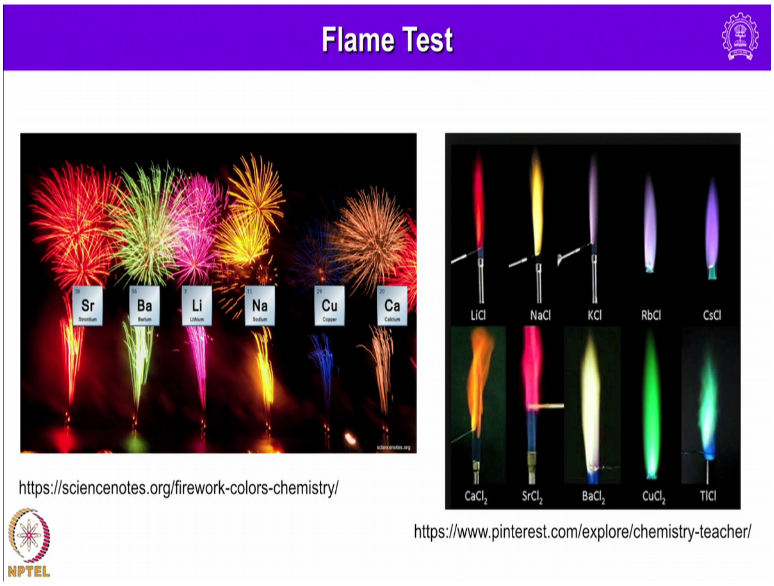

So, this is the flame test you can see here. So, calcium strontium and barium all I have shown and.

In fact, because of these vibrant colors they are also used in fireworks.

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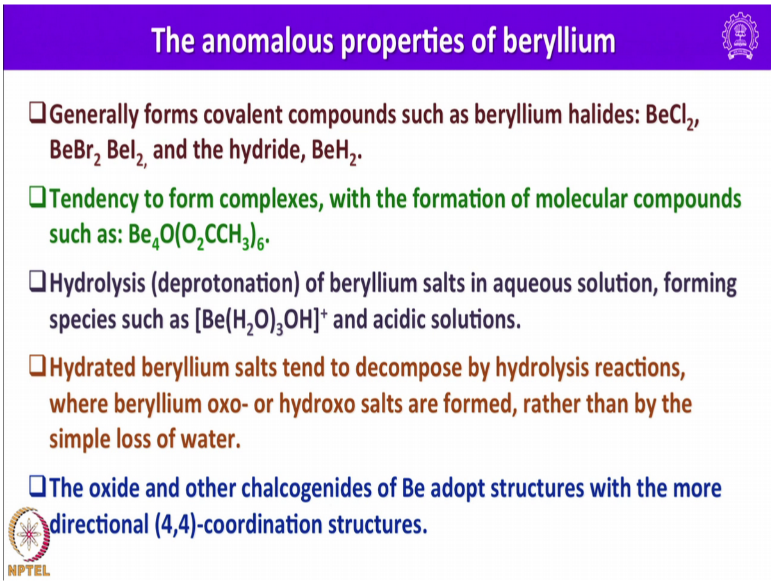

So, before I proceed to consider the reactivity of alkaline earth metals let us look into the difference in the properties of beryllium from the rest of the elements and; that means, the anomalous properties of beryllium should be looked into and let me discuss those properties generally beryllium forms covalent compound such as beryllium halides Be l2 Be Br2 beryllium iodide and also with hydrogen it forms covalent hydride BeH2 and they have a tendency to form complexes because of larger hydration enthalpy with the formation of molecular compounds such as beryllium acetate hydrolysis of beryllium salts in aqueous solution leads to the formation of species such as Be H2O thrice OH plus acidic solutions and hydrated beryllium salts tend to decompose by hydrolysis reactions where beryllium oxo and hydroxo salts are formed rather than by the simple loss of water.

So, that is the specialty of beryllium and the oxide and other chalcogenides of beryllium adopt structures with more directional coordination structures; that means, essentially they form some coordination compounds very similar to trans metal coordination compounds having preferably 4 coordination. So, beryllium forms many stable organometallic compounds as well including dibethyl bore beryllium, diethyl beryllium and di butyl tertial butyl beryllium and also it falls berylliosis similar to ferrocene; that means, bis cyclo pentadienyl beryllium compound and of course, since I am devoting a few lectures for the organometallic chemistry of main group elements that time I will be elaborating more about the synthesis and stability and structural aspects and both beryllium and aluminum form covalent hydrides and halides the analogous compounds of other group 2 elements are essentially ionic in nature.

The oxides of beryllium and aluminum are amphoteric whereas, the oxides of rest of the group elements are again basic this is also the trend very similar to what we saw in case of lithium in the presence of excess of hydroxide ions beryllium.

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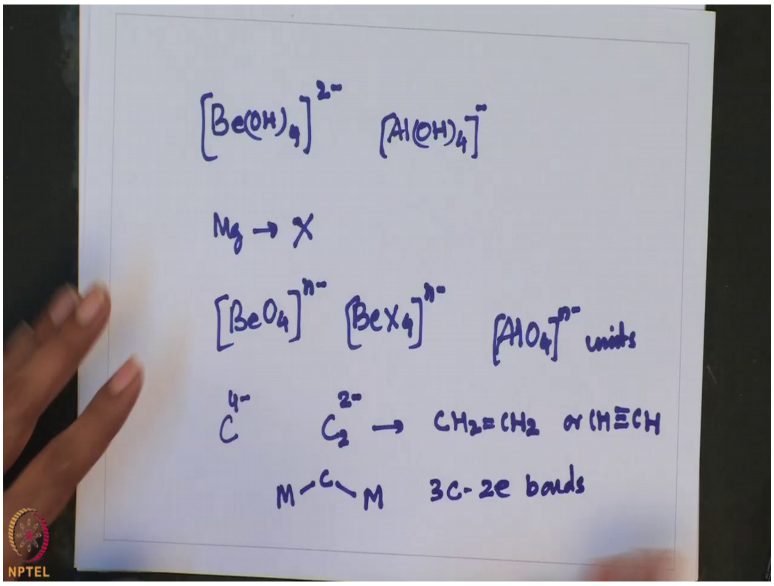

And aluminum form tetrahydroxy species like Be OH 4 times 2 minus of course, aluminum forms similar soluble hydroxide no equivalent chemistry is observed for whereas, magnesium does not show any of these properties and both elements form structures based on linked tetrahedra. So, beryllium forms structures built from minus and Be X4 x minus tetrahedral and aluminum also forms numerous aluminates and alumino silicates containing Al O4 n minus units.

So, this shows the similarities in the reactions and properties of beryllium with aluminum and both elements form carbides that contain C4 minus ion of course, in carbides these ions will be there and which on hydrolysis are reaction with water produce methane the other group 2 carbides contain essentially C2 2 minus ion and produce ethylene this essentially gives ethylene or acetylene of course, those things I will discuss later when the corresponding carbides are treated with water and alkyl compounds of beryllium and aluminum are electron deficient compounds that contain bridges; that means, essentially this is nothing, but 3 centered 2 electron bonds. So, this is quite common in case of alkyl beryllium and aluminum compounds and they undergo association to form one dimensional chain.

So, I will be elaborating later about the more details about this one, let us now continue with the chemical reactivity of group 2 elements smaller size compared to alkaline metals you should remember alkaline earth metals have smaller size compared to alkali metals.

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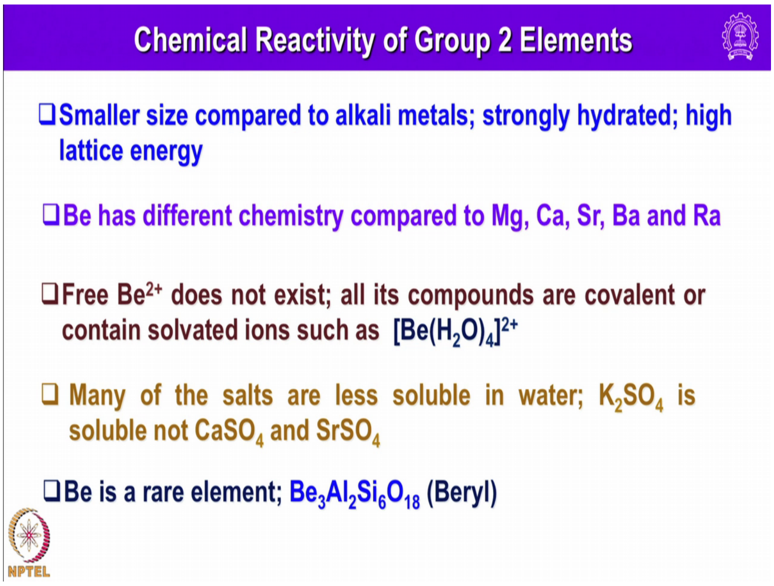

And they are strongly hydrated and they have high lattice energy compared to group 1 elements and in fact, beryllium has a different chemistry compared to it is heavier congeners free beryllium 2 plus ion does not exist all it is compounds are covalent or contain solvented ions.

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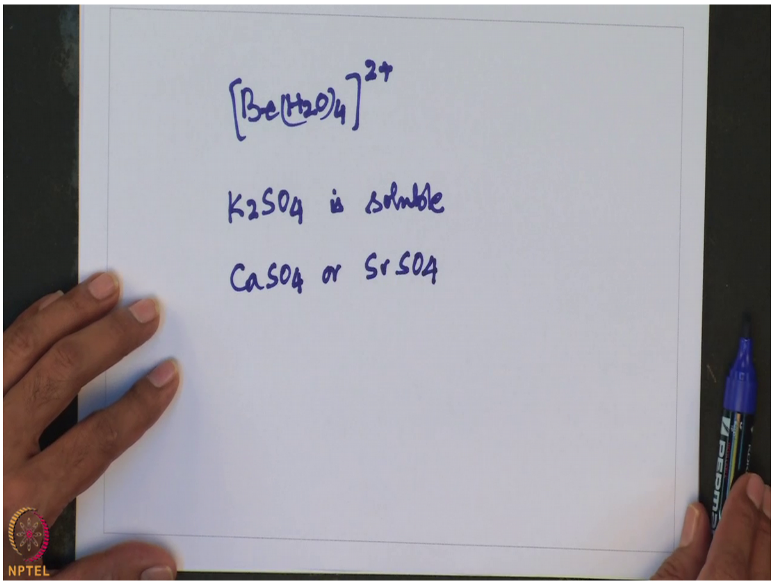

Such as yes; that means, it is very difficult to isolate free beryllium 2 plus ion many of the salts are less soluble in water K2 SO4 is soluble many of the group 2 salts are less soluble in water K2 SO 4 or NA 2 SO 4 if you take they are soluble in water whereas, Ca SO 4 or strontium SO 4 are insoluble. In fact, that trend increases down the group. In fact, most of the barium salts are insoluble and beryllium is a rare element and it is ore is important ore or source is beryl Be3 Al 2 Si 6 O18 of course, let me stop here in my next lecture I will be continuing the chemistry of main group 2 elements and begin my lecture with group 2 hydrides, have a pleasant inorganic chemistry reading until then.

Thank you.