Main Group Chemistry
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Lecture – 35
Chemistry of Group 14 Elements

Welcome to MSB lecture series on Main Group Chemistry. In my last lecture I was discussing about group 14 oxides and I was discussing about carbon monoxide. Let me continue from where I had stopped.

Carbon monoxide is a very toxic gas and the poisoning effect or toxicity of carbon monoxide arises from the formation of a very stable complex with haemoglobin with the consequent inhibition of O 2 transport in the body. That means, when we inhale carbon monoxide instead of oxygen binding to haemoglobin to take it to myoglobin and release, what happens? It forms, and that is reversible process absorption of oxygen or formation of a coordination compound of oxygen with haemoglobin iron is a reversible process whereas when CO binds it binds 3 hundred times stronger than oxygen as a result this is a very stable complex. And once all iron atoms in haemoglobin are utilised in form a very strong carbon monoxide complexes essentially the oxygen supply is cut off and this is where the toxicity of CO comes into picture if we inhale.

The oxidation of CO 2 CO 2 oxidation of carbon monoxide to carbon dioxide by a mixture of iodine MNO 2 and CAO 2 and AGO 2 at ambient temperature can be performed. So that means, the oxidation of CO to CO 2 by a mixture of iodine MNO 2, CAO and AG2 at ambient temperature, CO can be oxidized to CO 2 when its treated with some of the metal oxides that method we use in extraction of metals from the corresponding oxide ores. The CO molecule has a very low brown state basicity and also very negligible Lewis acidity towards neutral electron pair donors. So, despite its weak Lewis acidity; however, CO is attacked by strong Lewis bases at higher pressure and somewhat at elevated temperatures.

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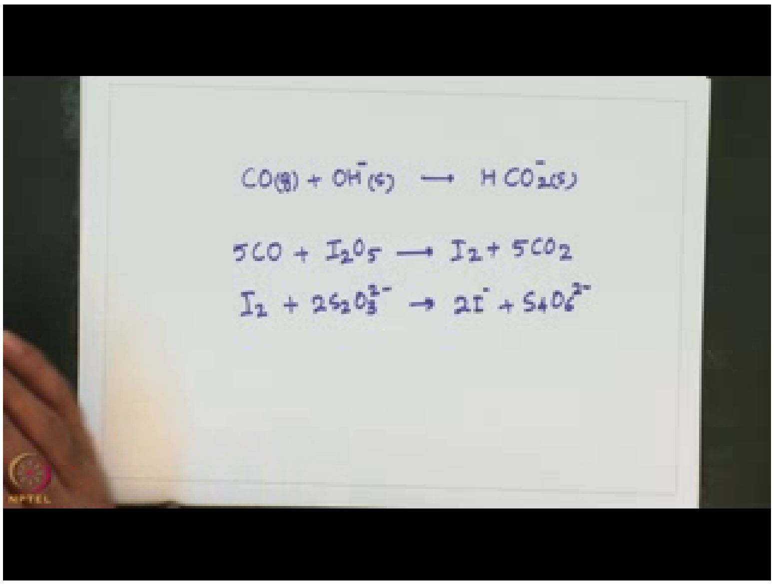

$$CO_{(g)} + OH^-_{(s)} \longrightarrow HCO^-_{2(s)}$$

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

So that means, if it takes CO, it can form something like this. This is essentially a format ion. The presence of alkyl or aryl group stabilizes the hydrides of all 3 elements. For example, if we take carbon monoxide and treat with I 2 O 5 iodine pent oxide it gives I 2 plus 5 CO 2 or one can take I 2 treat with thiosulphate ion it liberates iodide, so I minus.

So that means, the oxidation of CO to carbon dioxide is the basis of quantitative analysis for CO with the formation of I 2 which titrated against thiosulphate and the amount of CO is measured here. So, CO is similarly oxidised by a mixture of MNO 2 or cupric oxide and silver oxide at ambient temperature and this reaction is used in respirators.

And CO is also a very good reducing agent and can reduce most metals from their oxides to the metal. So, I will show you couple of examples here.

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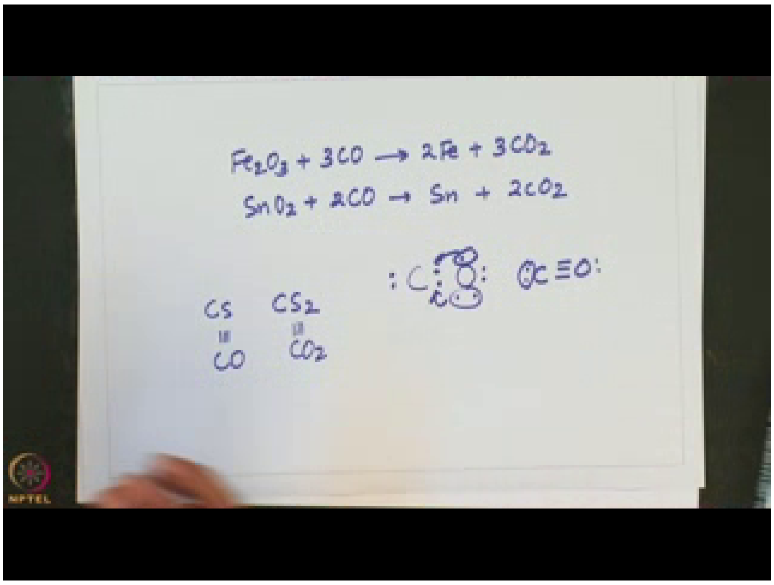

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$SnO_2 + 2CO \rightarrow Sn + 2CO_2$

For example, Fe 2 O 3 when it is treated with carbon monoxide it reduces iron to iron oxides to iron through the formation of CO 2 in that process CO get will get oxidised. Similarly Sn O 2 when it is treated with carbon monoxide it reduced to tin through the formation of carbon dioxide. So, this is where the utility of carbon monoxide comes as a reducing agent in metallurgy for the extraction of metals from the corresponding oxides.

Selected physical properties of CO and CO 2 I have given in the table that I am going to show for comparison. In fact, CO is the strongest known stable molecule and it confirms the efficiency of pi pi bonding between C and C. So, we have extensive pi pi bonding between carbon and oxide in fact, we have a triple bond that also I showed you through Lewis dot structure. For example, if we start writing Lewis structure. So, initially we get something like this and then if we write here then will be left with the 2 electrons here now octate is satisfied for this one. Whereas, octate is not satisfied, so 2 electrons moves here and 2 will move here and this leads to the formation of this one and this lone pair is responsible for carbon monoxide to behave as a ligand and here we have pi bonding is there. So, very strong pi bonding is there ok.

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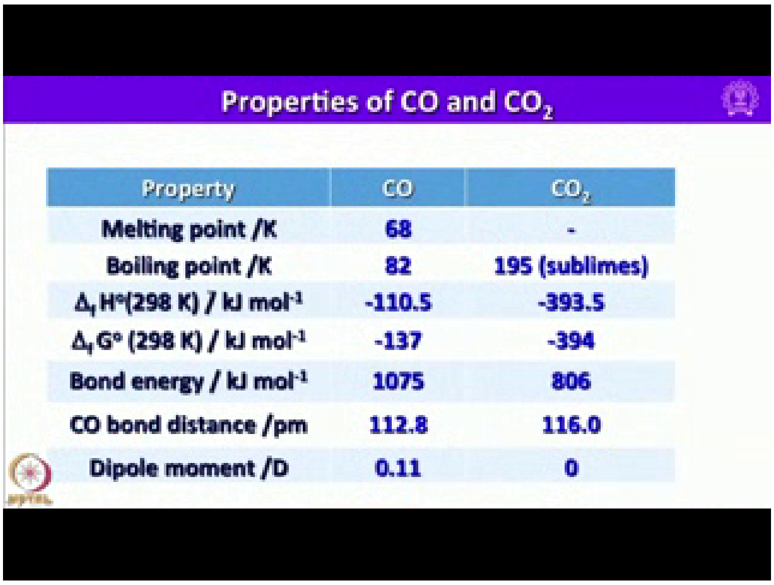

Properties of CO and CO_2

Property	CO	CO_2
Melting point /K	68	-
Boiling point /K	82	195 (sublimes)
$\Delta_f H^\circ$(298 K) / kJ mol^{-1}	-110.5	-393.5
$\Delta_f G^\circ$ (298 K) / kJ mol^{-1}	-137	-394
Bond energy / kJ mol^{-1}	1075	806
CO bond distance /pm	112.8	116.0
Dipole moment /D	0.11	0

So, you can compare some of the properties of carbon monoxide with carbon dioxide melting point is 68. So, boiling point is 82 and whereas, boiling point for CO 2 is 195 its sublimes 195 Kelvin. All these values are in Kelvin and here you can look into the enthalpy of formation it is minus 110.5 for CO whereas, this is more in case of this one. So, minus 393.5 and similarly one can look into delta G minus 137 whereas, in case of CO 2 it is almost more than 3 times all equal into 3 times minus 394 and bond energy is 1075 kilo joules per mole in case of carbon monoxide whereas, in case of carbon dioxide it is 806 CO bond distance 112.8 whereas, in case of CO we have 116. So, here we have a triple bond here we have a double bonds. So, that explains and dipole moment is 0.11 whereas, in case of CO 2 it is a linear symmetric molecule 0.

The sulphur analogue of carbon monoxide and carbon dioxide are known CS and CS 2; however, CS does not exist in its independent form, free state CS and CS 2 are also known CS does not have an independent existence CS is an unstable transient molecule and the CS 2 is endoergic. So, some complexes with CS 2 are exist and their structures are similar to those found by CO and CO 2 CS 2 undergoes hydrolysis and yields tri thiocarbonate ions very similar to carbonate tri thiocarbonate are thiocarbonate is CS 3 2 minus and this is very similar to CO 2 forming carbonate ion. And of course, CS 2 is a molecular substance similar to carbon dioxide. So, this is very similar to carbon dioxide and this is similar to carbon monoxide. The species CS as I mentioned is unstable because here if you think of having similar multiple bond between carbon and sulphur that is unstable because of the larger difference in the orbital 2 P orbital and 3 P orbital.

As a result what happens because of mismatch of orbital size this multiple bonding is not effective. CS does not have independent existence, but can be stabilized by coordination to a metal by using an appropriate reagent for generation of CS 2. The linear CS is a better sigma donor and pi acceptor then CO, but depends on electron richness of the metal and the type of the metal we are using and sourly transmittal complexes having CS are known. For example, I will give you the preparation of such complexes. Before that let me show you the possible coordination modes of carbon thiomonoxide.

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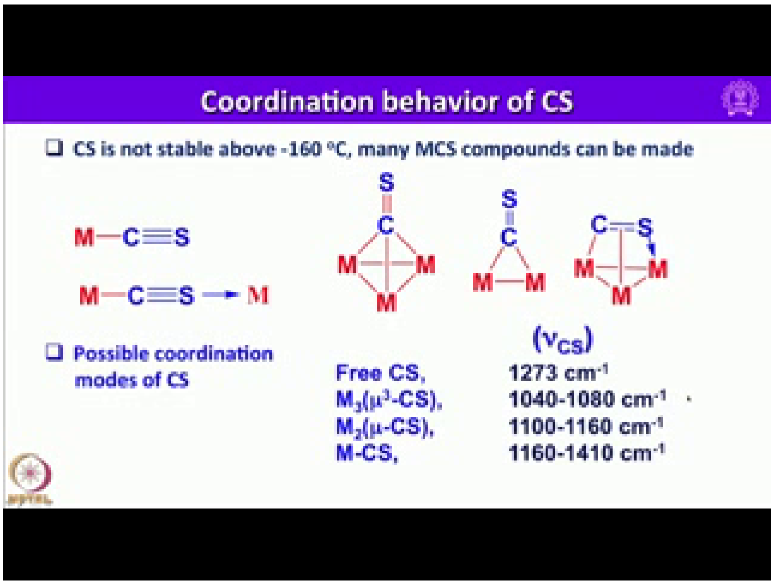

Coordination behavior of CS

- ☐ CS is not stable above -160 °C, many MCS compounds can be made
- ☐ Possible coordination modes of CS

	(ν_{CS})
Free CS,	1273 cm^{-1}
$M_3(\mu^3\text{-CS})$,	1040-1080 cm^{-1}
$M_2(\mu\text{-CS})$,	1100-1160 cm^{-1}
M-CS,	1160-1410 cm^{-1}

As I said carbon thiomonoxide is not stable above minus 160 degree centigrade and many thiocarbonyl compounds are known and they can have this kind of coordination modes it can be terminal. And since S is also a soft ligand with lone pair, it can also act as a bridging ligand one through c carbon lone pairs and another through sulphur lone pair and it can also bridge 3 metal centres or 2 metal centres and also it can involve in this kind of coordination.

And if you just look into the stretching frequency of free CS comes around 1273 centimetre inverse and when it is bridging 3 metal centres the value is in the range of 1040 to 1080 centimetre minus. And in case of dibridging it is 1100 to 1160 when it acts as a terminal ligand a stretching frequency of CS is around 1160 to 1410 it is little different from carbon monoxide as I had already mentioned this is a better sigma donor and a better pi acceptor compared to carbon monoxide.

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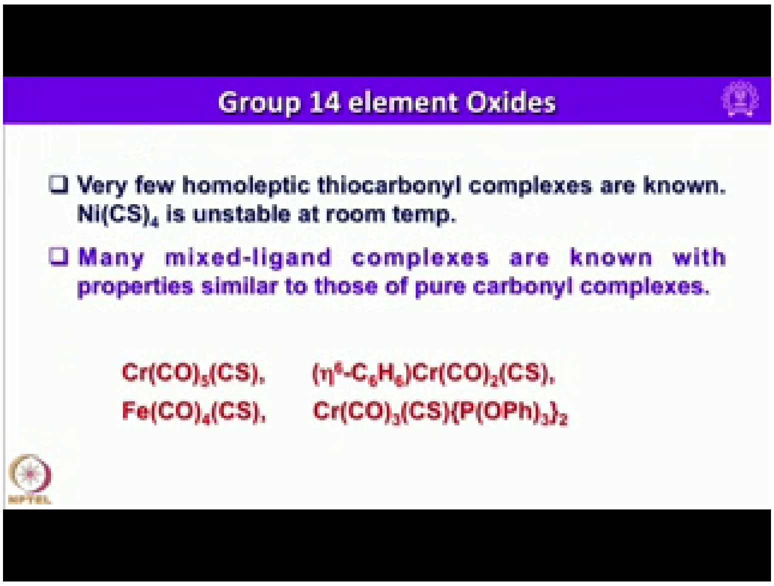

Group 14 element Oxides

- ❑ Very few homoleptic thiocarbonyl complexes are known. $Ni(CS)_4$ is unstable at room temp.
- ❑ Many mixed-ligand complexes are known with properties similar to those of pure carbonyl complexes.

$Cr(CO)_5(CS)$, $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CS)$,
$Fe(CO)_4(CS)$, $Cr(CO)_3(CS)\{P(OPh)_3\}_2$

So, let me this are some of the known compounds very few homoleptic thiocarbonyl complexes are known, like nickel tetracarbonyl is known similarly nickel tetra thiocarbonyl is can be made, but it is unstable at room temperature and many mixed ligand complexs are known with properties very similar to pure carbonyl complexes. Let me give you preparation of some of these compounds using 1 or 2 different routes.

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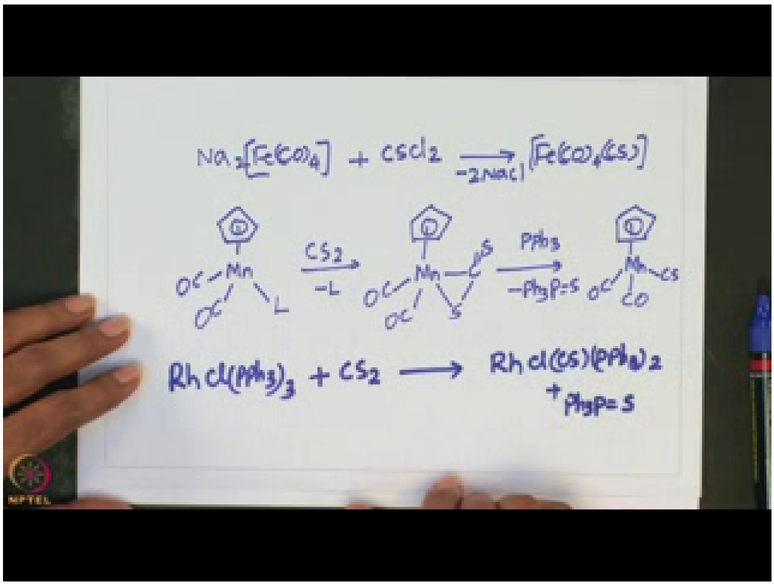

$$Na_2[Fe(CO)_4] + CSCl_2 \xrightarrow[-2NaCl]{} [Fe(CO)_4(CS)]$$

$$RhCl(PPh_3)_3 + CS_2 \longrightarrow RhCl(CS)(PPh_3)_2 + Ph_3P{=}S$$

Let us consider this one, anionic Fe CO 4 this one. When it is treated with CS Cl 2, the CSCl 2 is thiophosgene COCl 2 is known as phosgenes COCl 2 and if you replace oxygen with sulphur it is called thiophosgene when it is treated with Fe CO 4 anionic it leads to the formation of Fe CO 4 CS this is very similar to Fe CO 5 iron pentacarbonyl and here NaCl formed. So, one can also start with CS 2 for example, let us consider this cyclopentadienyl dicarbonyl manganese complex, let us say L is some ligand and treat this one with CS 2 it forms initially first L comes out. At this stage if we add triphenylphosphene and it will abstract sulphur and it forms sulphur tri phenyl phosphene sulphide and it leads to the formation of thiocarbonyl complex.

So, this is another way of generating in C 2 CS and utilising in the formation of a thiocarbonyl metal complex. If you consider wilkinson catalyst Rh Cl pph 3 thrice, this is a square planar complex, this is called wilkinson catalyst. This is used for hydrogenation and many catalytic reactions for a variety of organic transformations. So, this is when treated with carbon disulphide it forms Rh Cl CS pph 3 twice with the formation of this one. So, this is another method of preparing you now CS bond metal complexes. And you can see here many such compounds are known here; that means, there is a scope for preparation of thiocarbonyl complexes although it is very difficult to isolate CS.

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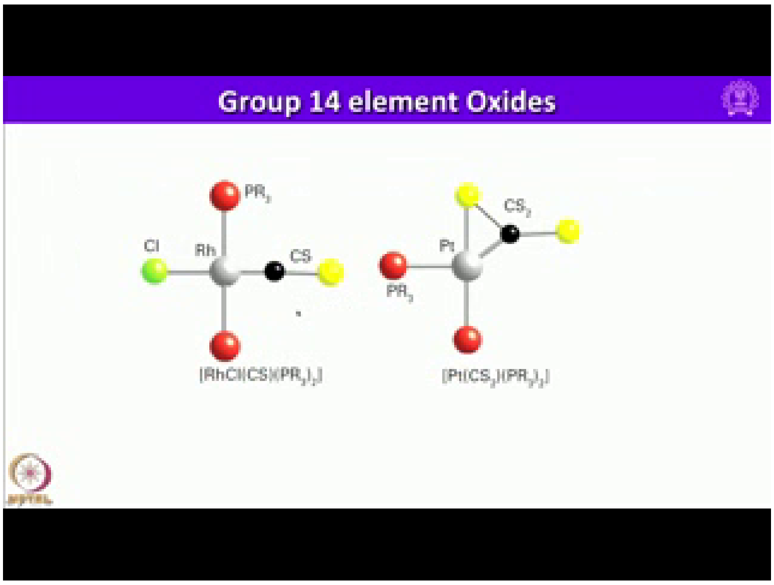

Group 14 element Oxides

$[RhCl(CS)(PR_3)_2]$

$[Pt(CS_2)(PR_3)_2]$

And this is the structure of the compound just now I wrote here this compound is very similar to vaskas compound where CO and Cl are trance to each other and we have 2 try fera phosphene trance to each other. So, here instead of carbon monoxide we have CS and also here CS 2 showing this kind of coordination with that also I wrote in case of manganese. So, structures are available for these compounds that indicates these compounds are quite stable and they can be crystallized.

And CO is very poisonous and much more reactive than nitrogen and it combines with halogens except iodine directly.

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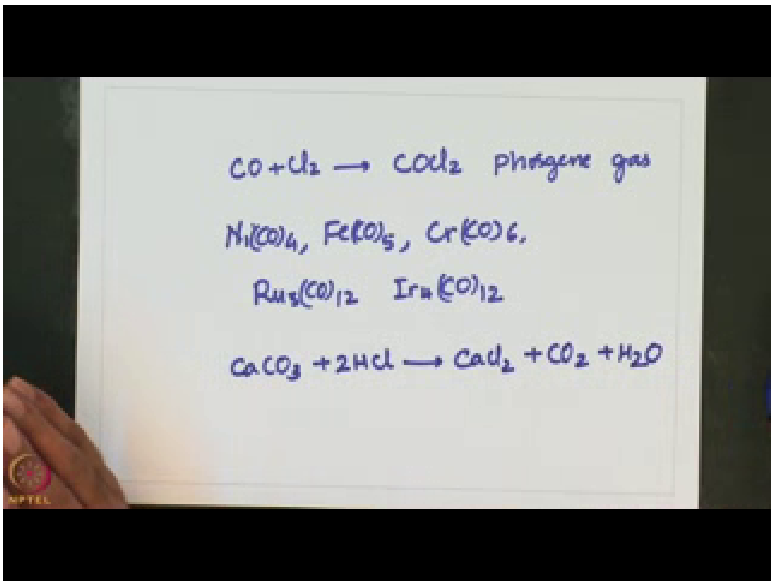

$CO + Cl_2 \rightarrow COCl_2$ phosgene gas

$Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$,

$Ru_3(CO)_{12}$ $Ir_4(CO)_{12}$

$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

For example, if you take CO and if you treat with Cl 2 it readily forms COCl 2 and its very poisonous gas it is called phosgene phosgene gas. So, one has to be extremely careful, if we have a source of carbon monoxide and if you have a source of halogen they should not be put together in a same place and in the same cupboard and if any spillage is there it is likely that there can be formation of phosgene. And CO is an excellent ligand in coordination chemistry and also in organometallic chemistry. For example we know homoleptic Ni CO 4 is known, chromium hexacarbonyl is known, iron penta carbonyl is known and chromium molybdenum tungsten hexa carbonyls are known group 6 and also clusters are known for example, Ru 3 CO 12 or even iridium. So many such compounds are known and you will be learning more in organometallic chemistry about these things.

CO compares well with triphenylphosphene or in particular tertiary phosphenes in its donor and acceptor properties. So, when we take carbon and burn in excess of oxygen that leads to the formation of carbon dioxide solid, carbon dioxide is called dry ice and it readily sublimes, but maybe kept in insulated containers for laboratory use and to perform reaction at low temperature. That means, we can use them in low temperature. But small scale laboratory synthesis of gaseous CO 2 involves this following reaction and CO 2 is the most stable oxide produced on an enormous scale industrially by the combustion of coal, oil or natural gas anytime we burn coal oil or natural gas, the by product is carbon dioxide.

One interesting thing about carbon dioxide is, is a very weak Lewis acid for example, only a small fraction of molecules are complexed with water to form carbonic acid H 2 CO 3 in acidic aqueous solution, but at higher P h OH coordinates to carbon atom. So, it forms hydrogen carbonate or bicarbonate. So, that can be represented using these equations.

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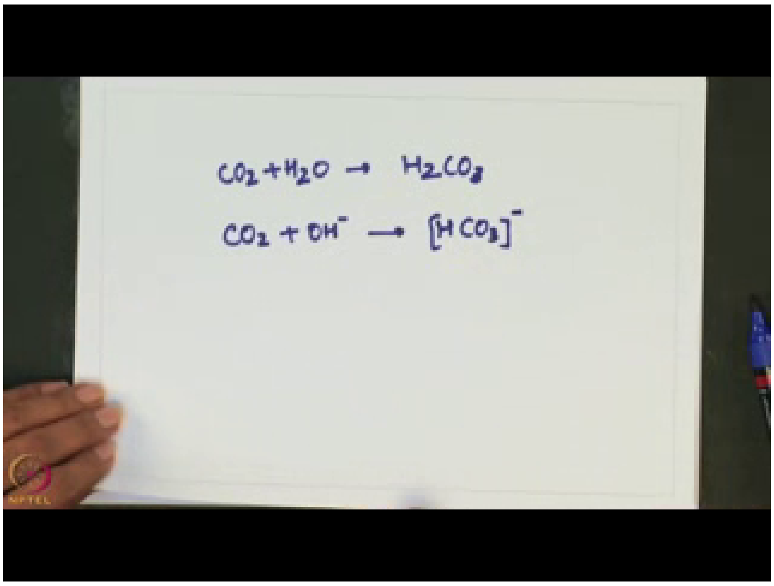

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$CO_2 + OH^- \rightarrow [HCO_3]^-$$

And in contrast to metal complexes of carbon monoxide metal complexes of carbon dioxide are not very common we have few compounds are known, but they are rare and for less important than those of metal carbonyls. And of course, if you find a way of making carbon dioxide complexes and then converting into some organic compounds probably that comes very handy in bringing down the carbon dioxide content provided we use cheaper metal such as iron and anyway the discussion on such matter is out of context as far as these lectures are concerned.

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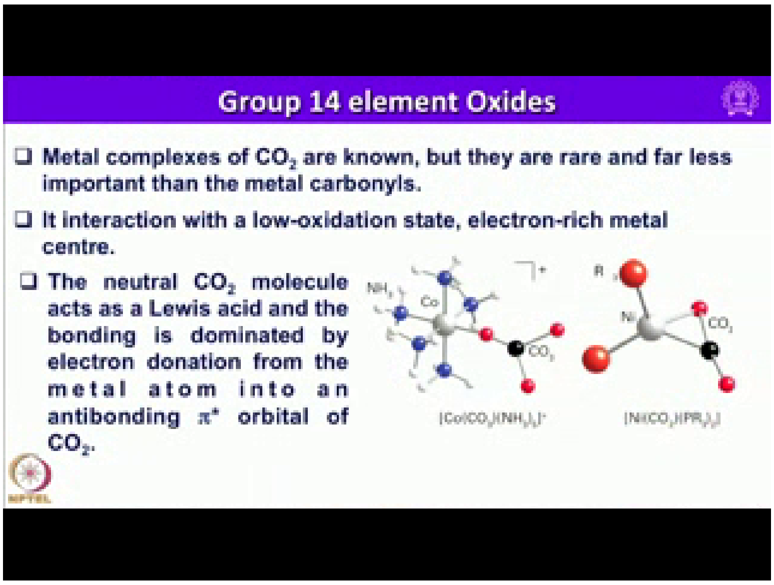

Group 14 element Oxides

- ❑ Metal complexes of CO_2 are known, but they are rare and far less important than the metal carbonyls.
- ❑ It interaction with a low-oxidation state, electron-rich metal centre.
- ❑ The neutral CO_2 molecule acts as a Lewis acid and the bonding is dominated by electron donation from the metal atom into an antibonding π^* orbital of CO_2.

Neutral carbon dioxide molecule acts as a Lewis acid and the bonding is dominated by electron donation from the metal atom into an antibonding pi star orbital of CO 2; that means, if at all if there is a binding is there it happens through this way. And of course, I have shown couple of examples here in which carbonate or carbon dioxide is binding in case of carbon dioxide you can see here it is binding to nickel very similar to carbon disulphide I showed in previous slide with platinum. So, here CO 3 binding can be seen here in this cobalt complex.

Carbonate ion is planar and processes D 3 H symmetry with all CO bonds are equal and measure 129 picometre and in fact, one can write 3 resonance structures for carbonate. For example, one can write here.

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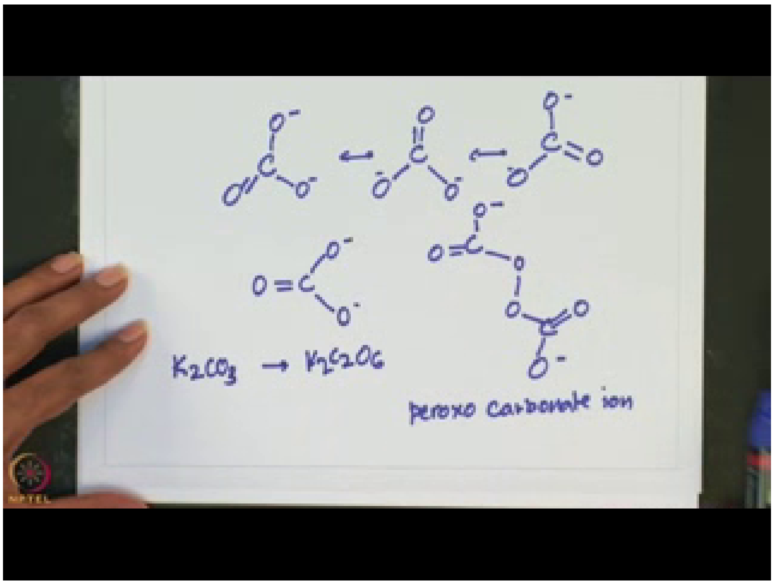

So, a delocalised bonding picture involving pi pi interactions is appropriate and valence bond theory describes the ion in terms of 3 resonance structures I have shown here the CO bond distance is longer than that in CO 2 and is consistent with a formal bond or drop 1.33 here. So, average.

So, most metal carbonates other than those of group 1 metals are sparingly soluble in water and here there is one more carbon oxide that you can see here. So, essentially a typical carbonate can be shown like this. So, one more is, this is peroxo carbonate ion. So, a general method of preparing peroxo salts can be used to convert K 2 CO 3 for example, to K 2 C 2 O 6 I have shown here. The electrolysis of aqueous K 2 CO 3 at 253 Kelvin using a high current density produces a salt believe to contain a peroxo carbonate ion. So that means, one can make this one starting from K 2 CO 3, K 2 CO 3 giving K 2 C 2 O 6, K 2 C 2 O 6 this is called peraxo carbonate, potassium peroxo carbonate and this is potassium carbonate.

A third oxide of carbon is carbon sub oxide having the composition

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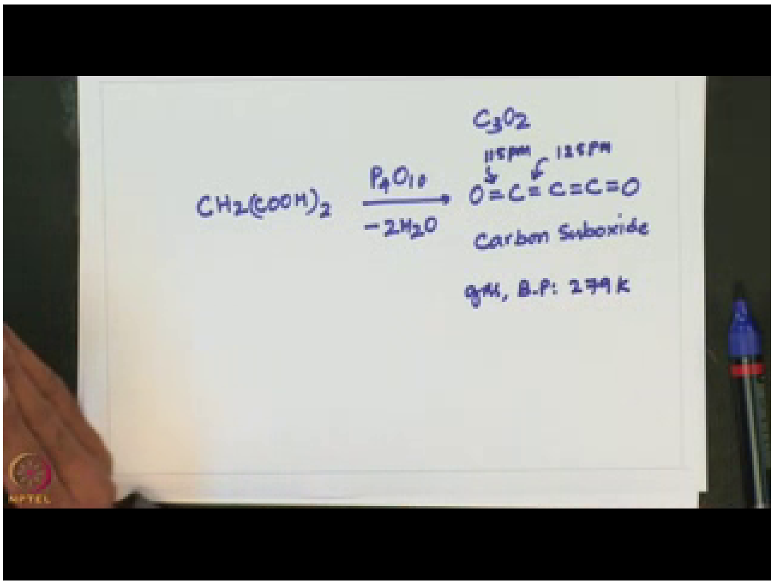

C 3 O 2 and one can prepare this one starting from malonic acid for example, on dehydrating malonic acid using P 4 O 10 phosphorus pentoxide essentially what we are doing is dehydration of malonic acid that gives this is. So, C 3 O 2 this is called carbon suboxide and here the carbon carbon distance if you look into it is 125 picometre whereas, oxygen to carbon distance is 1 hundred and fifteen picometre. And this is a gas boiling point 279 Kelvin gas and boiling point is 279 Kelvin and it polymerises about 288 Kelvin to form a red brown paramagnetic material.

Of course, the structure of carbon suboxide is usually described as quasi linear because IR spectroscopic and electron diffraction data for the gaseous molecule shows that the energy barrier to bending at the central carbon atom is only 0.37 kilo joules per mole that is very close to the vibrational ground state that is a reason this is called quasi linear.

And of course, the next one is silicon and silicon we have this SIO 2. You can see here SIO 2 is a non volatile solid and occurs in many different forms nearly all of which posses lattice structures constructed of tetrahedral SIO 4 building blocks. They will be something like this SIO 4 building blocks here and silicon is at the centre and that is connected to 4 oxygen atoms and each only will be having a negative charge essential SIO 4 minus.

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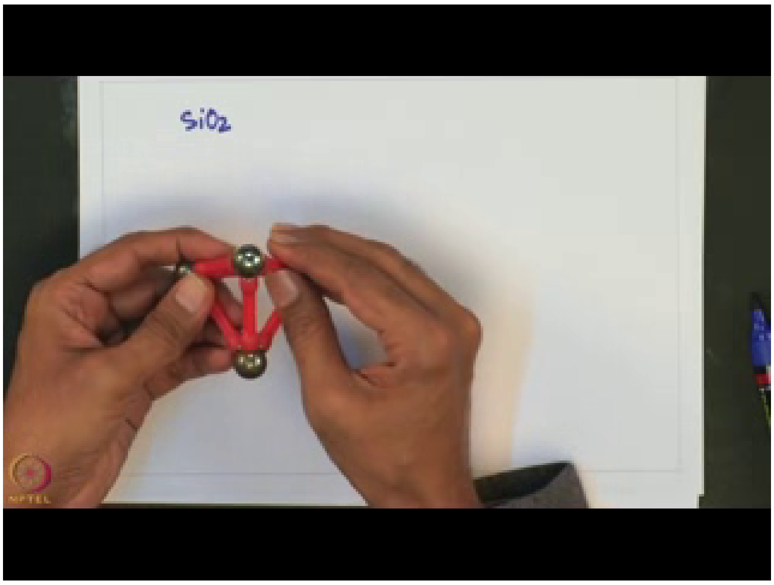

But overall when we look into that one we have a ratio of silicon to oxygen 1 is to 2 that is the reason formula is referred to as SIO 2. And each unit is connected to the next by sharing an oxygen atom to give SIO Si bridge something like this, something like this.

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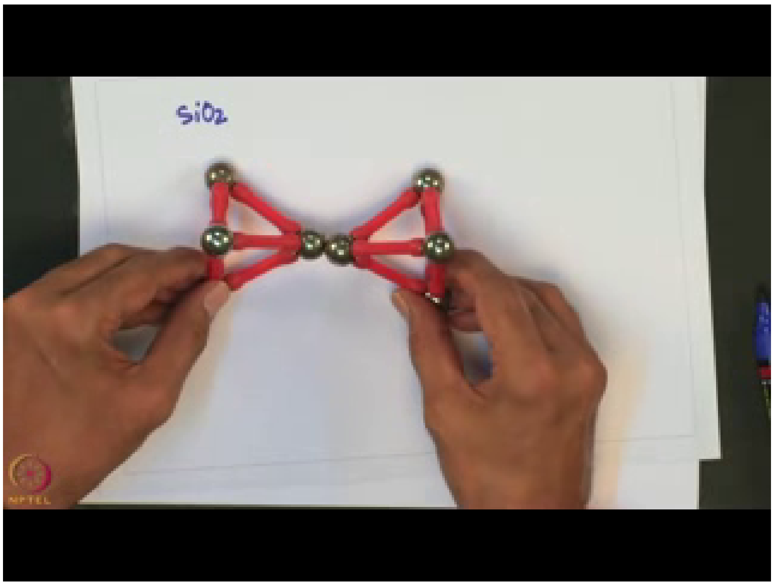

And you can see here at how one form of silica in different form of containing other elements main group elements as well as transfer elements that can be converted to something else shown in this chart here.

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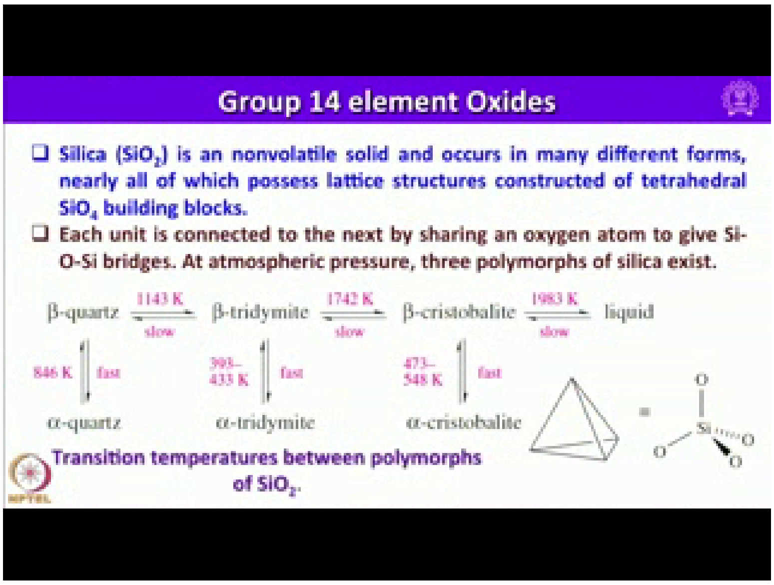

Group 14 element Oxides

- ☐ Silica (SiO_2) is an nonvolatile solid and occurs in many different forms, nearly all of which possess lattice structures constructed of tetrahedral SiO_4 building blocks.
- ☐ Each unit is connected to the next by sharing an oxygen atom to give Si-O-Si bridges. At atmospheric pressure, three polymorphs of silica exist.

Transition temperatures between polymorphs of SiO_2.

Beta quartz can be converted it into tridymite or cristobalite or alpha cristobalite or alpha tridymite or beta quartz can be converted into alpha quartz by altering the temperature. So that means, you can see a transition that occurs between polymers of silica or silicon dioxide. So, I would be discussing more aspects of silicon oxides in my next lecture. So, until then have a pleasant reading of group 14 chemistry, until I return with my next lecture.

Thank you very much.