Main Group Chemistry
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Lecture – 37
Chemistry of Group 14 Elements

Welcome to MSB lecture series on main group chemistry. In this lecture, I shall continue discussion on oxides of heavier group 14 elements. So, in my previous lecture, I was discussing about germanium oxide let me continue discussion on tin oxide.

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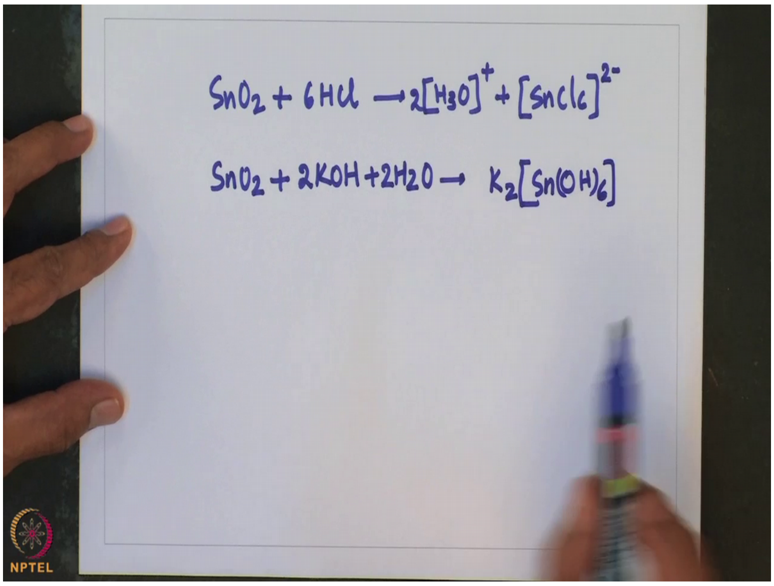

$SnO_2 + 6HCl \rightarrow 2[H_3O]^+ + [SnCl_6]^{2-}$

$SnO_2 + 2KOH + 2H_2O \rightarrow K_2[Sn(OH)_6]$

Tin oxide if we consider SnO 2 with tin in plus for state is soluble in many acids, but it exhibits amphoteric behaviour and also reacts with alkalis. Reaction occurs in strongly alkaline media to give a stagnate for example, SnO 2 when treated with hydrochloric acid, it forms hexachlorostanet, similarly when it is treated with KOH in aqueous medium, it gives again hydroxide hexahydroxystanet.

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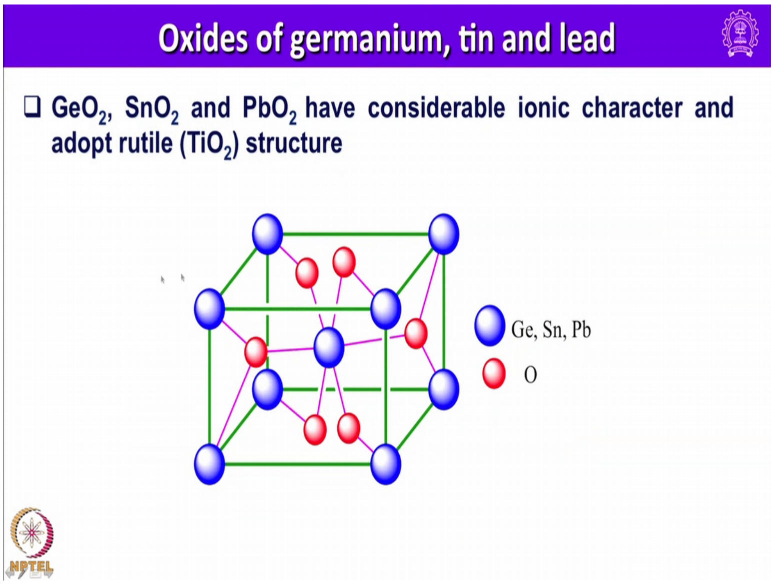

Oxides of germanium, tin and lead

- GeO_2, SnO_2 and PbO_2 have considerable ionic character and adopt rutile (TiO_2) structure

So, oxides of germanium, tin and lead are very similar to rutile structure, you can see here here these main group elements germanium tin or lead they are essentially are octahedraly surrounded by 6 oxygen atoms, were as oxygen is bridging or its tribridging in this fashion.

6 coordinated metal and 3 coordinated oxygen is the common feature of rutile structure or (Refer Time: 02:30) structure. These oxides as I showed are essentially amphoteric and dissolve in both acids and bases and of course, hydrated tin and lead 2 plus ions undergoes substantial hydrolysis.

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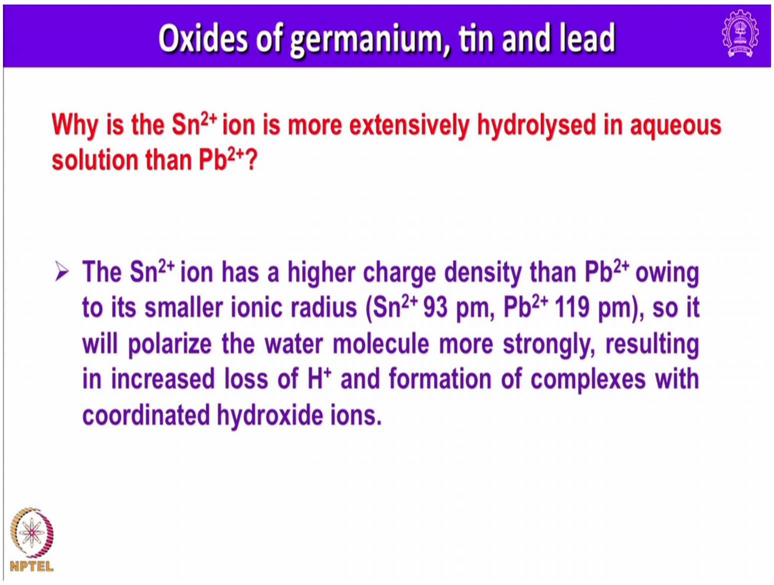

Oxides of germanium, tin and lead

Why is the Sn^{2+} ion is more extensively hydrolysed in aqueous solution than Pb^{2+}?

- The Sn^{2+} ion has a higher charge density than Pb^{2+} owing to its smaller ionic radius (Sn^{2+} 93 pm, Pb^{2+} 119 pm), so it will polarize the water molecule more strongly, resulting in increased loss of H^+ and formation of complexes with coordinated hydroxide ions.

So, I have a question here why is the tin 2 plus ion is more extensively hydrolyzed in aqueous solution, then Pb 2 plus. Answer is very simple, I read again answer I have given in the slide Sn 2 plus ion has a relatively larger charge density compared to lead 2 plus, owing to its smaller ionic radius. We can compare the ionic radius of tin with lead in case of tin 2 plus its 93 picometre, where as in case of lead 2 plus its 119 picometre. So, tin 2 plus polarises water molecule more strongly resulting in increased loss of H plus and formation of complexes with coordinated hydroxide ion; that means, here again the difference in the reactivity stems due to the fact that, tin has better chart 2 size ratio compared to lead being smaller in size so; that means, how the size of ions can have dramatic impact on some of these properties can be clearly seen from this example, I have a question here.

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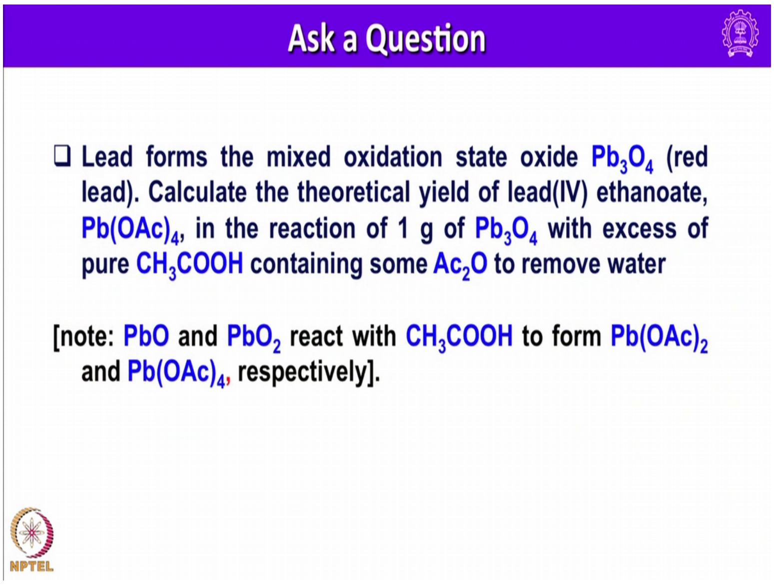

Ask a Question

- ☐ Lead forms the mixed oxidation state oxide Pb_3O_4 (red lead). Calculate the theoretical yield of lead(IV) ethanoate, $Pb(OAc)_4$, in the reaction of 1 g of Pb_3O_4 with excess of pure CH_3COOH containing some Ac_2O to remove water

[note: PbO and PbO_2 react with CH_3COOH to form $Pb(OAc)_2$ and $Pb(OAc)_4$, respectively].

The lead forms the mixed oxi state oxides; that means, if we consider Pb 3 O 4, you can see that we have 2 different type of lead ions. So, calculate the theoretical yield of lead 4 ethanoate or acetate in the reaction of 1 gram of Pb 3 O 4 with excess of pure acetic acid containing some quantity of acetic anhydride essentially the role of acetic anhydride is to remove water, to give back acetic acid. And note that Pb o and Pb O 2. So, Pb O plus 2 state and Pb O 2 plus 4 state react with acetic acid to form lead acetate, and lead tetra acetate respectively.

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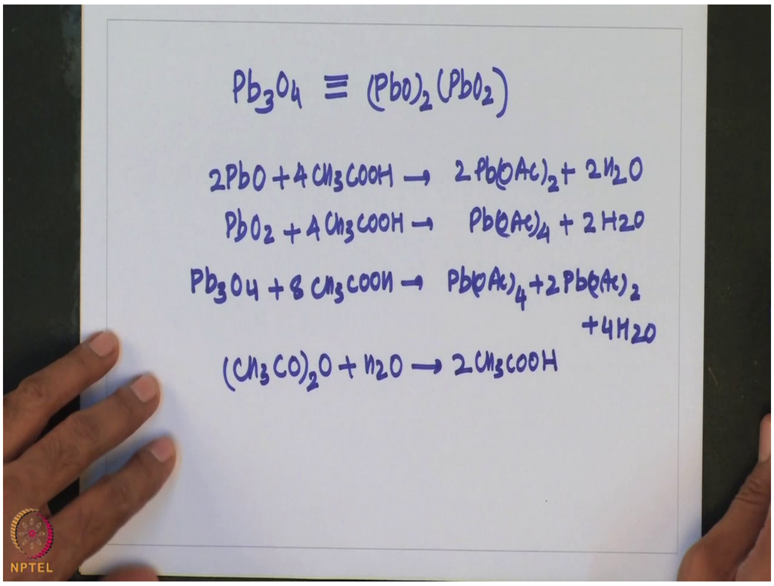

$$Pb_3O_4 \equiv (PbO)_2(PbO_2)$$

$$2PbO + 4CH_3COOH \rightarrow 2Pb(OAc)_2 + 2H_2O$$

$$PbO_2 + 4CH_3COOH \rightarrow Pb(OAc)_4 + 2H_2O$$

$$Pb_3O_4 + 8CH_3COOH \rightarrow Pb(OAc)_4 + 2Pb(OAc)_2 + 4H_2O$$

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

So, let me work out on this problem here me know that for example, composition of Pb 3 O 4 it is essentially combination of Pb O twice and Pb O 2. So that means, we have 2 lead atoms in plus 2 state and 1 lead atom in plus 4 state, leads to the composition of Pb 3 O 4 let us look into the reaction of Pb O as well as Pb O 2 with acetic acid, let first look into the reaction of 2 Pb O with 4 equivalents of acidic acid, it gives 2 Pb OAC this can also be written as OAc 2 times and here we get 2 equivalents of water.

Now let us look into the reaction of Pb O 2 with 4 equivalents of acetic acid, this gives essentially lead tetra acetate this over all reaction is Pb 3 O 4 plus 8 CH 3 C O OH this is giving Pb O AC 4 times plus 2 Pb O AC 2 times, plus 4 H 2 O. Essentially I have added up 1 and 2 so; that means, this is the overall reaction involving Pb 3 O 4 with acetic acid and of course, as I mentioned acetic anhydride role of acetic anhydride is essentially to extract this water to prevent the backward reaction. So, we need to add that many acetic anhydride here.

So, now calculate the molecular weight now. So, now, if we the molecular weight of P b 3 O 4, 4 is essentially 687.9.

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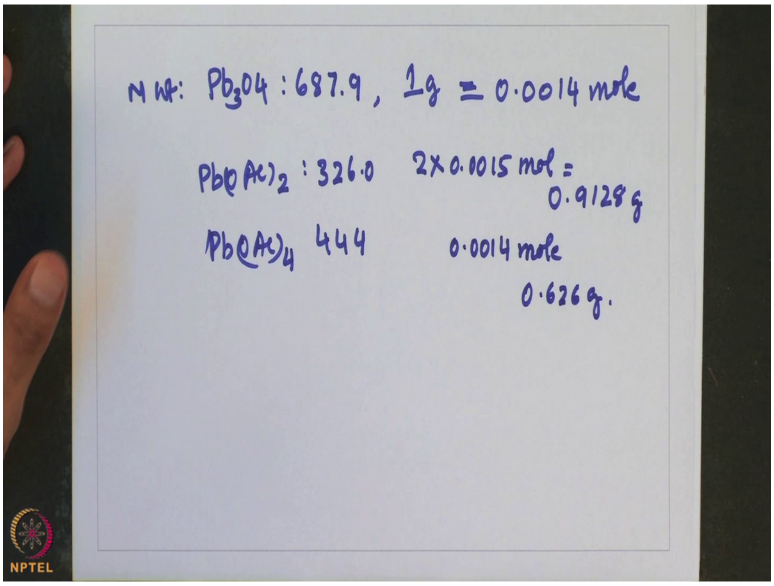

M Wt: Pb_3O_4 : 687.9, 1g = 0.0014 mole

$Pb(OAc)_2$: 326.0 2 × 0.0015 mol = 0.9128 g

$Pb(OAc)_4$ 444 0.0014 mole 0.626 g.

So that means, if you consider 1 gram that is equivalent to 0.0014 mole so; that means, Pb OAC twice is 326.0; that means, should form 2 into 0.0015 mole. So, that is equal to 0.9128 gram. So, then Pb OAC 4 times is molecular weight is 446 should form essentially 0.0014 mole. So, this accounts for about 0.626 grams. So, this how you can calculate the amount of lead acetate forms and lead tetra acetate formed in this reaction. Of course, we can also look into the uses of group 14 element oxides, silica glass operate is highly insensitive to thermal shock going to the low coefficient of thermal expansion of silica, and boro silicate glass that is essentially also known as Pyrex contains about 10 to 15 percent of B 2 O 3 and has a lower melting point than silica glass.

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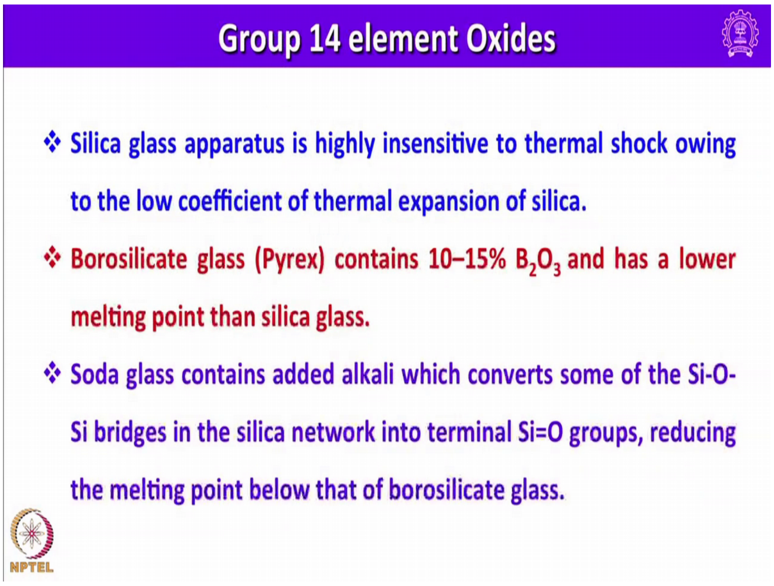

Group 14 element Oxides

- Silica glass apparatus is highly insensitive to thermal shock owing to the low coefficient of thermal expansion of silica.
- Borosilicate glass (Pyrex) contains 10–15% B_2O_3 and has a lower melting point than silica glass.
- Soda glass contains added alkali which converts some of the Si-O-Si bridges in the silica network into terminal Si=O groups, reducing the melting point below that of borosilicate glass.

And soda class contains added alkali which converts some of the Si O S i bridges in the silicon network into terminal SiO groups, reducing the melting point below that of borosilicate glass.

Now, let us look into the carbides, carbides are the numerous binary compounds of carbon with metals and metalloids which are classified as follows. Saline (Refer Time : 09:28) carbides or ionic carbides which are essentially formed by group 1 and group 2 elements, and also to an extent by aluminium and metallic carbides are essentially made up of trans elements, that is d block elements, and metalloid carbides are essentially found by boron and silicon and saline carbides means carbides of alkali metals and alkaline earth metals on hydrolysis essentially produce the corresponding hydrocarbons. For example, if you take simple carbide that gives methane, when it is hydrolysed and you can see the distribution of carbides in the periodic table.

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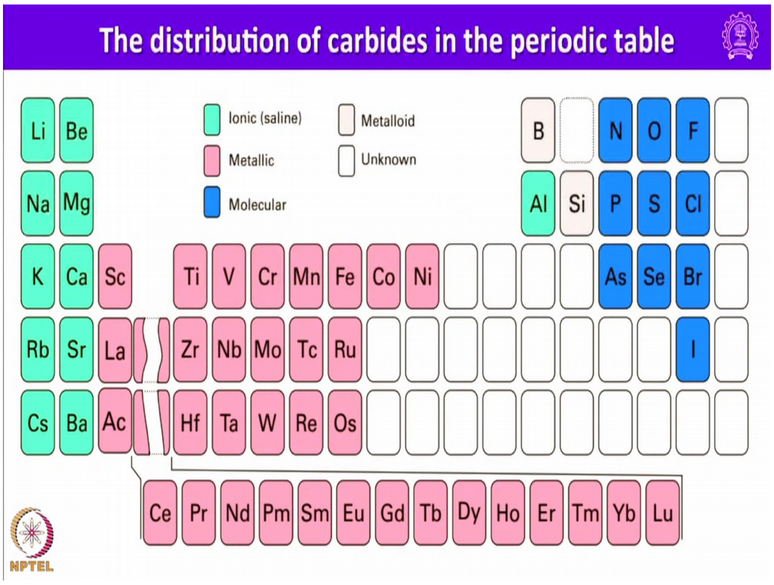

The distribution of carbides in the periodic table

🟩 Ionic (saline)
🟥 Metallic
🟦 Molecular
☐ Metalloid
☐ Unknown

You can see this saline hydrides saline carbides are ionic carbides are essentially formed by group 1 and group 2 elements, and to an extent aluminium, and then molecular carbon compounds are essentially formed by p block elements such as 50 group, 15, 16 and 17, they form a covalent carbon to the element bonds. And metallic ones are essentially formed by transmittals you can see here in this colour here, and metalloids are essentially by boron and silicon.

So, if this how we can classify the carbides of the elements in the periodic table by looking to the nature and the properties chemical as well as physical properties. And saline carbides are essentially formed by as I mentioned high electropositive metals, and non metal carbides are mechanically hot and are also semiconductors. Saline carbides of group 1 and 2 can also be divided into 3 sub categories.

Inter collection compounds for example, if we take alkali metals and pass their vapours into the graphite sheets around 300 to 400 degree centigrade, we get inter collected compounds. In case of potassium it is a k c 8; that means, the composition is one potassium atom for 8 carbon atoms, and here essentially potassium sheets between 8 carbon atoms 4 above and 4 below giving a sort of anti square prismatic structure for potassium. In case of calcium carbide calcium is placed in a octahedral environment. So, it goes and as of we have dicarbides having C 2 2 minus an ion or methanes having C 4 minus an ion. Graphite inter collection compounds are formed by group 1 metals, the dicarbides are formed by a broad range of electropositive metals that already I had discussed talking about the chemistry of group 1 and group 2 elements.

Let us look into the reactions of metal oxides with carbon. So, that also leads to the formation of carbides for example, if you take calcium oxide, and treat this one with carbon essentially it is a reduction process and; that means, that requires very high temperature of 2000 degree centigrade, it gives calcium carbide.

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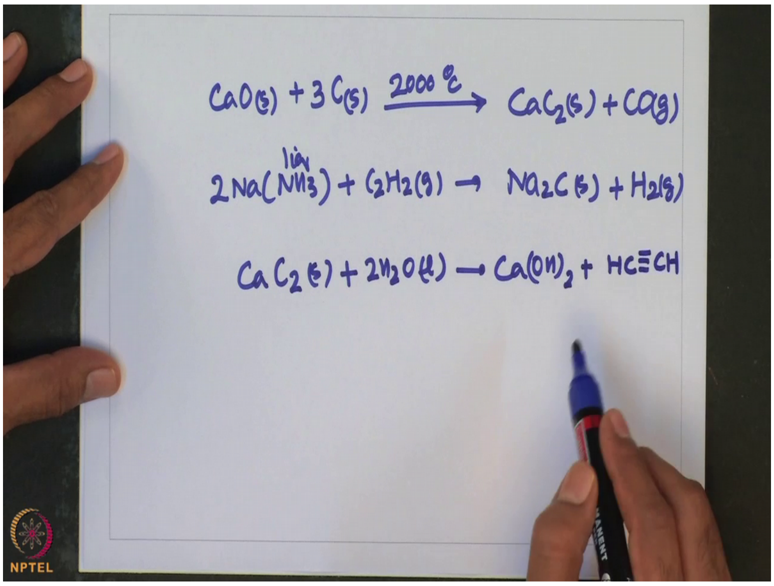

$$CaO_{(s)} + 3C_{(s)} \xrightarrow{2000\,°C} CaC_{2}(s) + CO(g)$$

$$2Na(\overset{liq}{NH_3}) + C_2H_2(g) \rightarrow Na_2C(s) + H_2(g)$$

$$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2 + HC{\equiv}CH$$

Of course, reaction of ethyne with a metal ammonia solution gives the corresponding carbide for example, if we take sodium in ammonia, liquid ammonia and treat this one with acetylene, it leads to the formation of N a 2 C solid plus H2 comes out. Of course, as I already discussed the chemistry of electropositive carbides in the respective groups, just let me write this reaction how they undergo hydrolysis. If it is treated with 2 equivalents of water, it forms calcium hydroxide plus acetylene comes out.

So, let us look into the compounds of group 14 elements with nitrogen.

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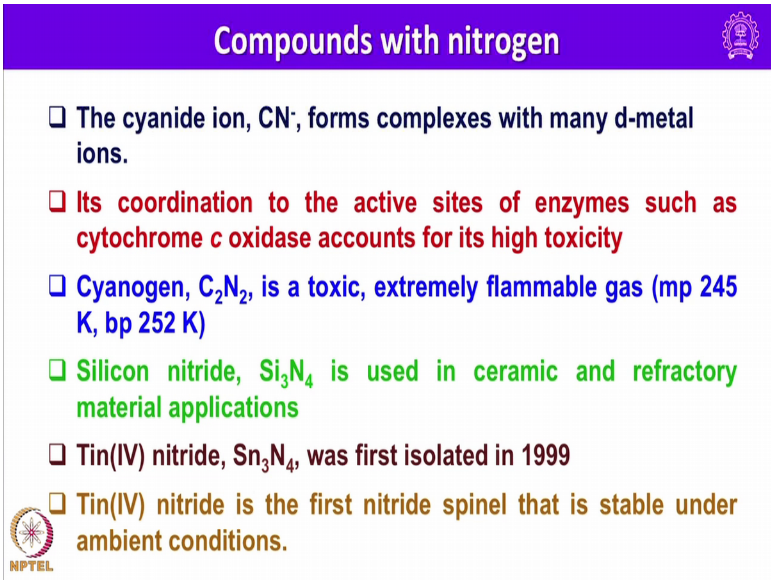

Compounds with nitrogen

- The cyanide ion, CN^-, forms complexes with many d-metal ions.
- Its coordination to the active sites of enzymes such as cytochrome *c* oxidase accounts for its high toxicity
- Cyanogen, C_2N_2, is a toxic, extremely flammable gas (mp 245 K, bp 252 K)
- Silicon nitride, Si_3N_4 is used in ceramic and refractory material applications
- Tin(IV) nitride, Sn_3N_4, was first isolated in 1999
- Tin(IV) nitride is the first nitride spinel that is stable under ambient conditions.

A cyanide is there very important in coordination chemistry, CN minus forms a numerous complexes many d block metal ions, its coordination to the active sites of enzymes such as cytochrome, c oxidises oxidise accounts for its high toxicity. The toxic nature of cyanide in living beings or in human beings comes into picture, because it forms a very stable complex with cytochrome c oxidise that accounts for its high toxicity. Cyanogen is a toxic extremely flammable gas melting point is 245 Kelvin and boiling point is 252 Kelvin.

Silicon nitride Si 3 Ni 4 is used in ceramic and refractory material applications, tin 4 nitride that is Sn 3 N 4 was first isolated in 1999. Tin nitride is the first nitride spinel that is a stable under ambient conditions, cyanide is a pseudo halogen its chemistry resembles that of halogen atoms and its physical and chemical properties also resembles halogens that is the reason, they are called pseudo halogens. For example, aside is also called as pseudo halogen and it forms C 2 N 2.

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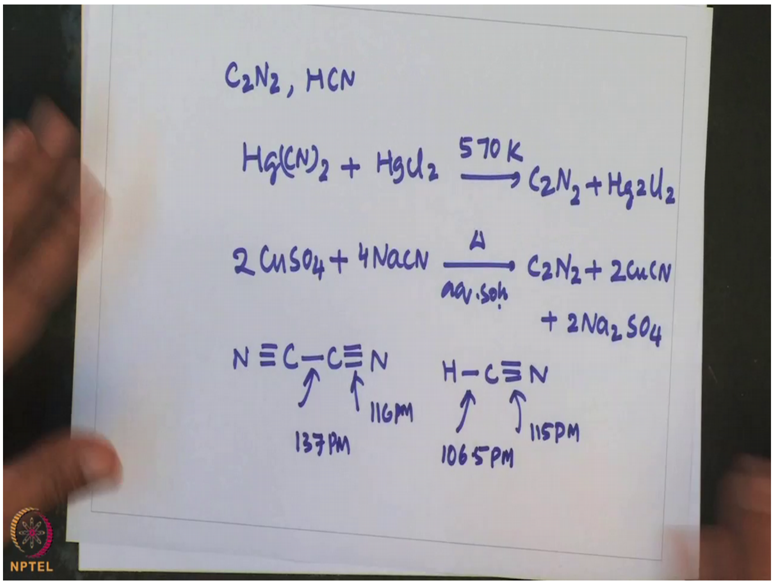

C_2N_2, HCN

$Hg(CN)_2 + HgCl_2 \xrightarrow{570\,K} C_2N_2 + Hg_2Cl_2$

$2CuSO_4 + 4NaCN \xrightarrow[aq.\,soln]{\Delta} C_2N_2 + 2CuCN + 2Na_2SO_4$

$N \equiv C - C \equiv N$

$H - C \equiv N$

HCN for example, if we take H g CN twice, and treat this one with H g c l 2 at 570 Kelvin, it gives cyanogen plus Hg 2 c l 2. One can also prepare this much static from copper sulphate for example, on heating the aqueous solution it gives C 2 N 2. So, cyanogen has a linear structure something like this and of course, very similar to here we can compare here the C triple bond N distance is bond distance is 115 picometre and here it is 116 marginal difference is there, and here this distance CC bond distance is 137 picometre here of course, here this CH bond distance is 1 point 106.5 picometre. Hence both are linear. Cynogen burns in air with a very hot and violent flame that is because of formation of carbon dioxide and N 2.

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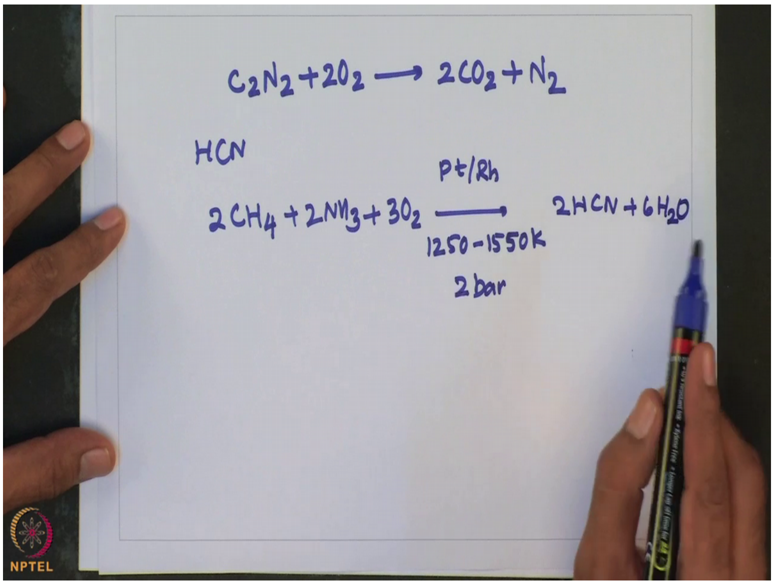

$C_2N_2 + 2O_2 \longrightarrow 2CO_2 + N_2$

HCN

$2CH_4 + 2NH_3 + 3O_2 \xrightarrow[1250-1550K \\ 2\,bar]{Pt/Rh} 2HCN + 6H_2O$

Hydrogen cyanide is extremely toxic and flammable colourless volatile liquid, and essentially one can prepare in large amounts by high temperature catalytic partial oxidation of methane and ammonia. We show you the method of preparation of hydrogen cyanide, platinum and rhodium catalyst and temperature required is very high 1250 to 1550 Kelvin, and 2 bar pressure. Mild oxidising agents convert cyanide to cyanogen, but with more powerful oxygen such as Pb O or neutral MNO 4 minus coverts c n minus 2 cyanide ion.

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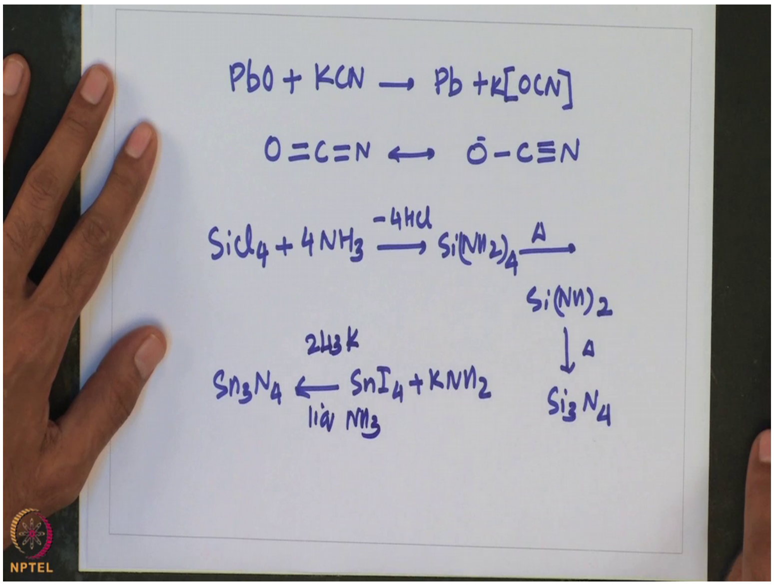

$PbO + KCN \longrightarrow Pb + K[OCN]$

$O=C=N \longleftrightarrow \bar{O}-C\equiv N$

$SiCl_4 + 4NH_3 \xrightarrow{-4HCl} Si(NH_2)_4 \xrightarrow{\Delta} Si(NH)_2 \xrightarrow{\Delta} Si_3N_4$

$Sn_3N_4 \xleftarrow[liq\ NH_3]{243K} SnI_4 + KNH_2$

So, for example, silicon nitride Si 3 N 4 is a white chemically inert amorphous powder which can be prepared by reaction or combining silicon and nitrogen at very high temperature. For example, one can also start from tetrachloro silane, for example, on treatment of tetrachloro silane with ammonia, leads to the formation of amide compound which on further heating gives this compound and which on further heating gives essentially Si 3 N 4.

Similarly, Sn 3 N 4 can also be made by starting from Sn I 4 plus KNH 2. Of course, I am not balancing the equation, 1 can generally prepare by treating Sn I 4 with potassium amide; that means, potassium in liquid ammonia at 243 Kelvin.

Sulphides of group 14 elements are quite well known, disulfides of carbon.

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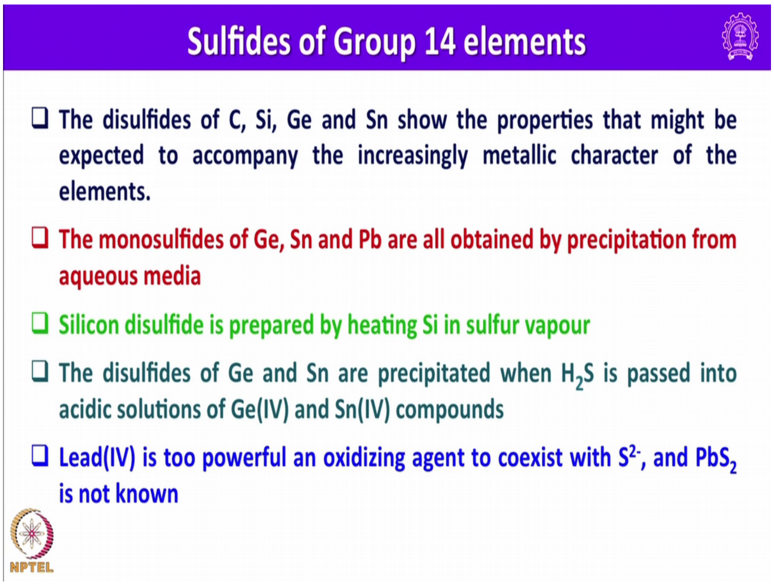

Sulfides of Group 14 elements

- ☐ The disulfides of C, Si, Ge and Sn show the properties that might be expected to accompany the increasingly metallic character of the elements.
- ☐ The monosulfides of Ge, Sn and Pb are all obtained by precipitation from aqueous media
- ☐ Silicon disulfide is prepared by heating Si in sulfur vapour
- ☐ The disulfides of Ge and Sn are precipitated when H_2S is passed into acidic solutions of Ge(IV) and Sn(IV) compounds
- ☐ Lead(IV) is too powerful an oxidizing agent to coexist with S^{2-}, and PbS_2 is not known

Carbon disulphide silicon germanium and tin show the properties that might be expected to accompany, the increasingly metallic character of the elements. The mono sulphides of germanium tin and Pb all are obtained by precipitation from aqueous media, silicon disulphide is prepared by heating silicon in sulphur vapour, the disulfides of germanium and tin are precipitated when H 2 S is passed into acidic solution of germanium or tin 4 compounds, lead 4 is too powerful an oxidizing agent to coexist with S 2 minus. So, hence Pb s 2 is not known, similar to Pb O 2 of course Pb O 2 one can make whereas, in case of sulphur Pb S 2 is not known.

When shaken with solutions of group one metal sulphides, carbon disulphide dissolves readily to give tri thiocarbonates having composition m 2 c s 3 that contain essentially a thiocarbonate ion.

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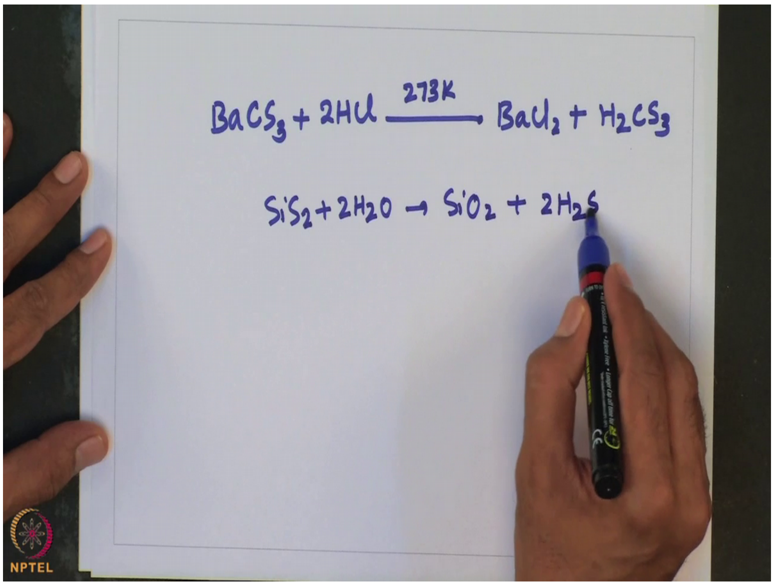

$$BaCS_3 + 2HCl \xrightarrow{273K} BaCl_2 + H_2CS_3$$

$$SiS_2 + 2H_2O \rightarrow SiO_2 + 2H_2S$$

For example, barium thiocarbonate when it is treated with the Hc l at 273 Kelvin, it gives B a c l 2 plus thio carboxylic acid and of course, silicon disulphide is prepared by heating, sulphur in sulphur vapour with silicon both the structure of this and the chemistry of Si O 2 show no parallels with SiO 2 and s i s 2 is instantly hydrolyzed. So, SiO 2 is very stable towards hydrolysis whereas, s i s 2 readily undergoes hydrolysis to form SiO 2 plus 2 H 2 S. Some of the sulphides of tin and germanium have cluster structures for example, if you consider G e 4.

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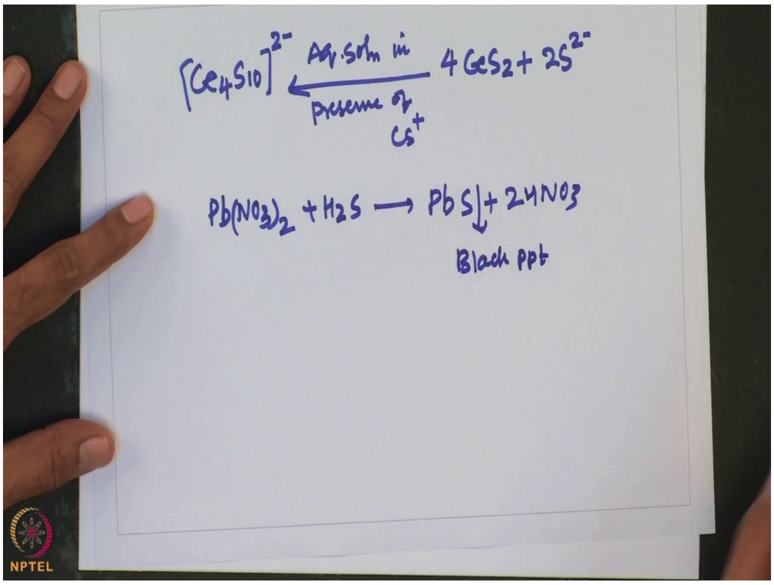

$$[Ge_4S_{10}]^{2-} \xleftarrow[\text{Cs}^+]{\text{Aq. soln in presence of}} 4GeS_2 + 2S^{2-}$$

$$Pb(NO_3)_2 + H_2S \longrightarrow \underset{\text{Black ppt}}{PbS\downarrow} + 2HNO_3$$

S 10 2 minus which can be prepared starting from germanium sulphide, with sulphide source essentially c c m sulphide one can use aqueous solution in presence of c c m plus; c c m sulphide one can use aqueous solution of c c m sulphide and germanium sulphide when they mixed together it leads to the formation of Ge 4 S10 2 minus lead 2 sulphide occurs naturally as galina Pb s and that adapts sodium chloride lattice, and it forms a block precipitate so; that means, in the qualitative test formation of lead sulphate from the corresponding salts is used as a identification or qualitative test for the cations for example, if you take lead nitrate treat this 1 with H 2 S, aqueous solution of lead nitrate when is bubbled with H 2 S gas, it gives Pb s plus 2 HNO 3 and this is a black precipitate. So, this indicates presence of some of these sulphophillic metal ions.

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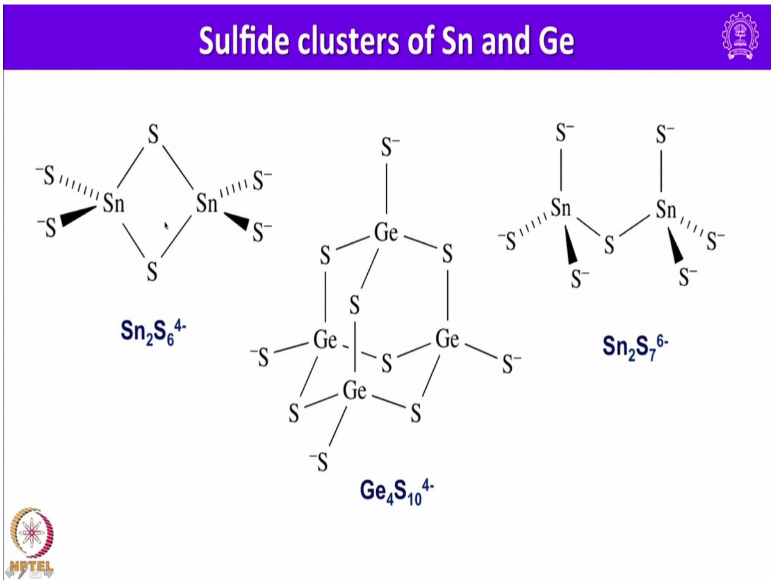

Sulfide clusters of Sn and Ge

$Sn_2S_6^{4-}$

$Ge_4S_{10}^{4-}$

$Sn_2S_7^{6-}$

The structure of few of this higher sulphides I have here Sn 2 S 6 4 minus here G e 4 S 10 has a bi cage structure or it is it is similar to piro structure Sn 2 S 7, 6 minus very similar to pyrosilicate and of course, halides of group 14elements are also quite well known.

The stability of tetra halaomethanes decreases from Cf 4 to c i 4, the rates of nucleophilic displacement increases greatly from fluorine to iodine and lie in the order like this.

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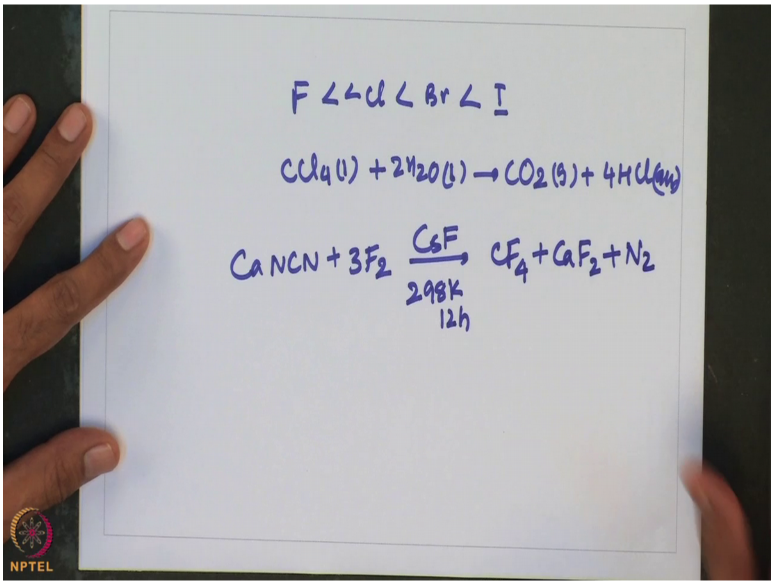

$F << Cl < Br < I$

$CCl_4(l) + 2H_2O(l) \rightarrow CO_2(g) + 4HCl(aq)$

$CaNCN + 3F_2 \xrightarrow[298K\ 12h]{CsF} CF_4 + CaF_2 + N_2$

And of course, CF 4 and CCl 4 are thermodynamically unstable with respect to hydrolysis CCl 4 plus 2 H 2 O. So, carbon tetrafluoride is extremely inert and may be prepared by the reaction of silicon carbide with f 2 with second product being S i F 4. So, a convenient laboratory scale synthesis in of CF 4 involves the reaction of calcium cyanamide with fluorine.

So, let me stop at this stage continue discussion on group 14 halides in my next lecture, until then have a pleasant reading of group fourteen chemistry.

Thank you.