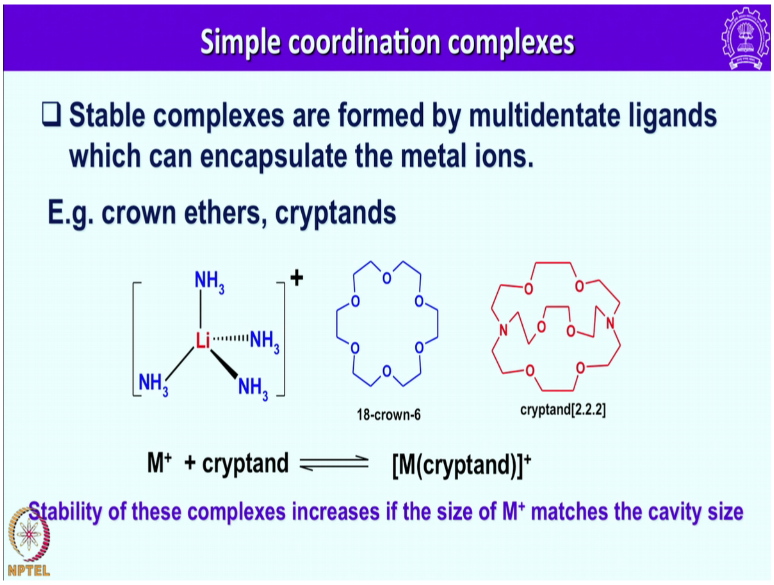
Main Group Chemistry
Prof. M.S. Balakrishna
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture - 18
Chemistry of Group 1 elements

Welcome to MSB lecture series on Main Group Chemistry. In my last lecture I was discussing about the interaction of alkali metals with the hydrogen and then with organic reagents and also I discussed about alkyl lithium reagents. Let me continue discussion on main group elements and their compounds.

So, alkali metal complexes such as halides form relatively very few complexes with neutral ligands for example, if we consider any of the transform metal halides on exposed to ligands such as water ammonia they readily form complexes having anywhere from 4 to 6 coordination number or even more in case of heavier d block elements. Here alkali metals form relatively very few complexes with neutral ligands, lithium salts are more soluble in solvents such as ethanol and ethers then those of other group members and lithium is 4 coordinate whereas, sodium and potassium prefer 6 coordination.

(Refer Slide Time: 01:38)



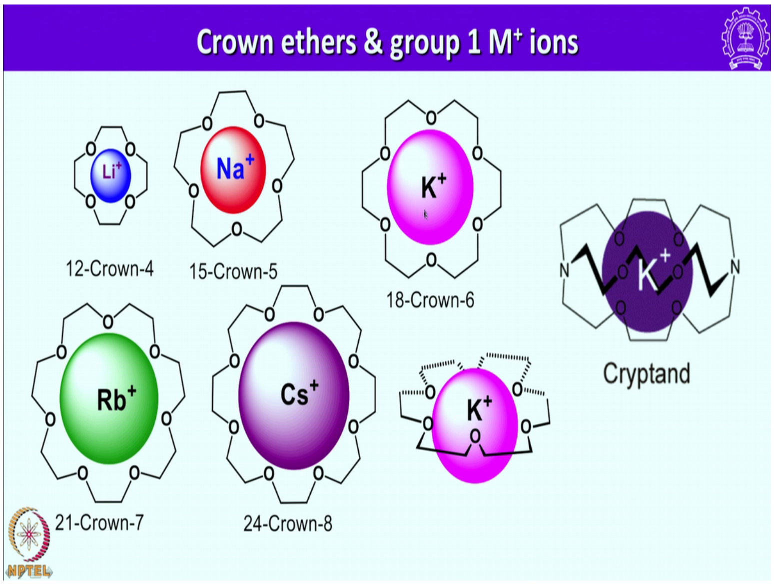
That means, stable complexes are formed by multidentate ligands which can encapsulate the metal ion in order to stabilize a cation coming from alkali metals one has to use a multidentate ligand which can encapsulate the metal ion.

So, in this context we have 2 type of ligands they are very very important in stabilizing alkali metal cations they are called crown ethers and cryptands. As I said lithium prefers 4 coordination, you can see here tetra mine lithium compound is shown here and these are all called crown ethers and cryptands. Here we can see in this cyclic ring we have oxygen and these oxygens are bridged by ethylene groups and in this case we have 6 oxygen atoms and this is called as 18 crown 6 whereas, in this case we have 2 nitrogen atoms flanked by 3 ether groups and this is called cryptand and its name you can see we have some numbers here cryptand in square bracket 2, 2, 2 this essentially represents between 2 nitrogen atoms we have in each chain we have 2 oxygen atoms 2 here, 2 here, 2 here

So, that refers to between 2 nitrogen atoms in each linker we have 2 oxygen atoms and for example, in one of the linker if we have 3 it can be 2 2 3 or 2 3 2 or 3 2 2. So, this is how it is referred. So, I will show you how we arrive at this number. For example, when you take a cation and you add cryptand. So, cryptand essentially encapsulates this cation in its fold through the coordination of nitrogen as well as oxygen with their lone pairs.

So, stability of these complexes increases if the size of M plus cation matches the cavity size if the cavity size is comparable to the size of the alkali metal cation then those compounds are more stable and especially when you want to stabilize some of these cations we have to go with precise crown ethers.

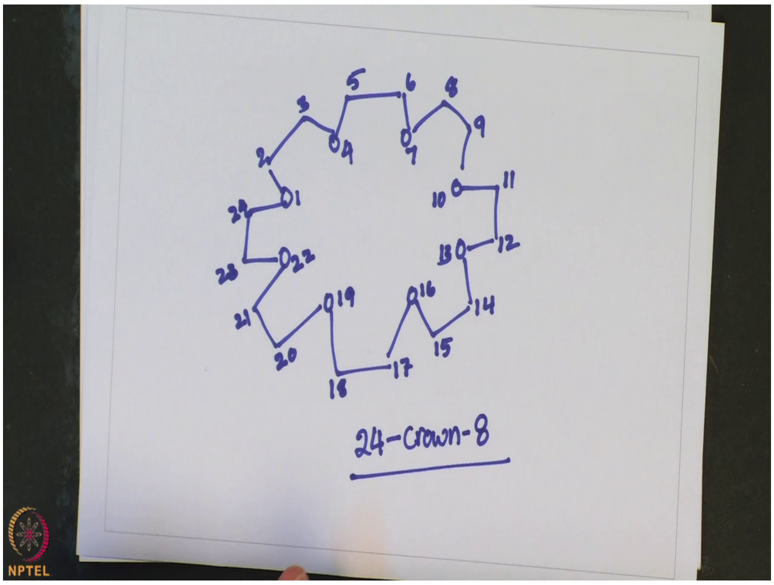
(Refer Slide Time: 04:11)



You can see here we have number of crown ethers for example, in order to stabilize lithium since it is a lithium ion is much smaller in size 2 crown 4 is sufficient, for sodium we need 15 crown 5, in case of potassium we need 18 crown 6 and we can see here in case of rubidium due to the larger size one can use 21 crown 7. Similar in case of cesium we require to stabilize cesium cation 24 crown 8 ether you can see here how this crown ether is encapsulating K plus ion and of course, here we have 3 such linkers are there with donor atoms such as oxygen in cryptand and in here they are flanking in this fashion essentially it is called encapsulation.

Now, let me come to the naming of these why we call 18 crown or 15 crown. Let me write one crown ether here.

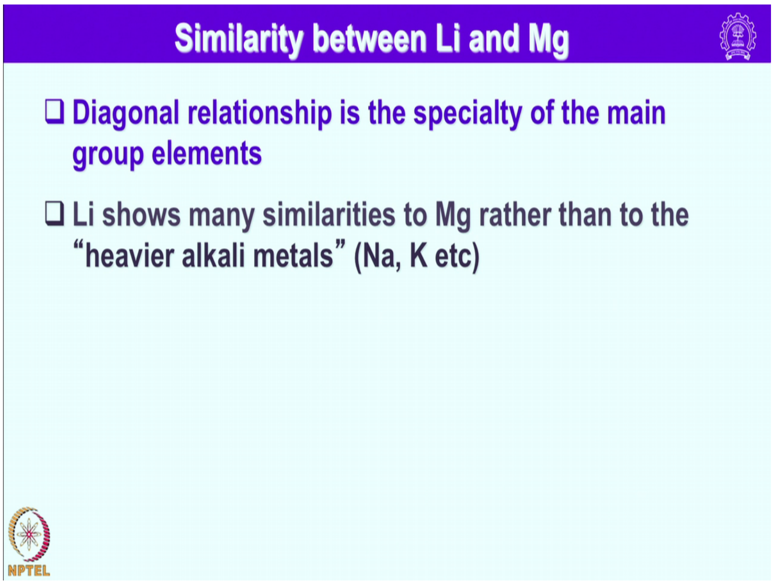
(Refer Slide Time: 05:24)



So, now, I have written some oxygen atoms, now connect them through ethylene linkers you start numbering from somewhere 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24; that means, we have a cyclic ring with 24 atoms in this ring. And in this one that is the reason we call it first we write 24 and since all these ethers are not planar they are folded or puckered and when they are puckered especially while capsulating a cation they appear like crown that is the reason term crown is used here and then this number represents home the number of oxygen atoms present here 1 2 3 4 5 6 7 8 are there. So, this is 8.

So, this is how one can name these ethers no matter how many ethylene groups are there and how many oxygen atoms are there. If 24 crown 8 in the same way one can write for all crown ethers. And let us look into some similarities between lithium and magnesium.

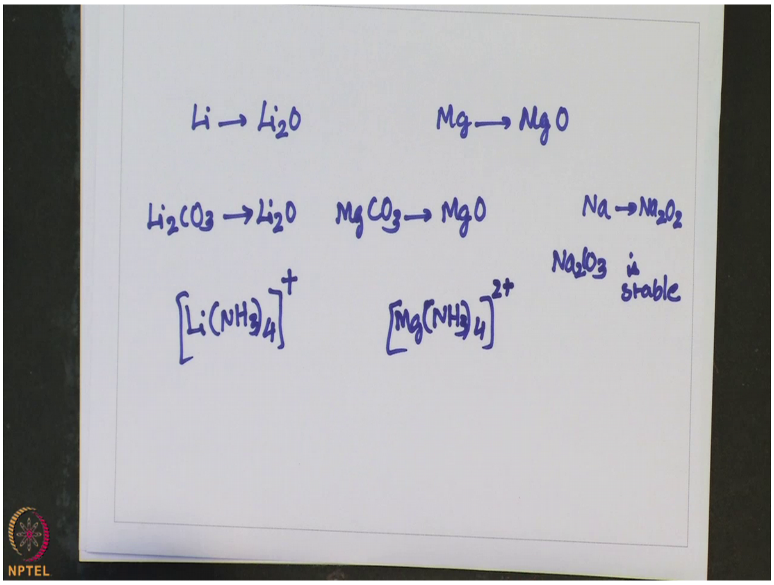
(Refer Slide Time: 07:25)



So, this is called diagonal relationship when we are comparing one naught one element from the group one down this is called diagonal relationship and this diagonal relationship is very very important in case of main group elements.

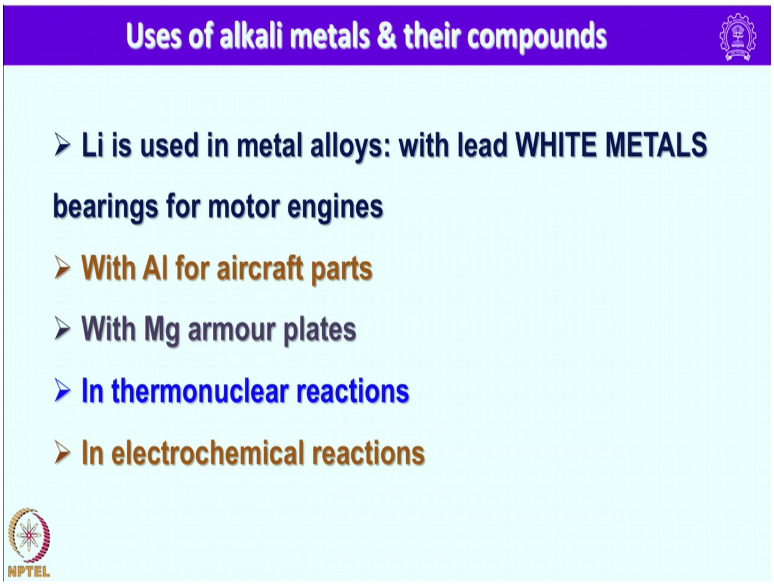
For example here lithium shows many similarities to magnesium rather than to the heavier alkali metals from its own group such as sodium and potassium. Let us look into few examples here let us see lithium forms lithium oxide, similarly magnesium forms magnesium oxide so; that means, lithium has a preference to form only oxide not peroxide in the same way magnesium has a preference to form magnesium oxide whereas, sodium forms sodium peroxide.

(Refer Slide Time: 08:03)



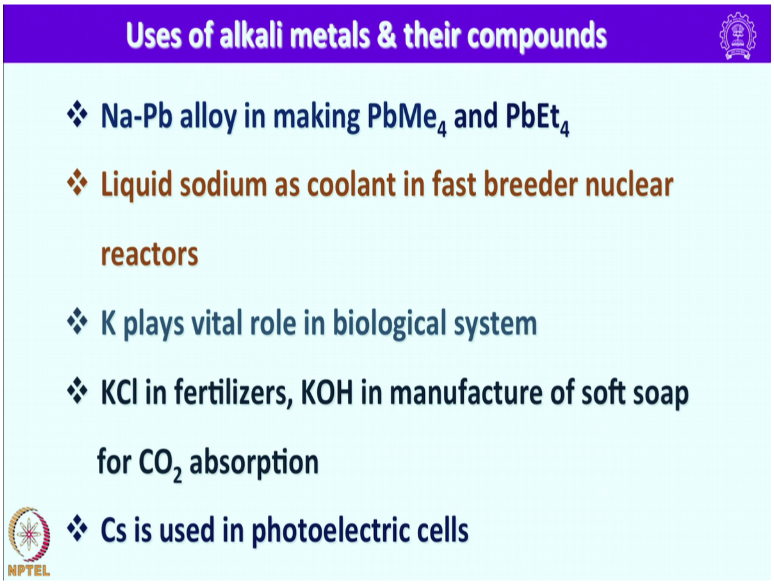
So, let us look into lithium carbonate on heating it readily gives lithium oxide plus CO 2. Similarly, magnesium carbonate on heating gives magnesium oxide and carbon dioxide whereas; Na 2 CO 3 is relatively more stable. And lithium forms a tetra mine complex like this similarly magnesium also forms tetramine complex time being these 3 examples are you know to show the similarities between lithium and magnesium when I start discussing the chemistry of alkaline earth metals I would come back again to show more similarities between lithium and magnesium.

(Refer Slide Time: 09:47)



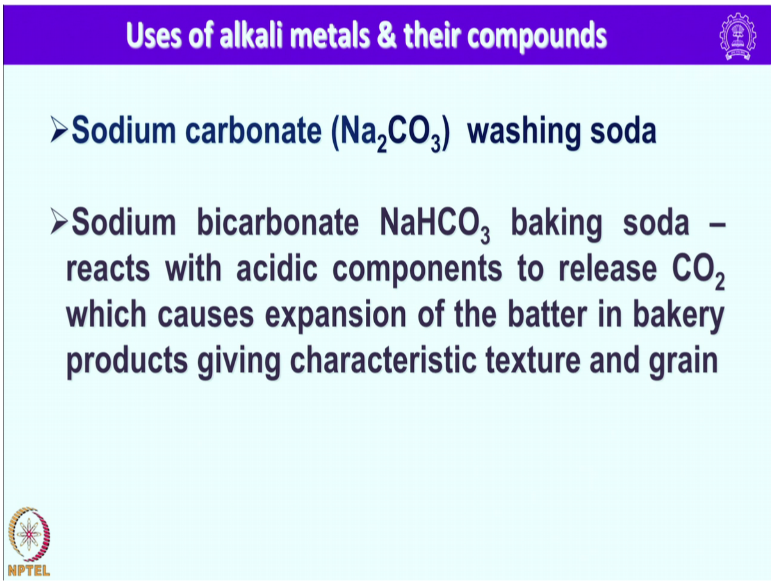
Now, let us look into the uses of alkali metals and their compounds. And lithium is used in metal alloys especially when it is combined with lead that leads to the formation of white metals and these white metals are used in bearings for motor a engines. When lithium is combined with aluminum it imparts hardness and since aluminum is lighter so they are used in aircraft parts. With magnesium used in armor plates and also lithium is used in lithium and some of the alkali metals are used in thermonuclear reactions and also they are widely used in electrochemical reactions.

(Refer Slide Time: 10:32)



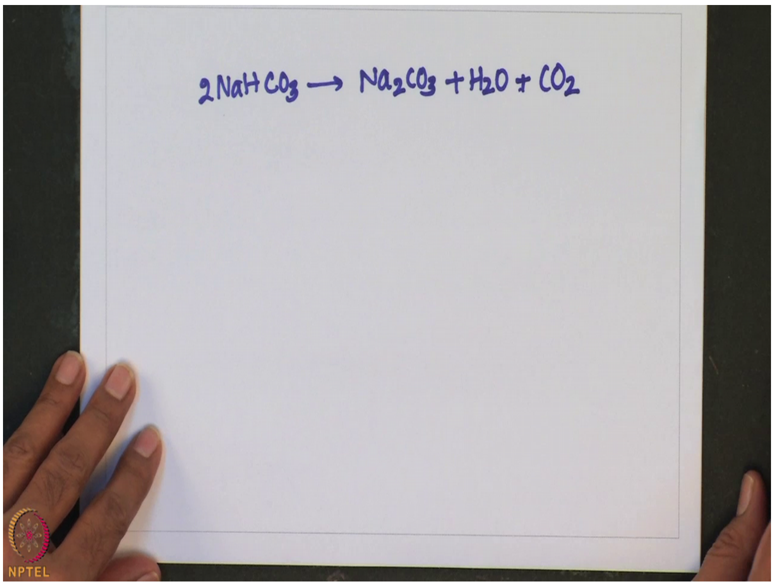
And sodium and lead alloy is used in making tetra methyl and tetra ethyl lead. And tetra methyl and tetra ethyl leads were used extensively about 10 to 15 years back as additives to petrol as anti knocking reagents. I would elaborate about this properties when I discuss the chemistry of group 14 elements and liquid sodium as a coolant in fast breeder nuclear reaction. So, liquid sodium is used as a coolant in fast breeder nuclear reactions and also potassium plays a very very important role in biological system along with sodium plus ions. And KCl is extensively used in fertilizers and potassium hydroxide is used in the manufacture of soap and also for CO 2 absorption and cesium is used in photoelectric cells and sodium carbonate washing soda and sodium bicarbonate is known as baking soda.

(Refer Slide Time: 11:40)



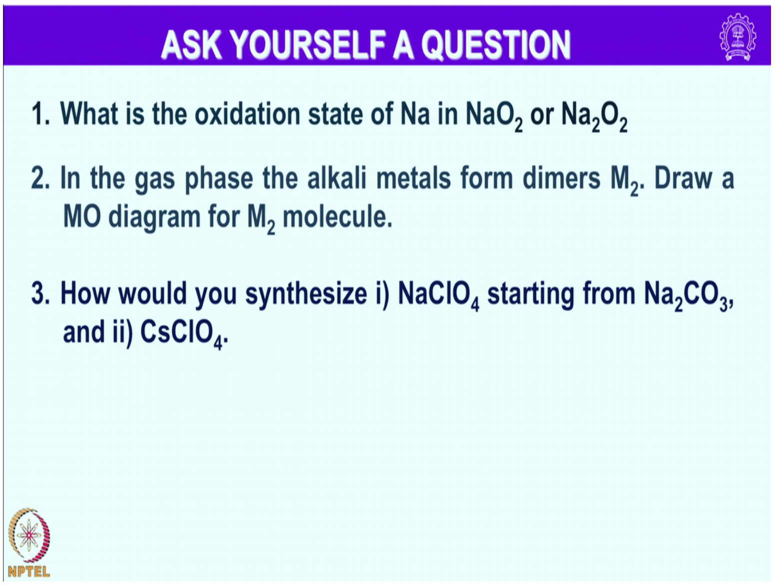
So, this sodium bicarbonate reacts with acidic components to release carbon dioxide which causes the expansion of the batter in bakery products giving a characteristic texture and grain. Let us look into those reactions here. So, for example, sodium bicarbonate gives on heating sodium carbonate plus H 2 plus CO 2. So, this CO 2 is used in fermentation process and also in bakery products.

(Refer Slide Time: 12:07)



So, now, let us look into few questions here. So, what is the oxidation state of sodium in Na O 2 or Na 2 O 2. So, one should be able to tell simply by looking into the oxygen how many oxygens are there and what are the charges on them.

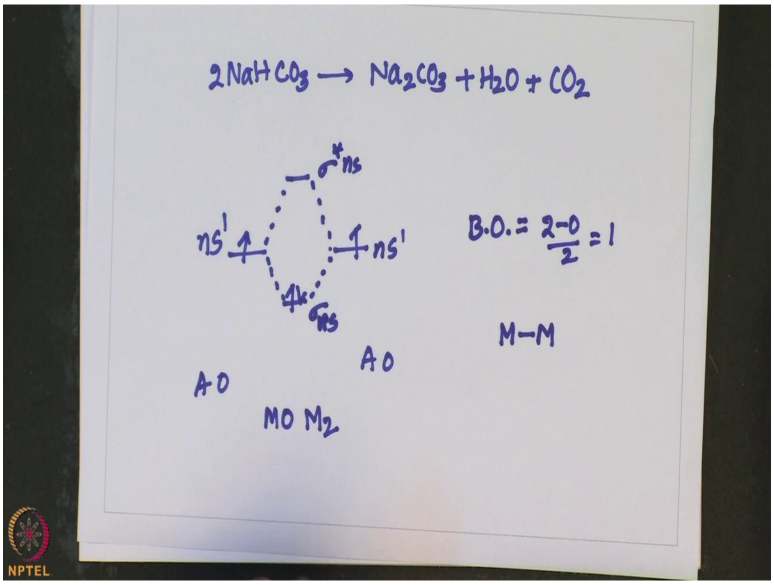
(Refer Slide Time: 12:30)



For example, if you take Na O 2. So, here O 2 2 minus it is a peroxide. So, you can say it is Na plus and in both the cases oxidate of sodium one can tell as Na plus because it cannot show higher oxygen states.

In the gas phase the alkali metals form dimers M 2. So, draw a MO diagram for M 2 molecules. So, while discussing the structure and bonding aspects especially while elaborating on molecular orbital theory I wrote MO diagram for dimmers of most of the group 1 and group 2 second row elements. So, in the same way one can write it its very simple since we have one electron in their valence shell, ns 1 can be written here we have one electron can be represented like this. So, another one is from another one electron.

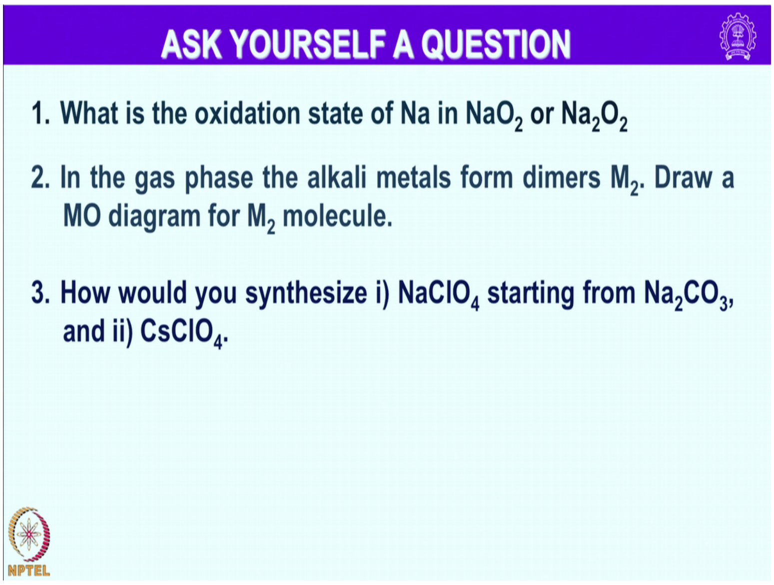
(Refer Slide Time: 13:35)



So, now, these two atomic orbitals will generate two molecular orbitals sigma ns and here sigma star ns. So, here these two electrons will be paired. So, now let us this is the MO diagram for M 2 species. Now let us look into the bond order of course, bond order by definition you know number of electrons in the bonding molecular orbitals minus number of electrons in anti bonding molecular orbitals divided by 2. So, here 2 minus 0 by 2 equals 1, yes it is possible to alkali metals to exist in the form of a dimer. So, this is the answer.

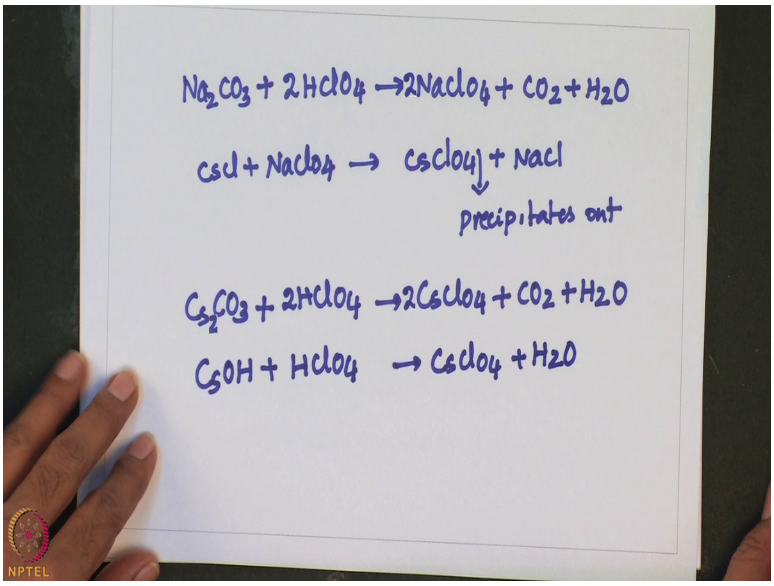
How would you synthesize sodium per chloride starting from sodium carbonate and cesium per chloride?

(Refer Slide Time: 14:52)



The next question is how would you synthesize sodium per chloride starting from sodium carbonate and then cesium per chlorate. So, now, let us look into the preparation of sodium per chlorate and cesium per chlorate. So, starting from sodium carbonate sodium carbonate let us treat sodium carbonate with per chloric acid. So, it can give directly sodium (Refer Time: 15:27) chlorate with a liberation of CO 2 and water.

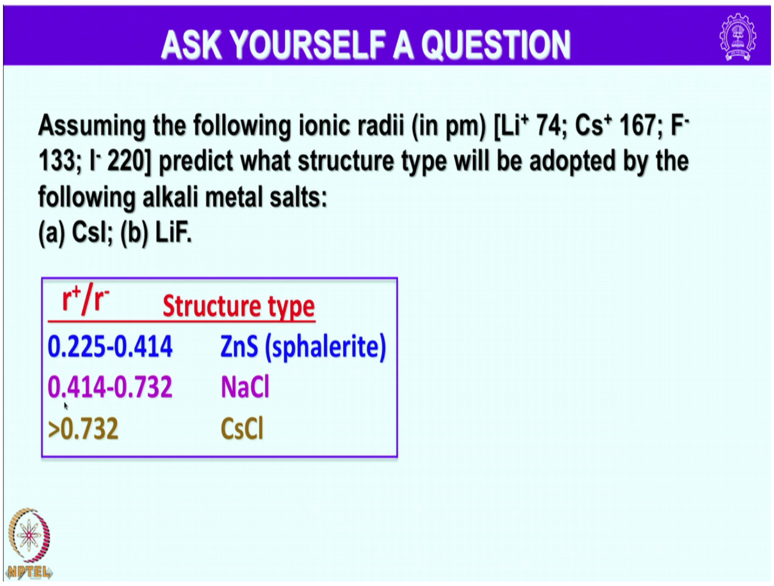
(Refer Slide Time: 15:15)



So, this is how one can directly react sodium carbonate with per chloric acid to generate sodium per chlorate. Cesium chlorate can be reacted with sodium per chlorate here. So, here in this case what happens cesium per chlorate readily precipitates out as a result that can be separated from sodium chloride. Or one can also start from cesium carbonate in a similar fashion to that of sodium reaction sodium, sodium carbonate reaction treat cesium carbonate with per chloric acid it gives cesium per chlorate plus CO 2 plus H 2 O. One can also start conveniently from cesium hydroxide for example, CsOH plus H Clo 4 gives CsCl O 4 plus H 2 O; that means, we have several options while making sodium per chlorate or cesium per chlorate.

So, now, another question is there.

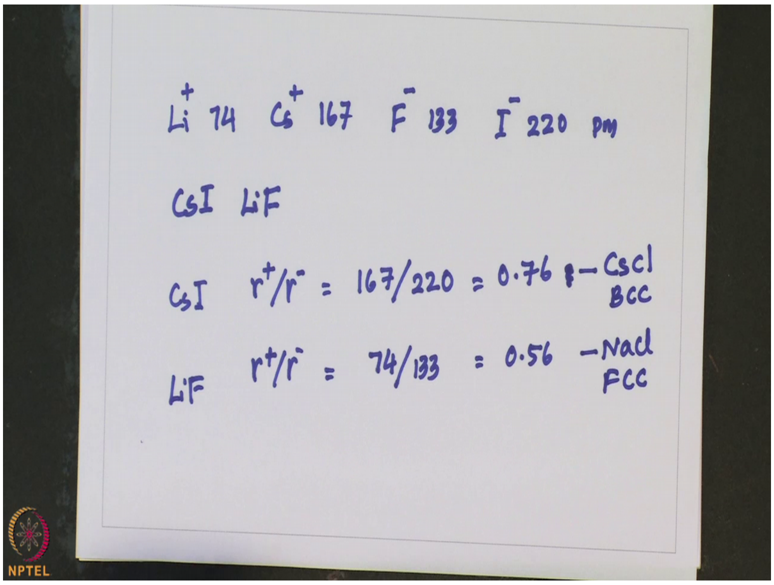
(Refer Slide Time: 17:16)



Assuming the following ionic radii in p picometry given for example, lithium plus 74 picometer and cesium is plus is 167 picometer and also for fluoride it is 133 picometer and iodide it is 220 picometer. So, using this data predict the structure type for the compounds given there, that is using this data predict the structural types of cesium iodide and lithium fluoride. So, the given values are there.

So, what is given here is lithium plus it is 74 and cesium plus 167 picometer and then we have fluoride it is given 133 and then iodide it is 220. So, all are picometers.

(Refer Slide Time: 17:55)

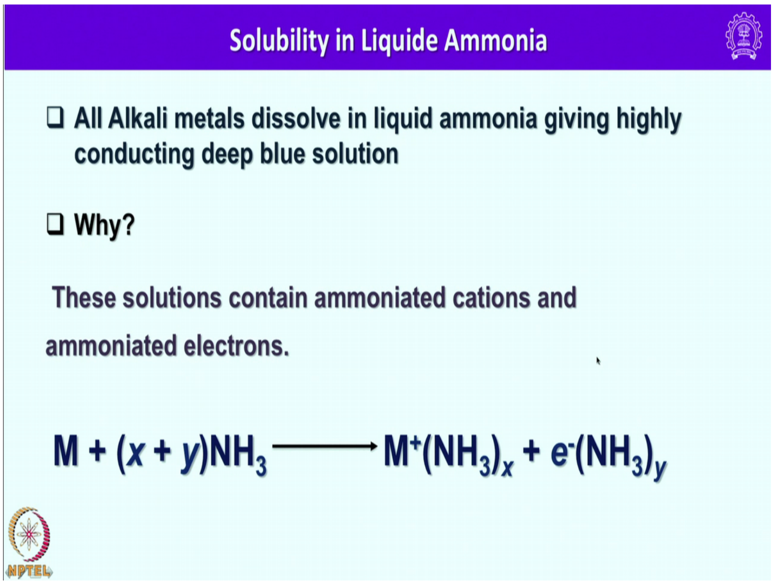


So, now we have to find out cesium iodide and lithium fluoride structural type. So, now, we have to use the radius ratio rule and also I have already listed here for example, if the radius ratio comes in this range between 225 to 0.414, you can always tell that the structure is similar to zinc sulphide or sphalerite or if the value is between 414 to 0.414 to 0.732 it will have FCC structure or if it is greater than 0.732 it will be BCC structure. Let me do the calculation.

So, for cesium iodide, r plus over r minus equals 167 divided by 220 this comes around 0.76 value and then lithium fluoride let us consider this ratio again we have 74 and then fluoride is 133. So, this comes around 0.56. Now we shall compare this one by comparing we can say it is greater than 1. So, it has CsCl structure, this has very similar to CsCl structure that is body centered cubic structure whereas, this is 0.56, 0.56 means it comes in the range of sodium chloride type structure that is it is BCC and this is FCC. So, of course, one can conveniently use this method to predict the structural types for any given alkali metal salt.

Let us look into the solubility of alkali metals in liquid ammonia.

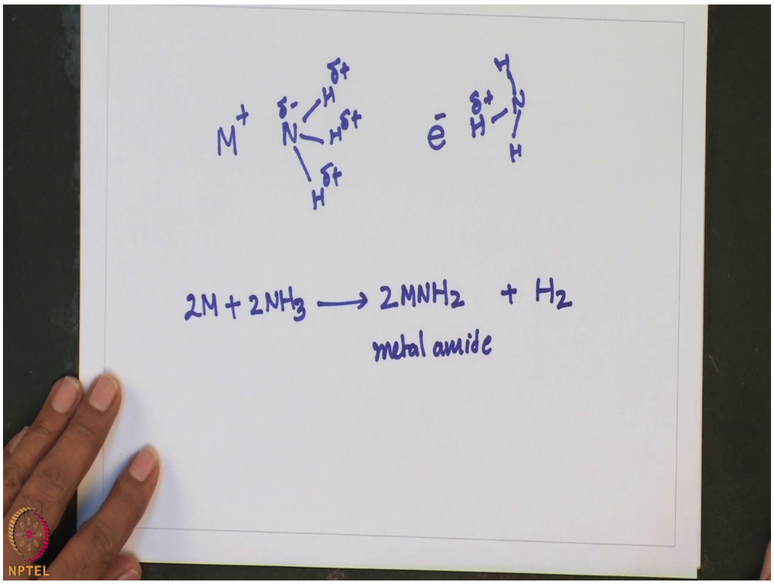
(Refer Slide Time: 20:17)



All alkali metals dissolve in liquid ammonia giving highly conducting deep blue solution, why this happens, why the color is blue. So, these solutions contain essentially ammoniated cations and ammoniated electrons they are represented in this fashion I have shown here.

So, let us say M has x plus y quantity of ammonia on addition on mixing them it forms cation is separated having surrounded by x number of ammonia and here the electrons are also surrounded by y amounts of ammonia. So, why that happens? So, is essentially in the solution what happens you know that I showed you the reaction in which sodium amide is formed electrons are leached out these electrons are essentially what happens surrounded by ammonia and this cations are also surrounded by ammonia they form ammonia complex whereas, electron also forms complex only thing is that direction of the atoms are very different for example, ammonia if we take NH 3 in case of when M is there this will be minus. So, orientation will be in this fashion because negative it is going towards the negative dipole is going towards cation and it forms a complex whereas, in case of electron this negatively charged, so hydrogen atoms will be directing in this fashion.

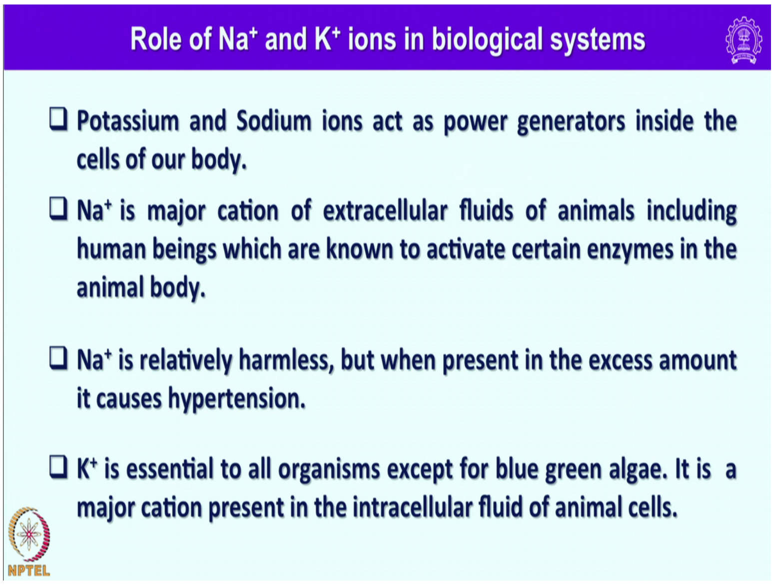
(Refer Slide Time: 21:33)



So, you can see the direction. So, in both complexes are there involving M plus with ammonia and here electrons with ammonia. So, as a result, when ordinary light falls on this ammoniated electrons they essentially get excited to higher levels by absorbing energy corresponding to red region of the visible light. As a result transmitted light is blue which imparts blue color to the solution and of course, on standing this blue solution liberates hydrogen slowly and this is due to the reaction that leads to the formation of metal amide already I had written I will write again here plus 2 NH 3 here 2 MNH 2. So, this is metal amide and plus H 2 comes out.

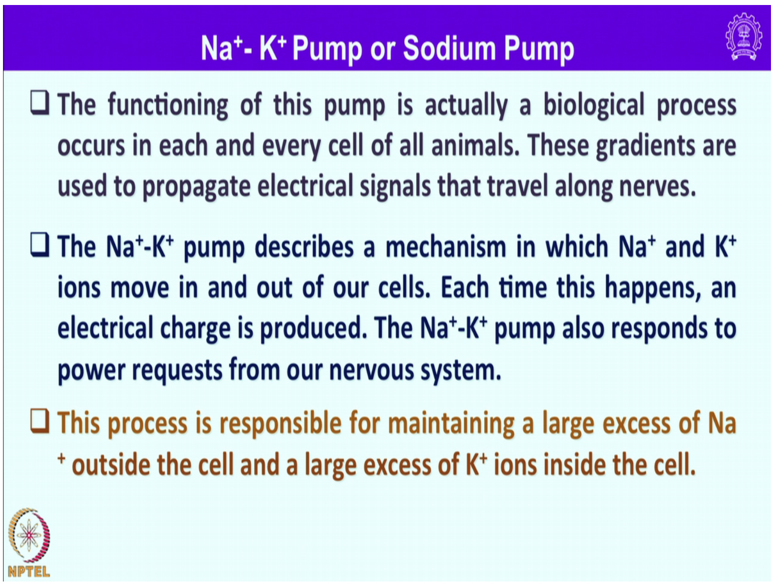
Now, let us look into the role of sodium and potassium ions in biological system they are very very important in living beings.

(Refer Slide Time: 23:21)



Sodium and potassium ions act as power generator inside the cell of our body. Sodium plus is major cation of extra cellular fluids of animals including us human beings and which are known to activate certain enzymes in the animal body. Sodium plus is relatively harmless, but when it is present in large excess it causes hypertension and potassium ion is very essential to all organisms except for blue green algae and it is a major cation present in the intracellular fluid of animal cells. You should remember potassium is present in the intracellular fluid of animal cells whereas, sodium is concentrated majorly in extracellular fluids of animal cells.

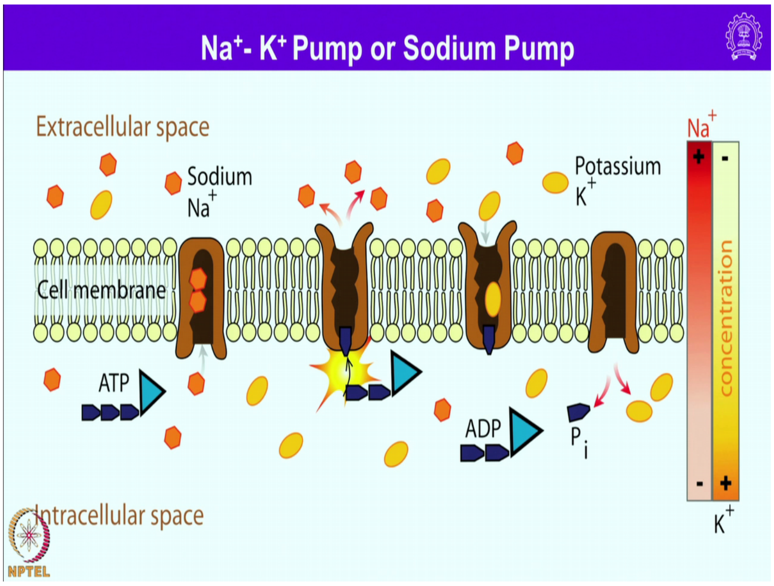
(Refer Slide Time: 24:17)



So, there is another term we come across in biology or biological process that is called sodium pump or sodium ion potassium ion pump. So, how it functions let us look into it. The functioning of this pump is actually a biological process it occurs in almost all cells of all animals these gradients are used to propagate electrical signals that travel along nerves. The sodium plus and potassium plus pump essentially describes a mechanism in which sodium plus and potassium ions move in and out of our cells, each time this happens an electrical charge is produced. This sodium and potassium pump also responds to power requires from our nervous system.

So, this process the pumping process is responsible for maintaining a large excess of sodium plus ions outside the cell and a large excess of potassium ions inside the cell that you can see in the diagram I have shown here, you can see here.

(Refer Slide Time: 25:27)



This is where the sodium ions are there and this is the potassium ions are there and this is whatever is shown is intercellular space, intracellular space and this is extracellular space. In extracellular space sodium concentration is more sodium ion concentration is more and intracellular space potassium ion concentration is more.

So, let me stop at this stage and continue discussion on chemistry of alkali metals in my next lecture. So, have a pleasant reading of inorganic chemistry.

Thank you.