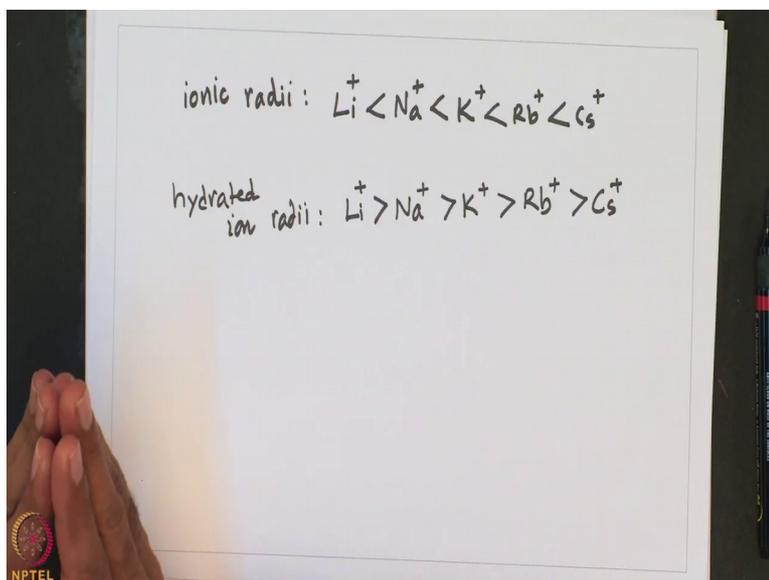


**Main Group Chemistry**  
**Prof. M. S. Balakrishna**  
**Department of Chemistry**  
**Indian Institute of Technology, Bombay**

**Lecture - 19**  
**Chemistry of Group 1 elements**

Welcome to MSB lecture series on main group chemistry, in my last lecture I was speaking about chemistry of group one elements. Let me continue from where I had stopped let me begin with a question; let us look into the ionic radii of group one elements it follows this order let us look into the hydrated ion radii hydrated ion radii.

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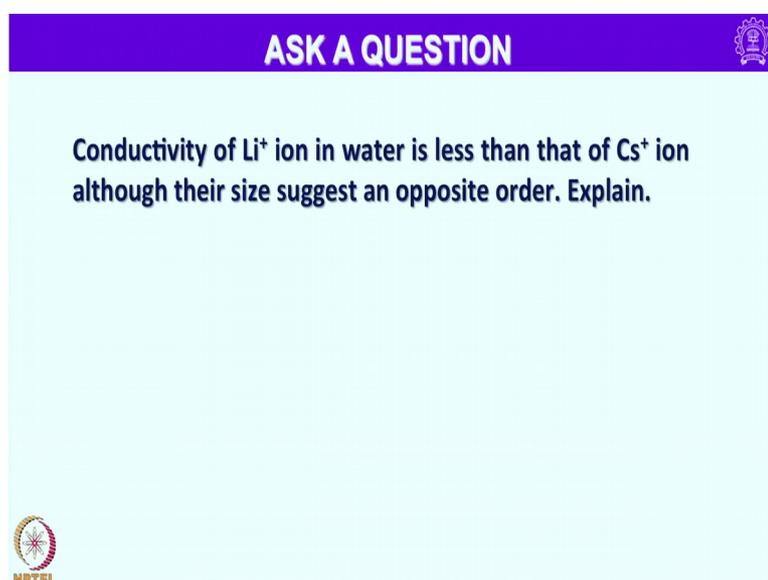
This follows a different trend exactly opposite trend. So, we have to look into it what is the reason for this, one let us look into first ionic radii. So, here we know that the size of atoms increases down the group, as a result what happens the relative energy of the cations also after removing the valence electron also should increase. So, this is according to the periodic trend and classification.

So, that is correct. So, lithium is the smallest and cesium is the largest ion. So, ionic radius increases, but what is happening here is, in case of hydrated ions radius decreases. So, this is because as charged to size ratio decreases when we go from lithium to cesium, hydration enthalpy also decreases. When the hydration enthalpy decreases they have less and less tendency to get hydrated or coordinated to water molecules; that means, lithium

shows because of larger charge to size ratio, it shows more hydration energy and coordination will be more efficient with lithium, and from lithium to cesium when you go across go down the group this hydration.

So, the coordinating ability decreases. As a result what happens surrounding the ions less and less number of water molecules should be there as a result what happens? The hydrated radius; obviously, decreases. So, this is because of the decrease in the hydration enthalpy, when the hydration enthalpy decreases they lose ability to get coordinated with ligands such as water, as a result in its coordination sphere less number of water molecules will be there as expected the hydrated radius will decrease.

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**ASK A QUESTION**

**Conductivity of  $\text{Li}^+$  ion in water is less than that of  $\text{Cs}^+$  ion although their size suggest an opposite order. Explain.**

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So, let us look into another question, here conductivity of lithium plus ion in water is less than that of cesium plus ion, although their size suggest an opposite order explain. This is exactly what I was explaining in my previous question to the previous question, just recall again whatever I said the smaller the size of the ion, the greater is the degree of hydration. When the size is small the degree of hydration is more, thus lithium plus ion with smallest size and highest charge to size ratio shows largest hydration enthalpy among all group one elements. So, the degree of hydration decreases on moving down the group that is from lithium to cesium plus. Due to the difference in degree of hydration ionic radii of hydrated alkali metal ions decreases from lithium to cesium, thus the ionic radii in aqueous solution decreases in the order.

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**Why I should Learn Main Group Chemistry**

**Potassium salts: resources and commercial demand**

World production of potash (strictly, potash refers only to KOH) rose from 0.32 Mt in 1900 to >50 Mt in 2007, with major producers being Canada and the former Soviet Union, followed by Germany. About 95% of the potash produced is destined to be used in the form of fertilizers. Now its production is ~70 Mt

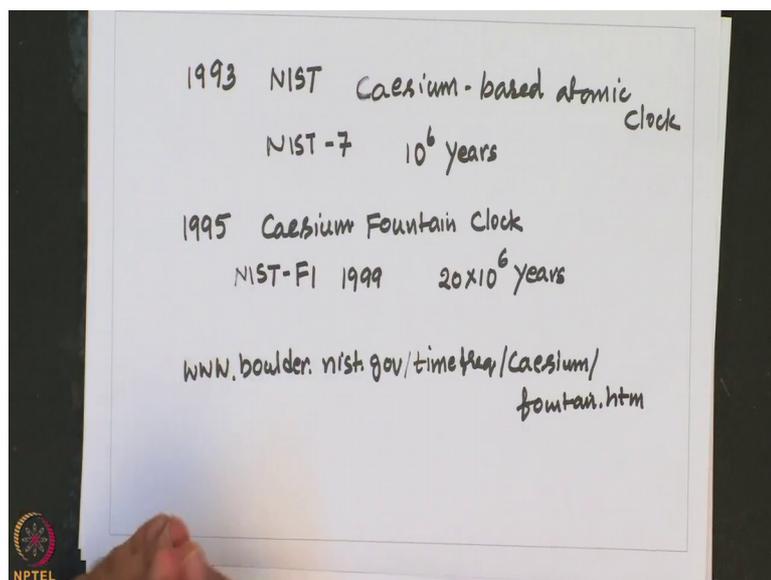


So, now sometime after learning inorganic chemistry or main group chemistry or transition metal chemistry, always some questions comes to your mind. Why I should learn main group chemistry main group elements or main group chemistry is an important branch of inorganic chemistry, and we come across utility of main group elements and their compounds in all walks of our life. So, let me disclose some of those things as we progress with this course.

Let us look into some aspects concerned with the main group elements especially group one elements. So, let us look into the potassium salts and the resources and commercial demand. So, world production of potash or potassium hydroxide rose from 0.32 metric ton in 1900 to around 50 metric ton in 2007 with major producers being Canada and the former Soviet Union USSR followed by Germany, and about 90 percent of potash that is produced worldwide is used in fertilizer manufacturing.

So, now the potash production is around 70 metric tons. So, that shows the importance of potassium salts especially potassium hydroxide, let us look into one more important aspect that revolves around cesium, keeping time with cesium what does it mean?

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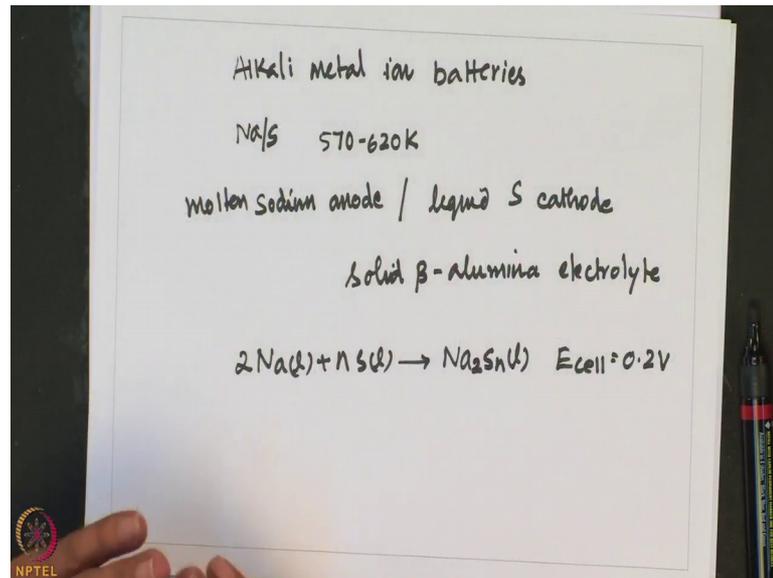


In 1993 so, national institute of standards of technology that is NIST and brought into use a cesium based atomic clock called this is called NIST 7, which kept international standard time to within one second in 10 to the power of 6 years; that means, the accuracy is one second in 10 to the power of 6 years.

So, this indicates the kind of accuracy we are looking into. So, the system depends upon repeated transitions from the ground to a specific excited state of atomic CS, and the monitoring of the frequency of the electromagnetic radiation that is emitted in 1995, the first cesium fountain clock that is called cesium fountain clock was constructed at the Paris observatory in France, a fountain clock also called as NIST F-1 was introduced in 1999 in the US to function as the countries primary time and frequency standard and NIST F-1 fountain clock is accurate to within one second in 20 into 10 to the power of 6 years. While earlier cesium clock observed cesium atoms at ambient temperatures cesium fountain clock use lasers to slow down and cool the atoms to temperature approaching 0 Kelvin for an online demonstration you can also look into the website.

So, here if you. So, this can give you more information of course, I have taken this information from (Refer Time: 10:04) in chemistry book by c e house craft and a g shark you can get more information from this website. So, another important application of alkali metals is in ion in alkali metal ion batteries.

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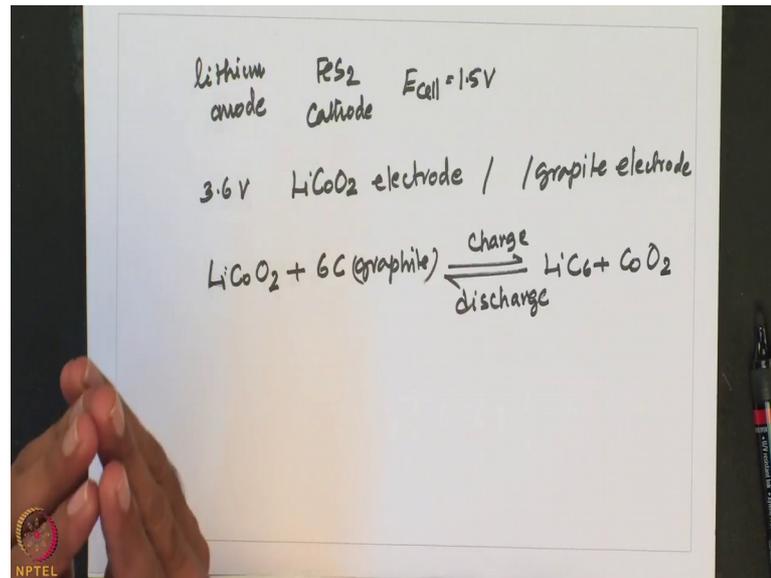
A sodium sulphur battery operates around 570 to 600 and 20 Kelvin and consists of a molten sodium anode and liquid sulphur cathode separated by a solid beta alumina electrolyte.

So, the cell reaction overall cell reaction I am going to write here liquid form, because its operates at such a high temperature 570 to 620 kelvin.

So, we are considering sodium molten sodium and liquid sulphur and here is 0.2 volts. So, and this is reversed when the battery is recharged by changing the polarity of the cell (Refer Time: 12:14) with the sodium sulphur battery in electric vehicles are quite promising, but further development is essentially needed to commercialize it. The high operating temperature is the major drawback with this sodium sulphide cell and of course, several properties of lithium including its highly negative reduction potential makes it much more suitable in battery industry.

For example if you consider lithium ion sulphide battery, that contains a lithium anode.

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Anode and ferrous sulphide cathode the E cell is 1.5 volts, and it finds uses in small devices such as cameras an important advancement in battery technology has been the development of lithium ion batteries, the lithium ion battery has a cell potential of 3.6 volts and consists of a lithium cobalt oxide electrode, and that is separated from a graphite electrode by a solid electrolyte across which lithium ions can migrate when the cell is charging.

The lithium plus ions are inter (Refer Time: 14:10) by graphite essentially  $\text{LiC}_6$  we call it because lithium is 6 coordinated, when the lithium vapors are positive between graphite at about higher temperature, lithium atom sit in between the graphite having a coordination of 6 carbon atoms; that means, lithium assumes an octahedral geometry having 3 carbons below and 3 carbon. So, essentially that s the reason the composition we call it as  $\text{LiC}_6$ . So, here lithium ions are intercalated by graphite and written to the  $\text{LiCoO}_2$  electrode when the cell is discharged the cell reaction can be written in this fashion cobalt oxide.

So, the crucial factor in this battery is that both electrode are able to act as hosts for lithium plus ions, and the system has been termed as rocking chair as lithium accelerates between both sides of this one. So, essentially both the electrode so; that means, we have 2 host materials and both of can take lithium while charging and discharging. So, lithium ion batteries have applications in laptop notebooks,

computers mobile phones and portable audio video devices and have potential use in electrical car as well.

So, let me give some more information in this slide. So, lithium rechargeable battery.

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**Lithium batteries** 

- The lithium rechargeable battery, used in portable computers and phones, mainly use  $\text{Li}_{1-x}\text{CoO}_2$  ( $x < 1$ ) as the cathode with a lithium/graphite anode,  $\text{LiC}_6$ .
- Lithium ions are produced at the anode during the battery discharge. To maintain charge balance,  $\text{Co}^{\text{IV}}$  is reduced to  $\text{Co}^{\text{III}}$  in the form of  $\text{LiCoO}_2$  at the cathode.

The reactions occurring during battery discharge are:

Cathode:  $\text{Li}_{1-x}\text{CoO}_2(\text{s}) + x\text{Li}^+(\text{Sol}) + xe^- \longrightarrow \text{LiCoO}_2(\text{s})$

Anode:  $\text{C}_6\text{Li}_{1-x} \longrightarrow 6\text{C}(\text{graphite}) + \text{Li}^+(\text{Sol}) + e^-$

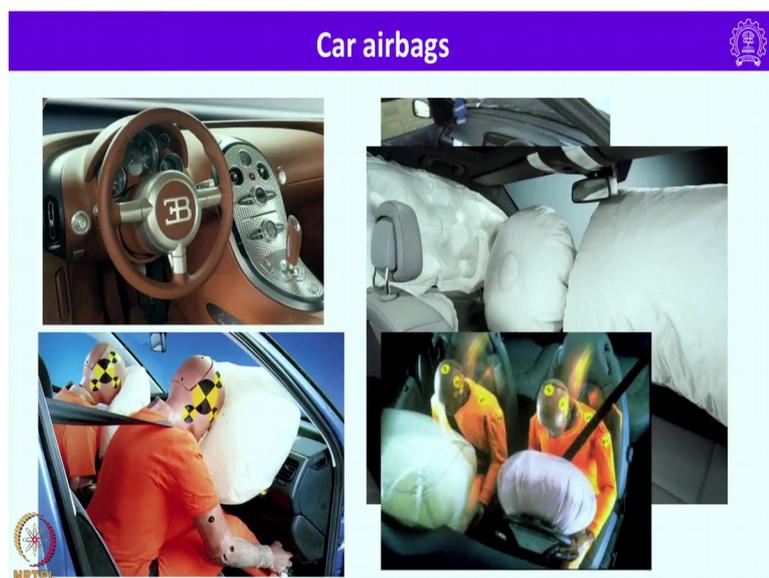


So, that I had mentioned mainly uses this lithium cobalt oxide as the cathode, with a lithium graphite anode as I mentioned there you are taking the composition of lithium to carbon as 1 is to 6. So, lithium ions are produced at the anode during the battery discharge to maintain charge balance, cobalt 4 is reduced to cobalt 3 in the form of  $\text{LiCoO}_2$ , if you look into species here cobalt is in plus 3 state at the cathode.

So, the reaction occurring during battery discharge is shown here. So, at cathode this is what the reaction happens and at anode this is the reaction. So, the battery is rechargeable because both the cathode and the anode can act as host for lithium ions, which can move back and forth and hence this battery is also called rock chair battery so; that means, charging and discharging can happen simultaneously.

So, let me come to another important application, you may be surprised to see why I have brought car airbags into the discussion, especially while discussing the chemistry of main group elements that is alkali metals of course, there is some chemistry behind this car bags, that has to do something with group one elements especially sodium. Let us look into it what it is, we can see this is the steering wheel of car.

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And here this is where the air bag is fixed in this one, we can see here. So, when there is an impact air bag start getting inflated, and this is how it happens and you can see how it protects the driver and co passenger you can see this one something like this. So, let us look into some technicality of car airbags before I come to the chemistry part; that means the utility of alkali metals in air bags ok.

So, let us look into how airbags work. Timing is very very important in airbags ability to deploy quickly enough to save a life in a head on collision. An air bag must be able to deploy in a matter of milliseconds, from the in shell collision impact and also we prevented from deploying when there is no head on collision; that means, when sudden application of brake is there or when the car moves over humps I have a small jerks and all those things should not leads to the opening of the airbag, the precautions has to be taken.

That means, the main component of the airbag system is a sensor that can detect only head on collisions, and immediately trigger the airbags deployment, the crash sensor essentially is a steel ball that slides inside a smooth bore next to the airbag. So, the ball is held in place by a permanent magnet or by a stiff spring which inhabits the balls motion when the car drives over bumps and pot holes.

So; that means, unless and otherwise there is a head on collision, the deployment of airbag should not take place. However, when the car decelerates very quickly as in a



This decomposes to form 2 N<sub>2</sub> and 3 equivalents of nitrogen. So, this nitrogen is responsible for deflating airbag so; that means, during this process we are getting elemental sodium, and elemental sodium is quite toxic and hazardous and it can also irritate skin oh. So, in that case we find a way to neutralize this one how it is done? You can see that in this is reaction one, in the reaction 2 I will show you how to neutralize the sodium that is released during the decomposition of sodium azide. So that means, along with sodium azide, we should also keep inside the airbag small quantity of potassium nitrate. This potassium nitrate reacts with sodium that is liberated during the decomposition of sodium azide to form sodium oxide potassium oxide plus extra nitrogen is also released this also helps in inflating the airbag. So, one more reaction is there.

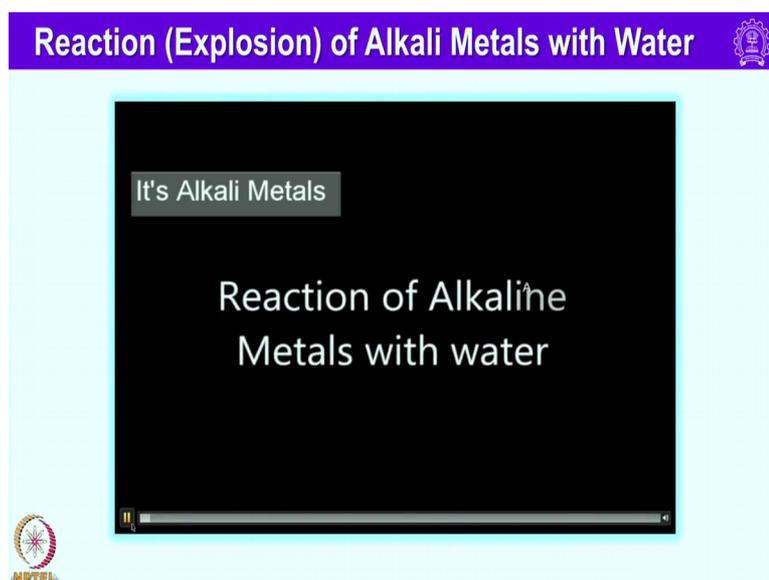
Now, we have to neutralize they are also quite hygroscopic and can be hazardous, now we have to find a way to neutralize them in reaction 3 I am going to show that one.  $K_2O + N_2O$  we are adding some silica  $SiO_2$  to neutralize both, what we get is sodium potassium silicate.

So, this is called alkaline silicate glass. So, at this stage if something happens to airbag and if any leakage is there, there will not be any damages to the life of an individual who is sitting in front of this airbag. So that means, a certain pressure is required to fill the airbag within milliseconds. Once this pressure has been determined the ideal gas law can be used to calculate the amount of  $N_2$  that must be generated to fill the airbag to this required pressure.

The amount of sodium azide in the gas generator is then carefully chosen to generate this exact amount of nitrogen gas. So, typically a car airbag has a capacity of 70 liters capacity of airbag is equals 70 liters approximately, and this requires about 130 grams of sodium azide. So, 130 grams means essentially if you just look into the molecular weight of sodium azide, it is essentially 23 plus 42 it is 65.

65 grams is equal to one mole, we need approximately 2 moles that is 130 grams 2 moles we need, and we need about thirteen grams of  $KNO_3$  so; that means, a typical airbag contain 130 grams of sodium azide and 13 grams of potassium nitrate, and then the equivalent amount of silica these things are there in the airbag this is how airbag works. I will show you this video.

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Reaction (Explosion) of Alkali Metals with Water

It's Alkali Metals

Reaction of Alkaline Metals with water

NPTEL

This slide features a purple header with the text "Reaction (Explosion) of Alkali Metals with Water" and a small logo on the right. Below the header is a video player window with a black background. The video player displays the text "It's Alkali Metals" in a grey box at the top left and "Reaction of Alkaline Metals with water" in white text in the center. A video control bar is visible at the bottom of the player. The NPTEL logo is located in the bottom left corner of the slide.

It gives some information about the nature of alkali.

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Reaction (Explosion) of Alkali Metals with Water

Lithium

NPTEL

This slide features a purple header with the text "Reaction (Explosion) of Alkali Metals with Water" and a small logo on the right. Below the header is a video player window with a black background. The video player displays the word "Lithium" in white text in the center. The NPTEL logo is located in the bottom left corner of the slide.

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## Reaction (Explosion) of Alkali Metals with Water



Metals for example, if lithium is put into water you can see how it ignites.

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## Reaction (Explosion) of Alkali Metals with Water

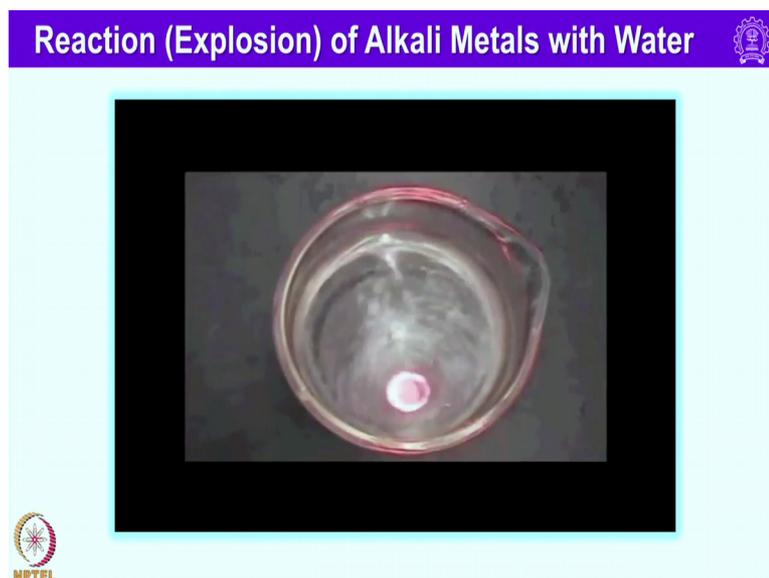


Sodium



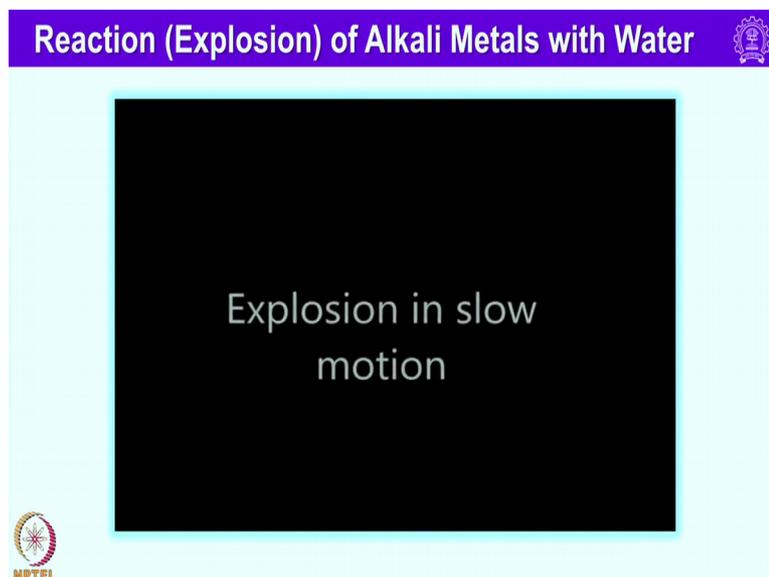
Now, let us look into the sodium what would happen.

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if you add little bit of sodium to water you can see it rigorously very vigorously it reacts and here the color whatever you are seeing is due to the liberation of  $H_2$  hydrogen gas, and that hydrogen gas combines with oxygen to form water highly exothermic and we can see this explosion in slow motion.

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Reaction (Explosion) of Alkali Metals with Water



youtube.com/periodicvideos

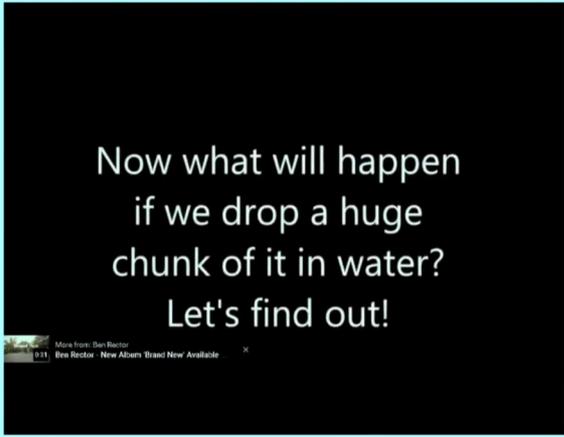
More from: Dan Recker  
Eye Recker - New Album Brand New Available



So, just look into it what would happen.

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Reaction (Explosion) of Alkali Metals with Water



Now what will happen  
if we drop a huge  
chunk of it in water?  
Let's find out!

More from: Dan Recker  
Eye Recker - New Album Brand New Available



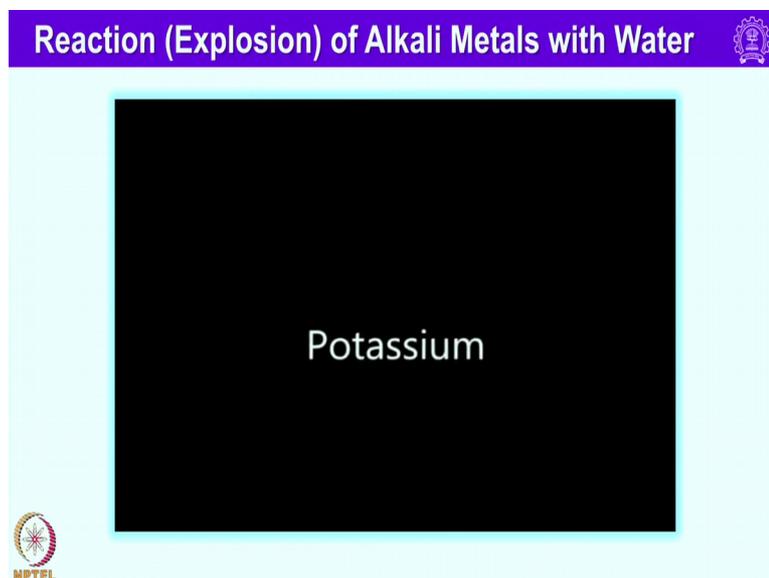
If you put a half a kilo of sodium into water of course, one should not try these things these are all tried.

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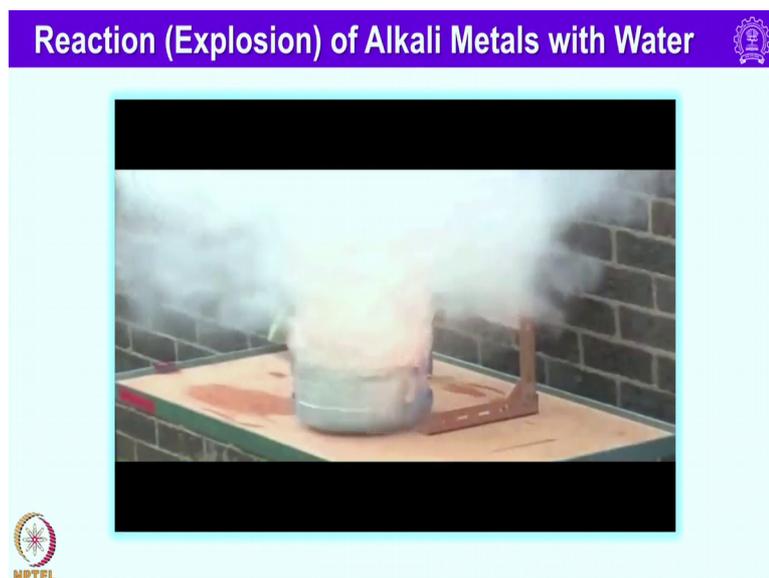
under taking all kind of safety norms and one should not try this kind of reactions because it can do damage to marine animals.

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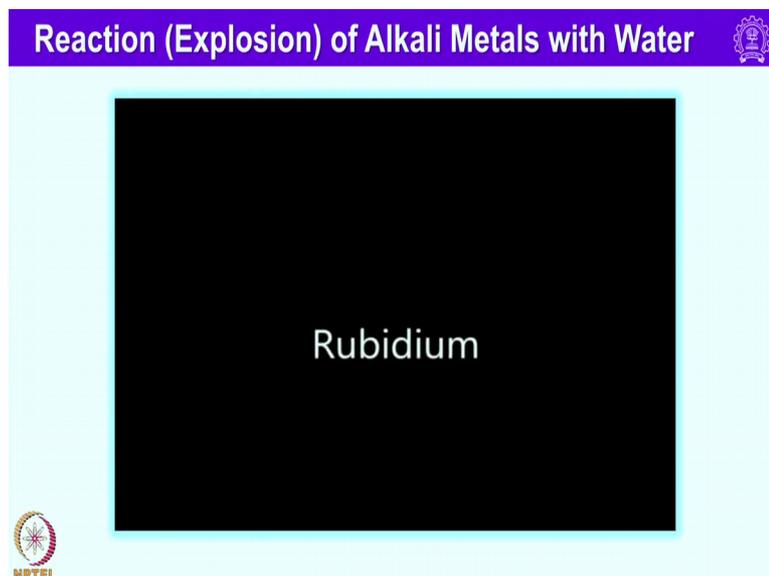
That shows the reactivity of

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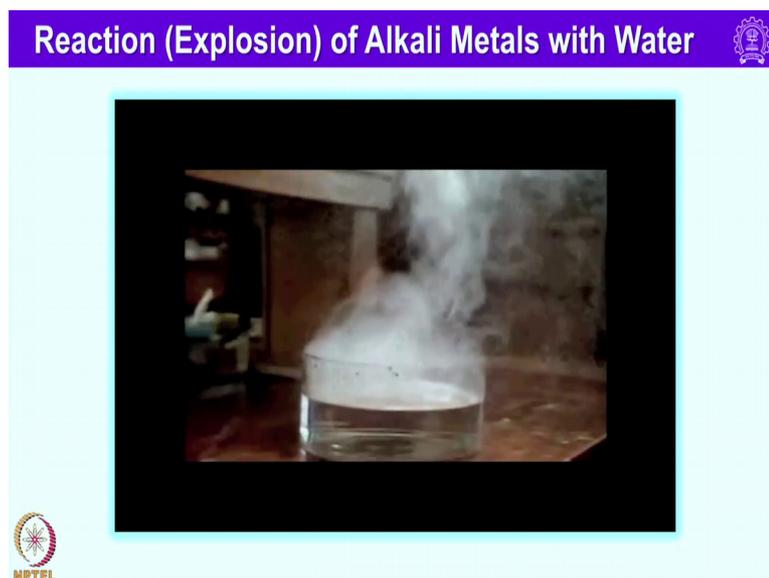
these.

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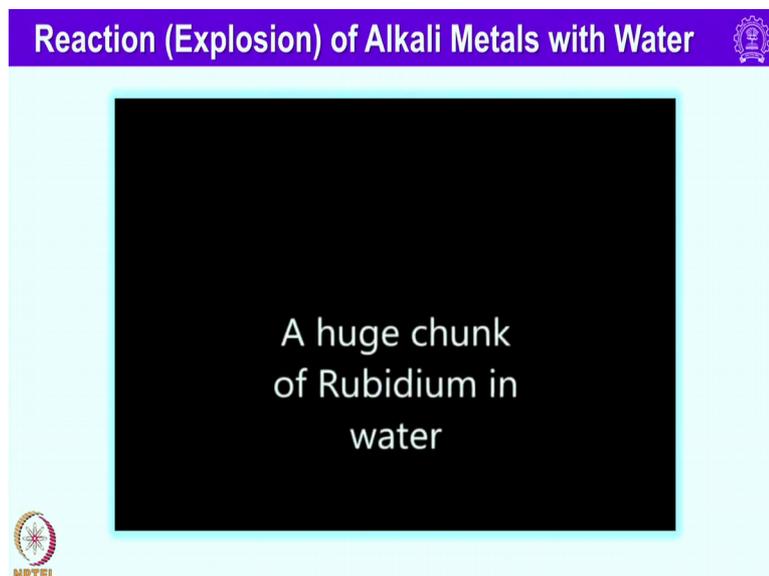
Alkali metals this is with rubidium.

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As I mentioned reactivity increases when you go down a group.

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That means reactivity of rubidium is much more drastic.

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Reaction (Explosion) of Alkali Metals with Water 



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Violent compared to sodium or potassium cesium

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Reaction (Explosion) of Alkali Metals with Water 

Caesium (or  
Cesium)

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is even more reactive,

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Reaction (Explosion) of Alkali Metals with Water 



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Reaction (Explosion) of Alkali Metals with Water 

Large volume  
of it

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So, let us before I conclude my lecture on chemistry of main group elements let me just give some idea about who discovered these alkali metals, you already saw how they look like this is how lithium looks like.

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### Who discovered Alkali Metals

The slide features a purple header with the title "Who discovered Alkali Metals" and the NPTEL logo. Below the header are five images: a piece of metal in a glass of water, a piece of metal being cut, two pieces of metal, a piece of metal being cut, and a piece of metal being cut. Below these images are four portraits of scientists: Johan August Arfwedson, Humphry Davy, Robert Bunsen, and Gustav Kirchhoff. Each portrait is accompanied by text describing their discovery of an alkali metal.

Johan August Arfwedson is credited with the discovery of lithium in 1817

Sodium was first isolated by Humphry Davy in 1807 by the electrolysis of sodium hydroxide, also potassium.

Rubidium and Caesium were discovered in 1861 and 1860 by Robert Bunsen and Gustav Kirchhoff, in Heidelberg, Germany.

Lithium is much lighter compared to rest of the alkali metals, you can see it is floating on hydro carbon and this was discovered by John August in 1870 and this is sodium, you can see that grey color is because of formation of sodium oxide layer on it.

Otherwise they should be looking like silver with shiny surface, and potassium is this one when you fresh melt it, it appears like a silver ball and both of them were discovered by Humphry Davy in 1807 of course, sodium he identified by the electrolysis of sodium hydroxide and same time he may also find out the existence of potassium, and then this is rubidium and cesium they are kept in a sealed vial these 2 are discovered by Robert Bunsen and Gustav Kirchhoff for Germany, and you must be familiar with Robert Bunsen's name in the schools and colleges we used to use Bunsen burner for doing flame test and other things, that Bunsen is the person who is responsible for discovering Bunsen burner.

With this let me summarize the chemistry of group one elements or.

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**Summary on Group 1 Elements** 

- **Group 1 elements and their compounds follow the Periodic Properties and Trends with very least or no variations**
- **Alkali metals are highly reactive, and form basic oxides and water soluble halides, containing  $M^+$  cations**
- **Among alkali metal compounds, whether Hydrides, Oxides, Halides or Organometallic compounds, ionic properties dominate the chemistry.**
- **However, lithium with its small size, shows partial covalent character in its many compounds and shows resemblance to magnesium (diagonal relationship)**



Group one elements and their compounds follow the periodic properties and trends, with very least or no variations they strictly follow the periodic trends. Alkali metals are highly reactive just now you witnessed in the in the slide I showed and form basic oxides, and water soluble halides containing  $m$  plus cations; that means, group oxide state is plus one and alkali metal compounds whether hydrides, oxides, halides or organometallic compounds ionic properties dominates the chemistry and most of them are ionic in nature.

However lithium with its small size and having a larger charge to size ratio shows partial covalent character, in almost all bonds that makes with other main group

elements. And it has more resemblance to magnesium rather than sodium or potassium. With this I conclude my lecture on group one elements in my next lecture I will be drawing your attention to the chemistry of group 2 elements, and till then have a pleasant time of reading inorganic chemistry.

Thank you very much.