Main Group Chemistry
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Lecture – 16
Chemistry of Group 1 elements

Welcome to MCB lecture series on chemistry of main group elements. Let me begin the discussion on group 1 elements, that is chemistry of group 1 elements group one elements are essentially called as alkaline metals and the electronic configuration is n s 1 that is they have one electron in their valence shell and as a result oxidation state of alkaline metals is plus 1.

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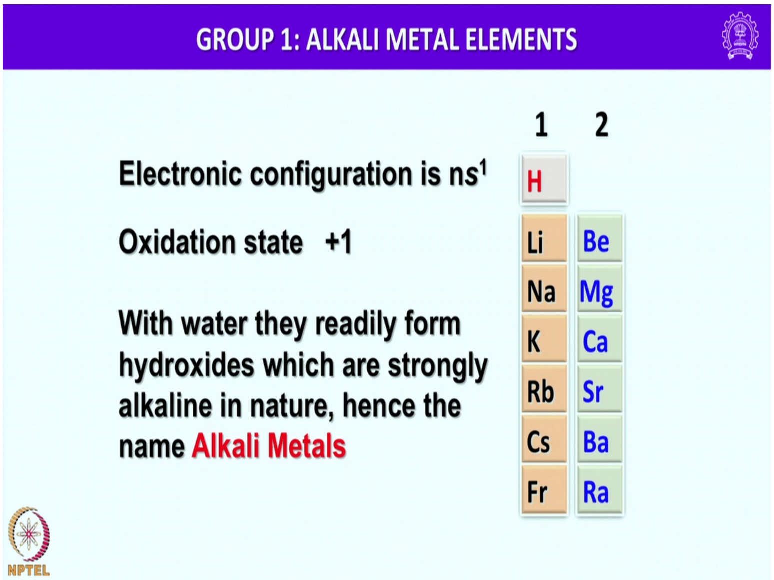

GROUP 1: ALKALI METAL ELEMENTS

Electronic configuration is ns^1

Oxidation state +1

With water they readily form hydroxides which are strongly alkaline in nature, hence the name **Alkali Metals**

1	2
H	
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba
Fr	Ra

And here I have listed all the alkaline metals in that group one of course, including hydrogen. Of course, I am not going to discuss about hydrogen I shall draw your attention to only lithium to francium and we have totally 6 elements lithium, sodium, potassium, rubidium, cesium and francium. To have some analogy with the next group element that is alkaline earth elements I have also listed here of course, that also starts with beryllium, magnesium, calcium, strontium, barium and radium and we come across some similarities between them those things I shall discuss when I move to group 2 chemistry.

The important feature of alkaline metals is the group all state is plus 1 and these metals readily react with water to form hydroxides and which are strongly alkaline in nature and hence the name alkali metals since they react very readily with water to form the corresponding hydroxides which are strongly basic in nature they are called alkali metals. Sodium and potassium are abundant whereas, lithium rubidium and cesium are less abundant and francium is highly radioactive and the longest lived isotope of francium is 223 francium that has about half life of 21 minutes, its half life is 21 minutes.

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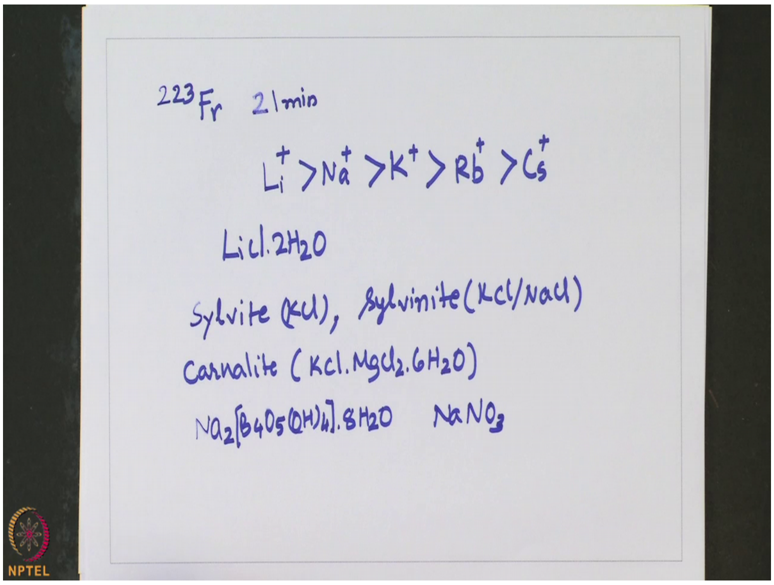

^{223}Fr 21 min

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$LiCl.2H_2O$

Sylvite (KCl), Sylvinite (KCl/NaCl)

Carnalite ($KCl.MgCl_2.6H_2O$)

$Na_2[B_4O_5(OH)_4].8H_2O$ $NaNO_3$

So, chemistry of lithium is little different from those of other group members owing to its small size. In fact, this trend we are going to see when we discuss chemistry group wise in each group the first element shows little different behavior both in terms of physical as well as chemical compared to the rest of the group members and lithium shows similarities to magnesium in terms of its properties usually known as diagonal relationship and sodium potassium calcium. Magnesium ions are in larger proportions in biological fluids and they perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

Here within a group the size is steadily increasing that you should remember and loosely held s electrons all these have n s 1 electronic configuration that is in the valence shell they have one electron these electrons are loosely held and hence they can be readily removed and as a result group one elements show very low ionization energy and all elements are electropositive and in fact, they are the most electropositive elements in the entire periodic table. So, they readily form m plus ions and m plus ions are smaller than m as expected because we are removing that lone electron present in the valence shell as a result effect in nuclear charge increases making the m plus cation much smaller in size compared to m.

And atomic and ionic radii increases down the group as the size increases it is expected, in fact, they have the largest size in their respective period or rows and ionization energy decreases down the group as the size steadily increases. And hydration enthalpy decreases down the group due to again increase in the ionic size; that means, if you look into the hydration enthalpy that follows this order maximum hydration enthalpy was shown by lithium and then sodium and then potassium and then rubidium and then cesium; that means, of course, you can also (Refer Time: 04:54) the size is increasing in this order and the size increases hydration enthalpy decreases. As a result they have less tendency to have an association of with water molecules. In fact, lithium plus has maximum degree of hydration and all lithium salts are hydrated for example, if you look into Licl it has 2 water molecules. Let us look into the occurrence.

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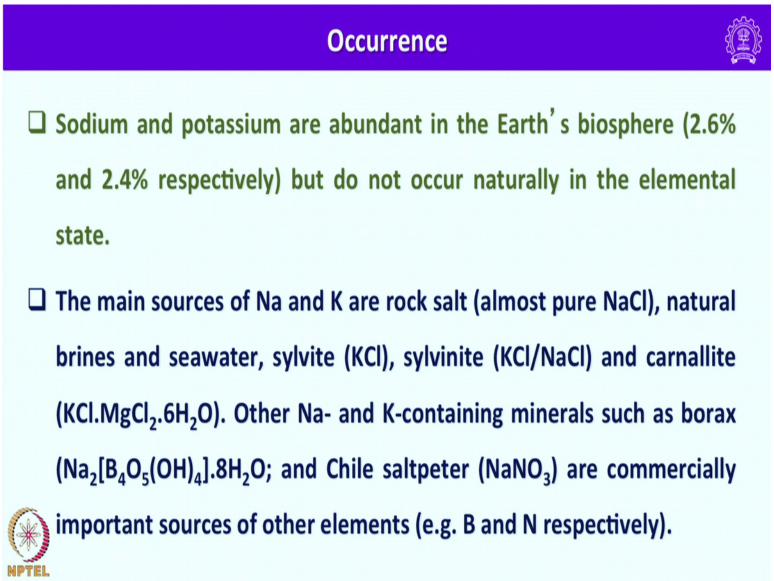

Occurrence

- ☐ Sodium and potassium are abundant in the Earth's biosphere (2.6% and 2.4% respectively) but do not occur naturally in the elemental state.
- ☐ The main sources of Na and K are rock salt (almost pure NaCl), natural brines and seawater, sylvite (KCl), sylvinite (KCl/NaCl) and carnallite ($KCl.MgCl_2.6H_2O$). Other Na- and K-containing minerals such as borax ($Na_2[B_4O_5(OH)_4].8H_2O$; and Chile saltpeter ($NaNO_3$) are commercially important sources of other elements (e.g. B and N respectively).

And sodium and potassium are abundant in the earth s biosphere accounts for about 2.6 and 2.4 percent respectively, but do not occur naturally in the elemental form. So, none of these alkali metals occur in elemental form because of their high reactivity. So, the main sources of sodium and potassium is essentially sea water and also in case of KCl and in case of both KCl and NaCl (Refer Time: 06:17) and (Refer Time: 06:18) it is a mixture of KCl MgCl 2 6 H 2 o. So, other sodium and potassium containing minerals such as borax and chilli salt (Refer Time: 07:08) that is NaNo 3.

So, these are the major sources of some of these alkali metals.

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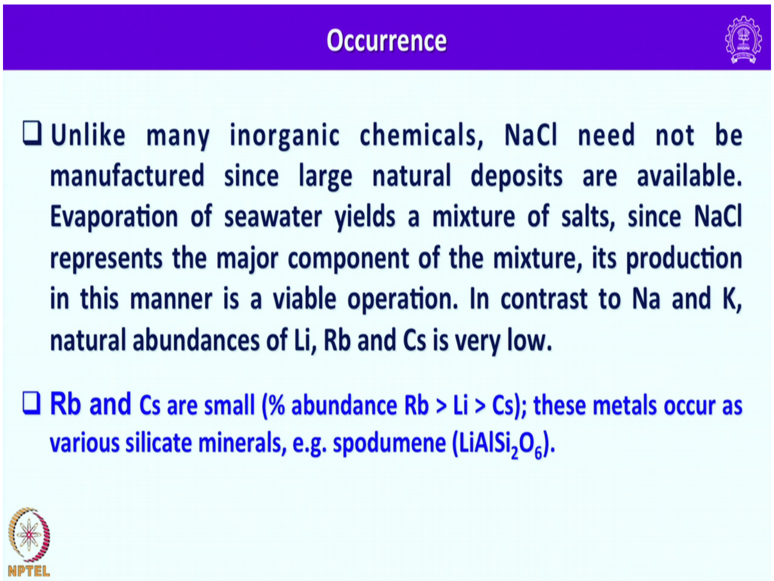

Occurrence

- Unlike many inorganic chemicals, NaCl need not be manufactured since large natural deposits are available. Evaporation of seawater yields a mixture of salts, since NaCl represents the major component of the mixture, its production in this manner is a viable operation. In contrast to Na and K, natural abundances of Li, Rb and Cs is very low.
- Rb and Cs are small (% abundance Rb > Li > Cs); these metals occur as various silicate minerals, e.g. spodumene ($LiAlSi_2O_6$).

So, unlike many inorganic chemicals sodium chloride need not be manufactured since large natural deposits are available. So, evaporation of simply evaporation of seawater yields a mixture of salts, since sodium chloride represents the major component of the mixture its production in this manner is viable operation. So, in contrast to sodium and potassium natural abundance of lithium rubidium cesium is very low and rubidium and cesium are very small or in trace quantities and these metals occur as various silicate minerals for example, spodumene LiAlSi 2 O 6, I have written there. So, from these some of these minerals the corresponding alkali metals are extracted.

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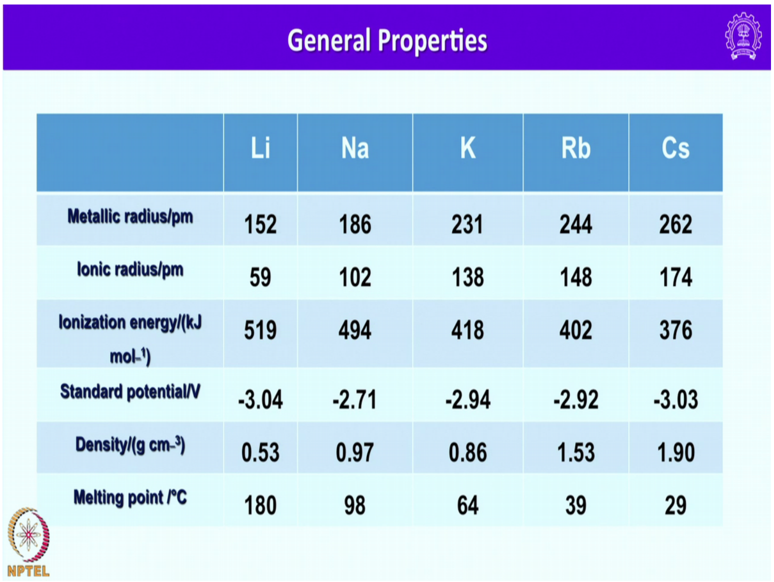

General Properties

	Li	Na	K	Rb	Cs
Metallic radius/pm	152	186	231	244	262
Ionic radius/pm	59	102	138	148	174
Ionization energy/(kJ mol^{-1})	519	494	418	402	376
Standard potential/V	-3.04	-2.71	-2.94	-2.92	-3.03
Density/(g cm^{-3})	0.53	0.97	0.86	1.53	1.90
Melting point /°C	180	98	64	39	29

Let us look into the general properties. I have listed here general properties for alkali metals and you can look into the metallic radius for all these elements. Metallic radius is steadily increasing as expected due to the increase in the size and consequently ionic radius is also increasing and with lithium showing 59 picometre and ionization energy also decreasing in this order because of increase in size ionization energy decreases with highest ionization energy is shown by lithium and standard potential is also shown here.

This is more or less comparable for all alkali metals and density also increasing as we go down the group and melting point is decreasing as we go down the group here. Melting point is more in case of lithium whereas, in case of sodium and potassium it steadily decreases.

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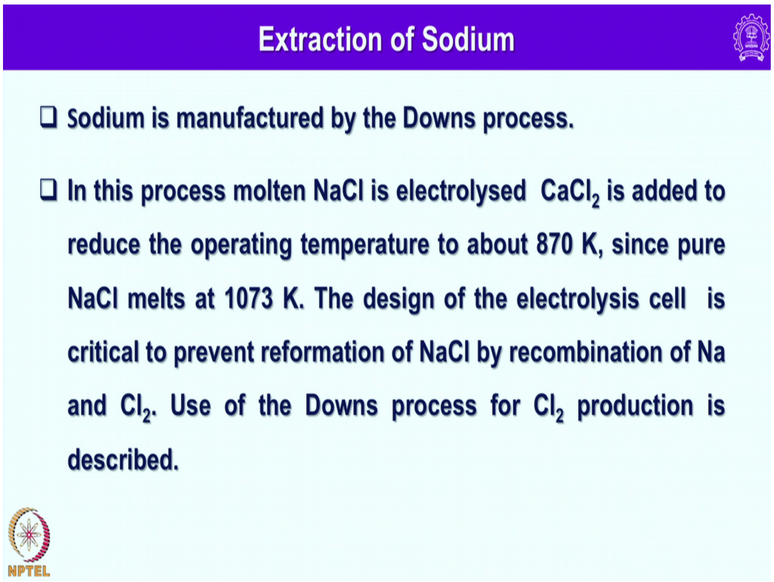

Extraction of Sodium

- ❑ Sodium is manufactured by the Downs process.
- ❑ In this process molten NaCl is electrolysed $CaCl_2$ is added to reduce the operating temperature to about 870 K, since pure NaCl melts at 1073 K. The design of the electrolysis cell is critical to prevent reformation of NaCl by recombination of Na and Cl_2. Use of the Downs process for Cl_2 production is described.

Let us look into the extraction of sodium and sodium is manufactured by the process called downs process and although we have plenty of sodium chloride is available we cannot simply do aqueous electrolysis to isolate to separate because its reactivity violent reaction with water that leads to the formation of sodium hydroxide we have to find an alternate method. So, this is essentially electrolysis, electrolysis method, but it is called fused electrolysis or molten electrolysis. In this process molten sodium is electrolyzed and here we are adding calcium chloride to reduce the operating temperature to about 870 Kelvin. If we simply consider sodium chloride its melting point is 1073 Kelvin in order to decrease the melting point calcium chloride is added and when the calcium chloride is added we all know the (Refer Time: 10:17) properties elevation in the boiling point (Refer Time: 10:19) in the freezing point when impurities are added.

So, here calcium chloride is added in considerable quantity to sodium chloride to reduce its melting point so that molten electrolysis can be carried out at operatable temperature and reaction condition. That design of the electrolysis cell is critical to prevent reformation of sodium chloride by recombination of sodium and chlorine.

Before that let us look into some facts that are concerned about down process as I mentioned we are adding some calcium chloride or barium chloride or (Refer Time: 11:01) chloride or in some cases sodium fluoride can also be added to reduce the temperature required to perform electrolysis in liquid phase. And sodium chloride melts at 801 degree centigrade or 1074 Kelvin, but a salt mixture can be kept liquid at a temperature as low as 505 degree centigrade, but for this one to achieve this low temperature one has to add considerable amount of calcium chloride. So, in this particular method downs method 33.2 percent sodium chloride is taken and 66.8 percent of calcium chloride is added. Almost 2 fold calcium chloride is added to bring down the melting point to 505 degree centigrade. So, that it can be conducted at that temperature without much problem.

If pure sodium chloride is used a metallic fog is formed in the molten sodium chloride which is impossible to separate. As a result we are using and of course, one is operating temperature and also at that condition whether the electrolysis cell we are using will be last longer all those things has to be considered and here for the same reason about fold calcium chloride is added to perform molten electrolysis.

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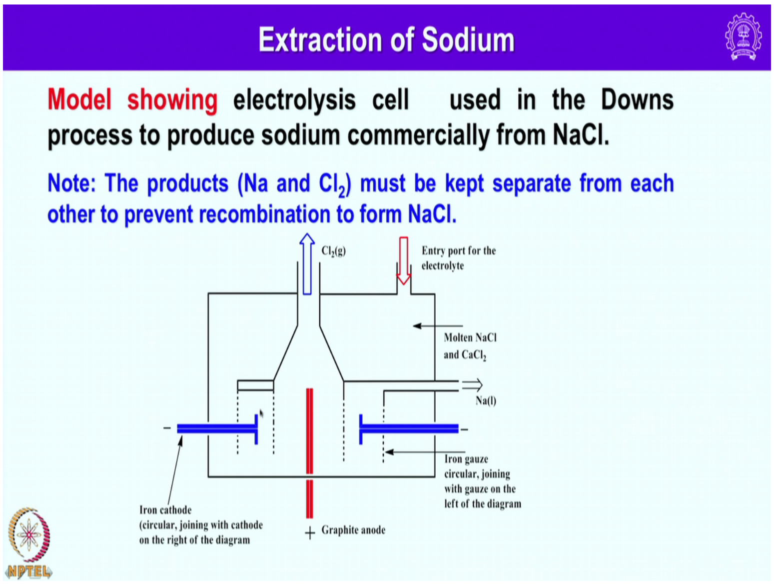

Extraction of Sodium

Model showing electrolysis cell used in the Downs process to produce sodium commercially from NaCl.

Note: The products (Na and Cl_2) must be kept separate from each other to prevent recombination to form NaCl.

And I am showing you the model representing electrolysis cell used in the downs process to produce sodium commercially from sodium chloride and the one thing one should remember is the products sodium and chlorine must be kept separate from each other to prevent recombination to form again sodium chloride.

This is the cell and you can see here we have this cathode, iron cathode and separate chamber is there and then a graphite anode is there and the chlorine that is liberated here goes off will separate it and then here this is the place where electrolyte is added. That means, molten sodium chloride and calcium chloride will be there and then here this is way out for sodium to take out sodium. So, this one essentially this essentially keeps in such a way that there is no recombination of sodium and chlorine.

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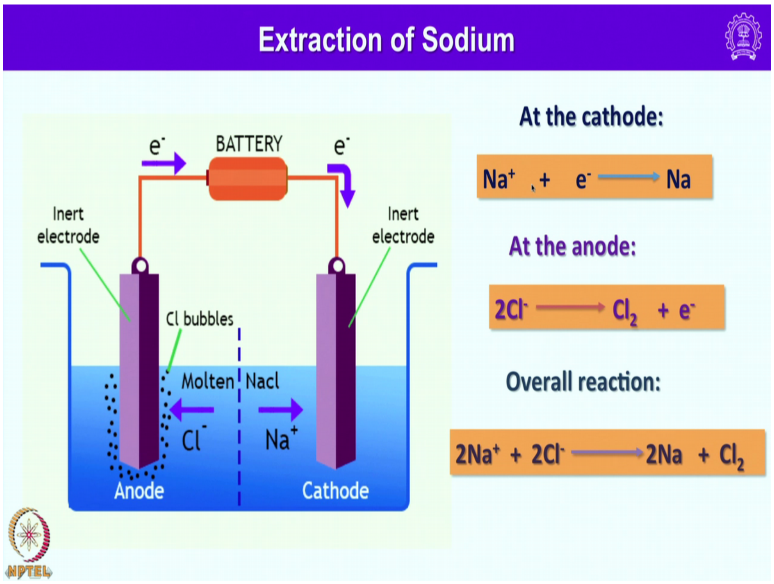

Extraction of Sodium

At the cathode:

$Na^+ + e^- \longrightarrow Na$

At the anode:

$2Cl^- \longrightarrow Cl_2 + e^-$

Overall reaction:

$2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2$

And this also shown in this figure, we can see here clearly and here anode and cathode are there at their well separated and sodium chloride is coming here, and inert electrode; and then whatever the sodium comes here it can be taken out. The overall reaction is given at cathode Na plus takes an electron to form sodium metal at the anode 2 Cl minus will be getting oxidized to Cl 2 and overall reaction is 2 Na plus plus 2 Cl minus gives 2 Na plus Cl 2 and both of them are separated at their respective electrodes.

The next the question is if we are performing electrolysis and reducing sodium is there any chance of calcium getting reduced of course, there is every possibility of calcium also getting reduced, but here we should look into the reduction potential.

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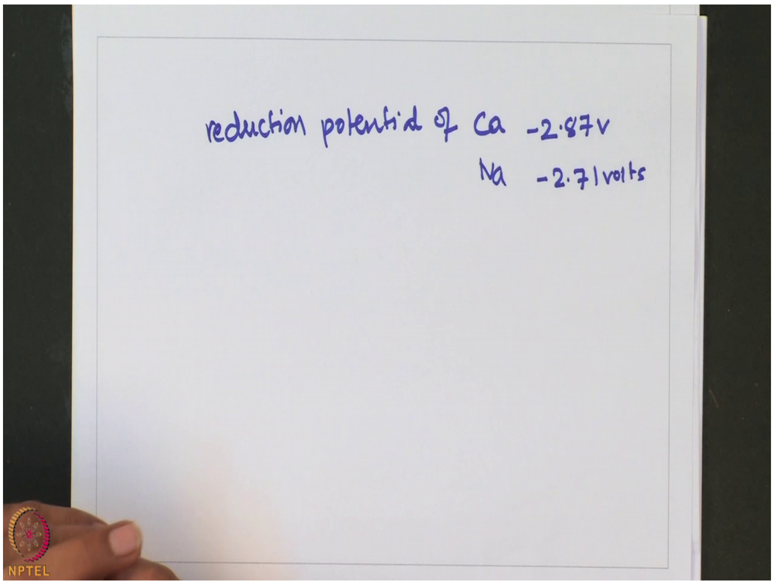

reduction potential of Ca -2.87v

Na -2.71volts

The reduction potential of calcium is minus 2.87 volts whereas, the reduction potential of sodium is minus 2.71 volts; that means, here by controlling the voltage we can ensure that only sodium is reduced and not calcium. So, this way a contamination of calcium can be prevented while reducing sodium.

So, we are essentially exploiting the difference in the reduction potential of calcium and sodium, and because of this control of voltage the sodium ions are reduced to metallic form in preference to those of calcium. So, due to the presence of only one valence electron metal metal bonds are weak and hence they are soft metals if they are soft metals that can be easily we can cut it indicates. We do not have extensive metal metal bonding that we come across in case of (Refer Time: 16:02) metals and of course, here we have only one electron in the valence shell it is not sufficient to make the metal metal bond stronger as a result they are all soft metals.

They import characteristic color to an oxidizing flame this essentially due to the excitation of s electron to the p orbital. That means, essentially when exposed when this alkaline metals are exposed to flame they import a characteristic colour that comes essentially because of excitation of the lone electron present in the valence shell to the higher orbital.

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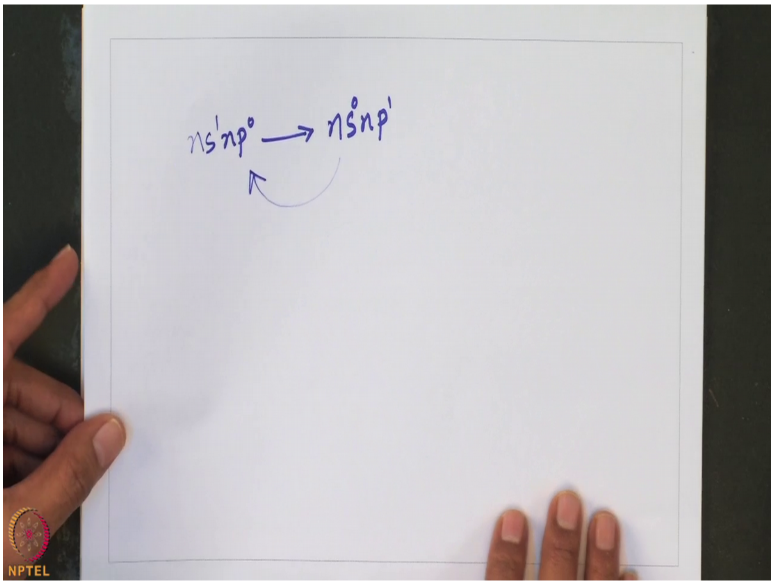

$$ns^1np^0 \rightarrow ns^0np^1$$

For example let us take n s 1 and we have n p 0 we do not have any electrons, on exposing to the flame this electron is excited and it goes to this one we will be having this kind of situation here and this excited electron will emit radiation in the visible region while returning to the ground state. So, when it comes back it emits in the visible region depending upon what electromagnetic radiation it emits that color is shown by these ions.

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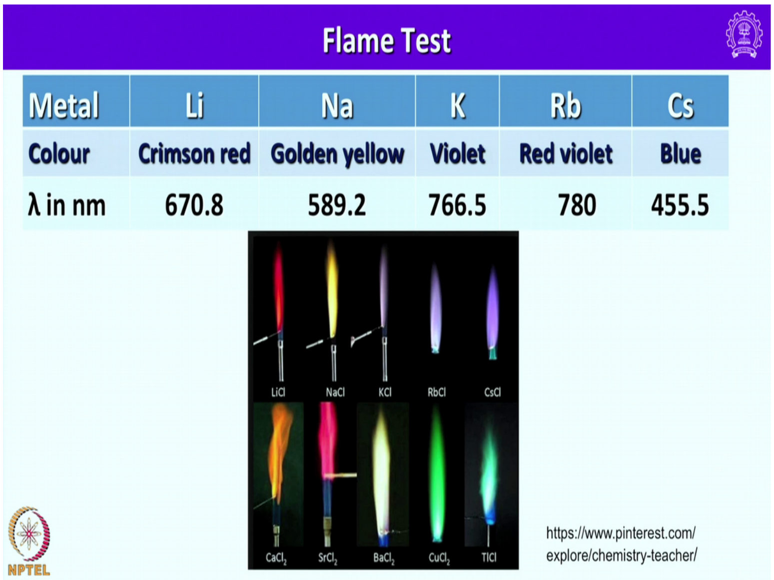

Flame Test

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Golden yellow	Violet	Red violet	Blue
λ in nm	670.8	589.2	766.5	780	455.5

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So, this is called flame test. So, of course, in the flame test they give a characteristic color. Lithium will impart crimson red color and the wavelength is 670.8 nanometer and sodium imparts golden yellow color and its wavelength is 589.2 and potassium imparts violet color 766.5 is the wavelength and rubidium shows red violet color and the wavelength is 780 nanometer and c c m shows blue color and the wavelength is 455.5. That means, it is a characteristic you know test we perform to identify these alkaline metals in a given salt and you can see here the different colors whatever I have mentioned is shown here crimson red, golden yellow and golden yellow and then violet and red violet and blue color respectively for lithium to cesium.

As I mentioned because of one electron metal metal bonds are not very strong, so all of them are (Refer Time: 18:37) soft solid can be cut with a knife except lithium, lithium is bit hard they are highly malleable and ductile. Silver lustre is essentially due to the presence of highly mobile electrons of the metallic lattice. In the lattice what happens this one electron present in the valence I have some sort of a stream of electrons they will be moving very freely over the surface giving a silver lustre to all these metals and a large size in their respective periods and size increases down the group. If you consider any period the large size is shown by this alkaline metals and ionization energy decreases down the group and all this alkaline metals show plus one oxidation state. And reducing character of all these alkaline metals increases from sodium to cesium and; however, (Refer Time: 19:32) lithium is the strongest reducing agent; that means, all alkaline metals are reducing agents.

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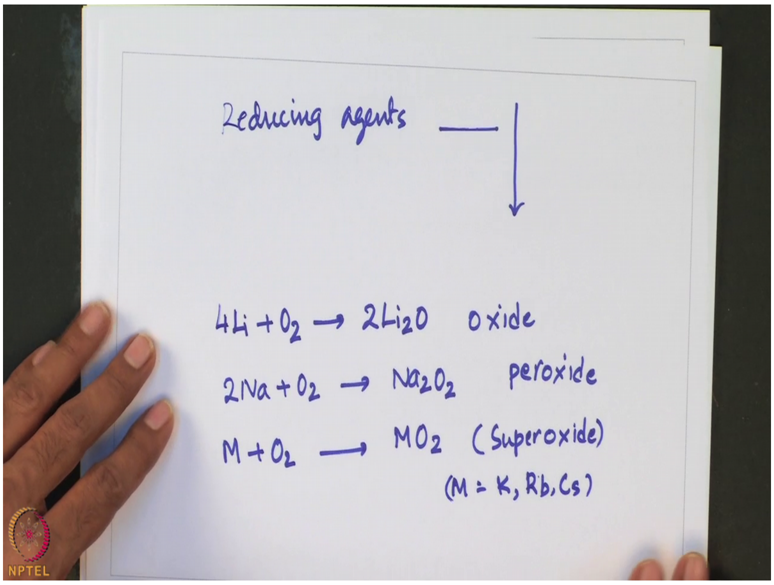

Reducing agents ⟶ ↓

$4Li + O_2 \rightarrow 2Li_2O$ oxide

$2Na + O_2 \rightarrow Na_2O_2$ peroxide

$M + O_2 \longrightarrow MO_2$ (Superoxide)

(M = K, Rb, Cs)

And this trend increases down the group and they have very low melting points due to weak metallic bonds and density increases from lithium to cesium except potassium being lighter than sodium. So, ionic character increases from lithium to cesium. So, ionic character whatever is there in whatever the compounds we make increases from lithium to cesium. In case of lithium with any element we react; that means, whether we will consider lithium, hydride lithium oxide or lithium halide there is some covalent character is there because of the smaller size. All these alkaline metals are good conductors of heat and electricity.

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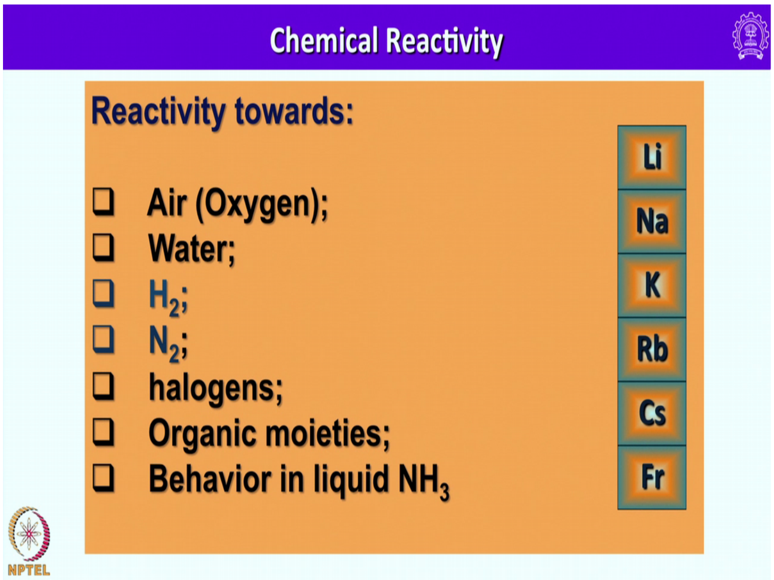

Chemical Reactivity

Reactivity towards:

- ☐ Air (Oxygen);
- ☐ Water;
- ☐ H_2;
- ☐ N_2;
- ☐ halogens;
- ☐ Organic moieties;
- ☐ Behavior in liquid NH_3

Li
Na
K
Rb
Cs
Fr

Let us while looking into the chemical reactivity, let us classify the reactions accordingly let how they interact with oxygen, how they interact with water and how they react with hydrogen and nitrogen and halogen or organic moieties and how they behave in liquid ammonia some of these aspects we shall see while looking into the reactivity.

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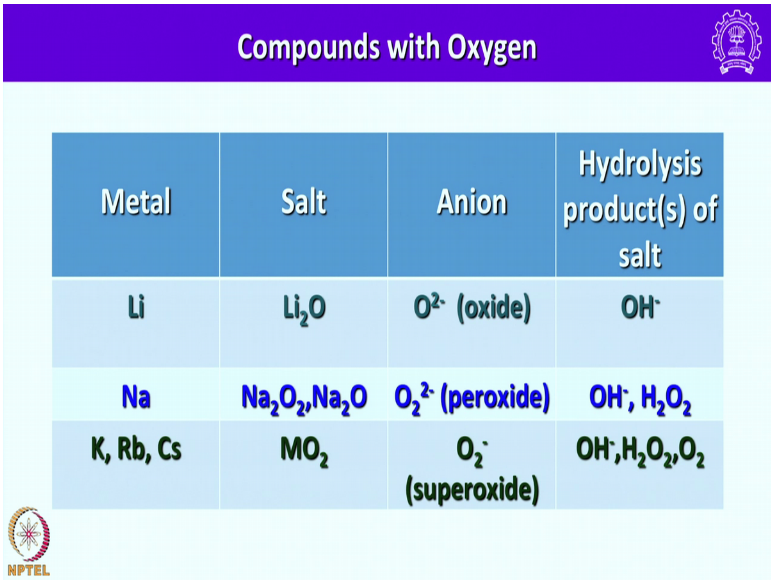

Compounds with Oxygen

Metal	Salt	Anion	Hydrolysis product(s) of salt
Li	Li_2O	O^{2-} (oxide)	OH^-
Na	Na_2O_2,Na_2O	O_2^{2-} (peroxide)	OH^-, H_2O_2
K, Rb, Cs	MO_2	O_2^- (superoxide)	OH^-,H_2O_2,O_2

So, here all these alkaline metals readily react with oxygen to form the corresponding oxides. For example, you can see here lithium forms lithium oxide and anion is O 2 minus and the hydrolysis product is OH minus that means, lithium oxide when it is reacted with water it gives lithium hydroxide. Similarly sodium it can form both sodium oxide and sodium peroxide and anion is peroxide in case of sodium peroxide and hydrolysis product can be hydroxide or H 2 O 2 and in case of potassium rubidium cesium all of them form super oxides and the anion is O 2 minus and in this case they can form their OH minus H 2 O 2 or O 2 on hydrolysis.

So, now let us look into the chemical properties. As I said all these elements react with oxygen and as a result when they are exposed to air the metal shining is tarnished essentially formation of a coating of metal oxide or hydroxide on their surface. When heated in excess of air lithium forms normal oxides sodium forms peroxides and other forms super oxides and potassium can form all 3 types of oxides, so its unique. Lithium forms only oxide sodium to an extent form it can form oxide as well peroxide whereas, potassium can form oxide, peroxide as well as super oxide and heavier alkaline metals form only super oxides.

So, let us look into the reaction with oxygen. For example, this is this is oxide because O 2 minus is there and sodium will form sodium peroxide, this is peroxide and M plus O 2 gives M O 2 is essentially super oxide. So, here M can be potassium rubidium or cesium.

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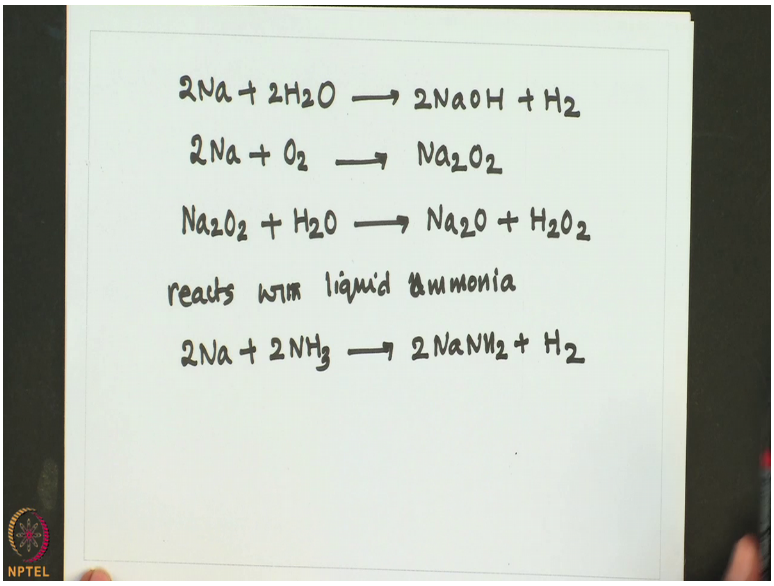

$2Na + 2H_2O \longrightarrow 2NaOH + H_2$

$2Na + O_2 \longrightarrow Na_2O_2$

$Na_2O_2 + H_2O \longrightarrow Na_2O + H_2O_2$

reacts with liquid ammonia

$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$

For example, let us consider 2 Na plus 2 H 2 O gives 2 NaoH plus H 2 is liberated similarly 2 Na when it reacts with oxygen it forms sodium peroxide Na 2 O 2 and when Na 2 O 2 is treated with water it forms Na 2 O sodium oxide and it forms H 2 O 2. Sodium also reacts with liquid ammonia 2 Na plus 2 NH 3 gives 2 NaNH 2 plus H 2. So that means, 2 equivalents of sodium reacts with 2 equivalents of ammonia to give 2 equivalents of NaNH 2 through the liberation of one equivalent of H 2.

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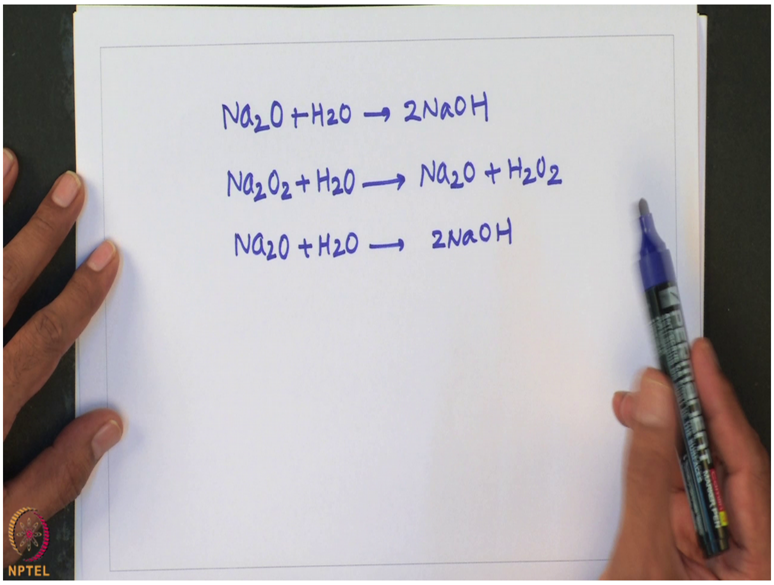

$Na_2O + H_2O \rightarrow 2NaOH$

$Na_2O_2 + H_2O \longrightarrow Na_2O + H_2O_2$

$Na_2O + H_2O \longrightarrow 2NaOH$

Let me elaborate only one reaction here before I conclude my talk. So, it forms sodium oxide also it forms oxide also the sodium oxide reacts with water to give sodium hydroxide. Similarly sodium peroxide can also form react step wise with water first if you treat with this one equivalent of water initially it forms sodium oxide plus H 2 O 2 is formed and next Na 2 O can they react with water to form 2 NaOH. So, one can that is the reason I showed you that it gives the products as H 2 O 2 as well as OH.

Let me stop a (Refer Time: 26:33). Let me discuss more chemistry in my next lecture. Until then have a pleasant reading of inorganic chemistry.

Thank you very much.