

Main Group Elements
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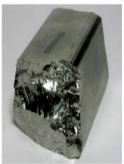





Lecture – 32
Chemistry of Group 14 Elements

Welcome to MSB lecture series on main group chemistry. Today let me drive your attention to the chemistry of group 14 elements. In my previous lecturer, I had concluded the discussion on group 13 elements. So, let me begin today with discussion on group 14 elements.

You all know that group 14 is in the centre of the main group elements consisting of 5 elements carbon, silicon, germanium, tin and lead and the electronic configuration. The valence shell of group 14 elements is $ns^2 np^2$ that is they have 4 electrons in their valence shell and of course, carbon is the 17th most abundant element in the earth's crust in nature. It is there in both free as well as in the combined state and coal, diamond and graphites and metal carbonates hydrocarbons and CO_2 are essentially the carbon containing entities substances and of course, carbon dioxide accounts for about 0.03 percent in air carbon is the most versatile among all elements in the periodic table.

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Who discovered group 14 elements

				
Carbon 1879	Silicon 1823	Germanium 1886	Tin 3000 BC	Lead
			Tin and Lead Discoverer unknown	
A L Lavoisier	Jöns Jacob Berzelius	Clemens Winkler		

NPTEL


And let us look into the discoverers of group 14 elements although carbon is known. It was actually identified by A L Lavoisier in 1879 and of course, silicon was discovered in

1823 by Berzelius and germanium by Clemens Winkler in 1886 and tin and lead are known since 3000 BC. We do not have clear information about who were responsible for discovering tin and lead because they are known since 3000 BC.

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Occurrence of group 14 elements

- ❑ Carbon occurs as diamond and graphite, and in several forms of low crystallinity. In 1996 Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl, and Harold Kroto for their discovery of a new allotrope of carbon, C_{60} , named *buckminsterfullerene*.
- ❑ Carbon occurs as carbon dioxide in the atmosphere, dissolved in natural waters and as the insoluble carbonates of calcium and magnesium.
- ❑ Elemental Si does not occur naturally, but it constitutes 25.7 % of the Earth's crust (Si is the second most abundant element after O) in the form of sand, quartz, rock crystal, flint, agate and silicate minerals.



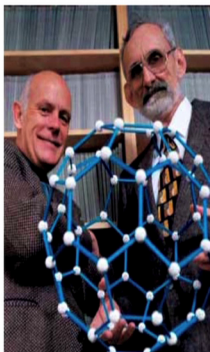

Carbon occurs as diamond and graphite and in several forms of low crystallinity in 1996 Nobel Prize in chemistry was awarded to 3 eminent scientist Richards Smalley, Robert Curl and Harold Kroto for the discovery of a new allotrope of carbon that is C_{60} is called fullerene named after buckminsterfullerene carbon occurs as carbon dioxide in the atmosphere dissolved in natural waters and also as the insoluble carbonates of calcium and magnesium are also found in earth crust as well as in water.

Elemental silicon does not occur naturally, but it constitutes about 25.7 percent of Earth's crust and of course, silicon is the second most abundant element after oxygen in the form of sand quartz rock crystal flint agate and silicate and several silicate minerals.

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Fullerene discovery


The Nobel Prize in Chemistry 1996



Robert F. Curl Jr.
Prize share: 1/3

Sir Harold W. Kroto
Prize share: 1/3

Richard E. Smalley
Prize share: 1/3




And these are the 3 people who won Nobel Prize in chemistry in 1996 for discovering fullerene; this is Robert Curle and this is Sir Harold Kroto and this is Richard E Smalley.

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Occurrence of group 14 elements

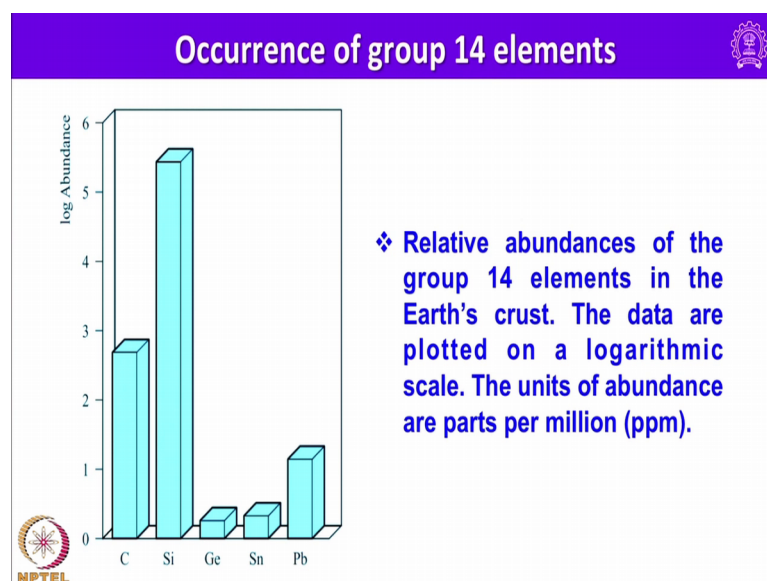
- Ge makes up only 1.8 ppm of the Earth's crust, being present in trace amounts in a range of minerals (e.g. zinc ores) and in coal.
- Sn is obtained from the mineral cassiterite, SnO_2 ,
- Pb is obtained from its sulfide ores such as: galena (PbS), anglesite (PbSO_4) and cerussite (PbCO_3).



Germanium makes up only about 1.8 p p m of the Earth's crust. So, it is its present in the trace amount in a range of minerals including zinc ores and also in coal.

And tin is obtained from the mineral cassiterite the composition of this one is SnO_2 ; it is a oxide ore and besides that it has all other impurities and lead is obtained from its sulphide ores such as galena is PbS are anglesite PbSO_4 and cerussite PbCO_3 .

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And you can just see the relative abundances of the group 14 elements in the Earth's crust. The most abundant one is silicon among all group 14 elements and germanium tin are in very small quantities.

Sources of natural graphite are supplemented by manufactured material found by heating powdered coke so; that means, essentially one can think of making artificial diamonds by heating coke to very high temperature for example, if the coke with silica when it is heated to 2800 Kelvin, one can get the artificial diamond and approximately 30 percent of the diamond that is required for industrial use in u s comes from the synthetic means and silicon not a very high purity can be extracted from silica that is silicon dioxide.

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Extraction of group 14 elements

- ❑ Sources of natural graphite are supplemented by manufactured material formed by heating powdered coke (high temperature carbonized coal) with silica at ≈ 2800 K. Approximately 30% of diamonds for industrial use in the US are synthetic.
- ❑ Silicon (not of high purity) is extracted from silica, SiO_2 , by heating with C or CaC_2 in an electric furnace.
- ❑ Impure Ge can be obtained from flue dusts collected during the extraction of zinc from its ores, or by reducing GeO_2 with H_2 or C.
- ❑ For use in the electronic and semiconductor industries, ultrapure Si and Ge are required, and both can be obtained by zone-melting techniques
- ❑ Tin is obtained from cassiterite (SnO_2) by reduction with C in a furnace.
- ❑ Pb is refined from its ores.



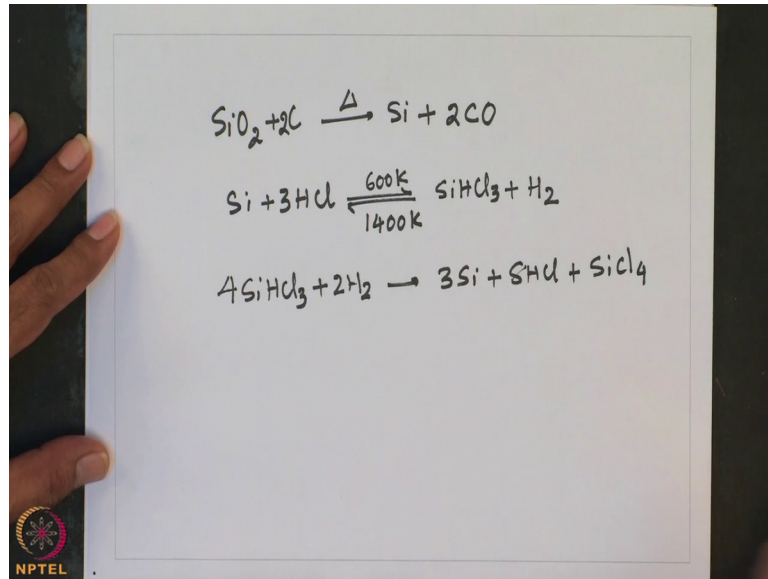
By heating with carbon or calcium carbide in an electric furnace impure germanium can also be obtained from flue dust collected during extraction of zinc from its ore or by reducing germanium oxide with hydrogen or carbon.

For use in the electronic and semiconductor industries, we need ultra pure silicon and germanium. So, they can be purified further using zone melting technique tin is obtained from cassiterite tin oxide by reduction with carbon in a furnace and of course, lead is refined from its ores.

And crude silicon is first converted to the volatile SiHCl_3 trichlorosilane which is then converted back to ultra pure silicon by using chemical vapour deposition called CVD and industrial CVD procedure involves passing SiHCl_3 that is trichlorosilane and hydrogen into the reaction vessel where they come into contact with the high purity silicon surface electrically heated to 1400 Kelvin; back reaction is highly endothermic and occurs on the surface of silicon to deposit additional silicon.

So, of course, melting point is 1687 Kelvin; a secondary product of the deposition reaction is essentially tetra-chlorosilane or silicon tetrachloride let me show you those reactions involved in this procedure.

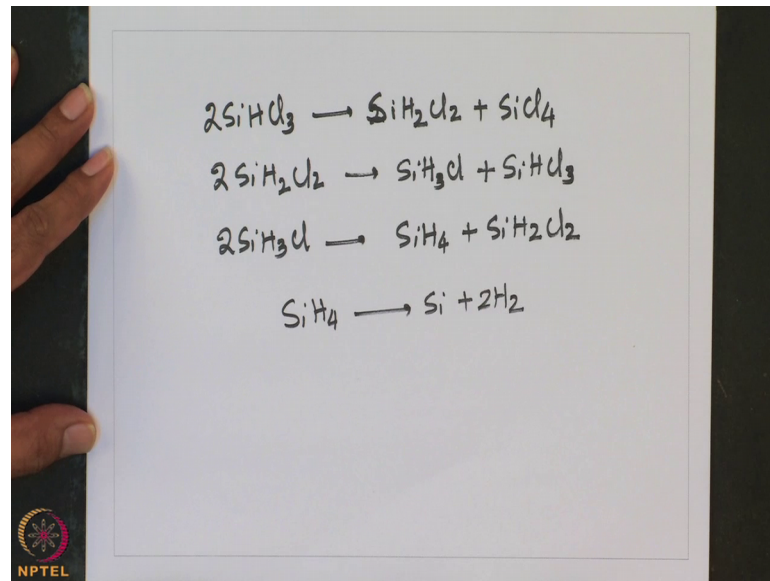
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So, SiO_2 is first treated with carbon to reduce it to silicon and then silicon is treated with HCl at 1600 Kelvin, you can reverse it at 1400 Kelvin. It gives trichlorosilane SiHCl_3 plus H_2 and then trichlorosilane is combined with H_2 to form silicon plus 8 HCl plus the by product as I mentioned SiCl_4 ; of course, SiCl_4 finds numerous applications this is one of the methods of getting SiCl_4 as well.

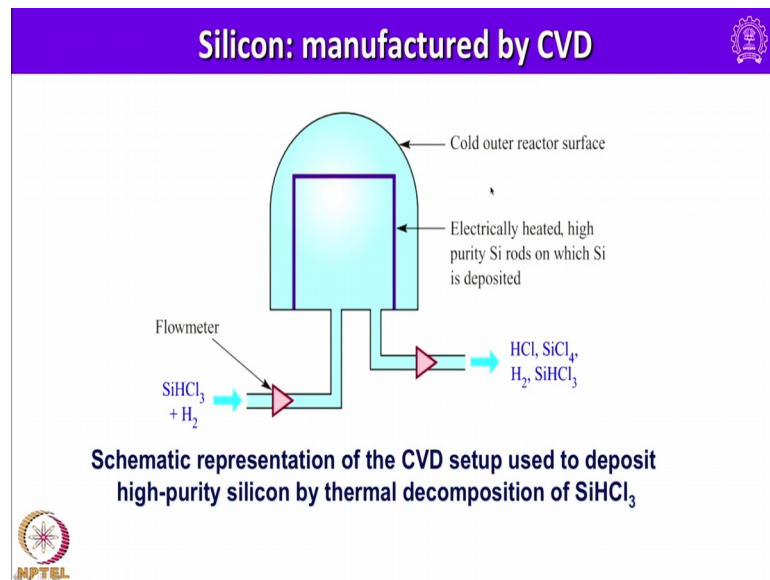
So, a more recently developed CVD process starts with SiH_4 instead of SiHCl_3 one can also prepare. So, a more recent method of CVD utilizes silane that is SiH_4 instead of trichlorosilane. So, I will show some reactions here to make silane; silane is much more volatile that is the reason in place of trichlorosilane simply silane is used.

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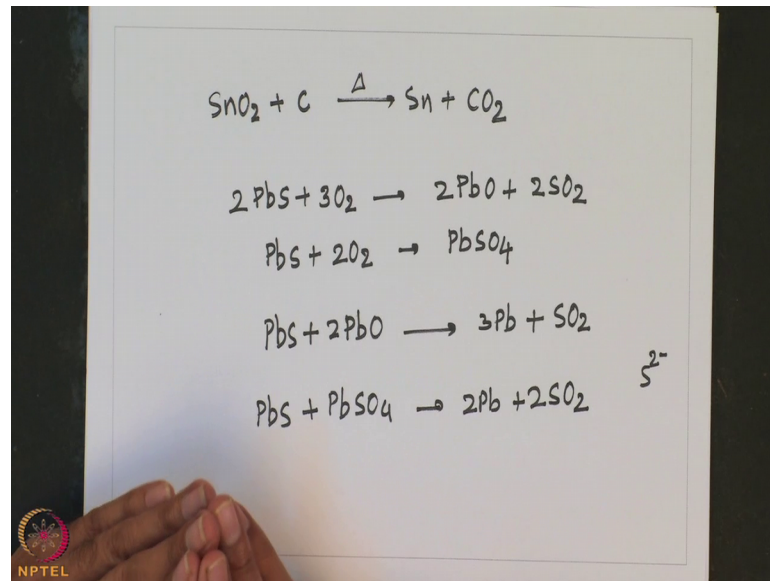
So, these are all redistribution reactions. So, SiH_4 can readily give Si plus 2H_2 , you can see here the a typical CVD setup is shown here ok.

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So, SiHCl_3 plus H_2 is passed here and of course, here we have a silicone surface is there on which silicon vapours will be deposited and then here all this gaseous substances will escape HCl , SiCl_4 , H_2 , SiCl_3 and they can be collected here through cooling or condensation.

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Though extraction of tin from its ore depends on redox chemistry here one can conveniently convert SnO_2 by using carbon as a reducing agent to get Sn. In case of lead the concentrated ore is roasted in a furnace at a moderate temperature the temperature of furnace is essentially controlled by regulating the air supply during roasting; that is lead sulphide is partly oxidised to lead monoxide and partly to lead sulphate for example,. So, this PbS can further react with oxygen and to form PbSO₄.

Now, more of galena can be added this is called self reduction to lead sulphide if you had lead oxide and the temperature is raised there will be reduction that is also called auto or self reduction in this process what happens lead sulphide is combined with lead oxide in absence of air to reduce Pb and thus SO_2 is formed here S^{2-} is essentially acting as a reducing agent S^{2-} acts as a reducing agent. Similarly, one can also combine PbS with PbSO₄ to give 2Pb plus 2SO₂. So, one of these methods can be conveniently used to get pure lead from the corresponding sulphide ore.

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Some physical properties of the group 14 elements					
Property	C	Si	Ge	Sn	Pb
Atomic number, Z	6	14	32	50	82
Ground state electronic configuration	[He] $2s^2 2p^2$	[Ne] $3s^2 3p^2$	[Ar] $3d^{10} 4s^2 4p^2$	[Kr] $4d^{10} 5s^2 5p^2$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
Enthalpy of atomization, $\Delta_a H^\circ(298\text{ K}) / \text{kJ mol}^{-1}$	717	456	375	302	195
Melting point, mp / K	>3823	1687	1211	505	600
Boiling point, bp / K	5100	2628	3106	2533	2022
Standard enthalpy of fusion, $\Delta_{\text{fus}} H^\circ(\text{mp}) / \text{kJ mol}^{-1}$	104.6	50.2	36.9	7.0	4.8
First ionization energy, $IE_1 / \text{kJ mol}^{-1}$	1086	786.5	762.2	708.6	715.6
Second ionization energy, $IE_2 / \text{kJ mol}^{-1}$	2353	1577	1537	1412	1450
Third ionization energy, $IE_3 / \text{kJ mol}^{-1}$	4620	3232	3302	2943	3081
Fourth ionization energy, $IE_4 / \text{kJ mol}^{-1}$	6223	4356	4411	3930	4083
Metallic radius, $r_{\text{metal}} / \text{pm}$	–	–	–	158	175
Covalent radius, $r_{\text{cov}} / \text{pm}$	77	118	122	140	154
Ionic radius, $r_{\text{ion}} / \text{pm}$	–	–	53 (Ge^{4+})	74 (Sn^{4+})	78 (Pb^{4+})
Standard reduction potential, $E^\circ(\text{M}^{2+}/\text{M}) / \text{V}$	–	–	–	-0.14	-0.13
Standard reduction potential, $E^\circ(\text{M}^{4+}/\text{M}^{2+}) / \text{V}$	–	–	–	+0.15	+1.69
NMR active nuclei (% abundance, nuclear spin)	^{13}C (1.1, $I = \frac{1}{2}$)	^{29}Si (4.7, $I = \frac{1}{2}$)	^{73}Ge (7.8, $I = \frac{3}{2}$)	^{117}Sn (7.6, $I = \frac{1}{2}$); ^{119}Sn (8.6, $I = \frac{3}{2}$)	^{207}Pb (22.6, $I = \frac{1}{2}$)

I have just displayed some physical properties of group 14 elements and you can see here enthalpy of atomisation is decreasing that indicates volatile nature of heavier group 14 elements and melting point also steadily decreasing and boiling point also decreases and standard enthalpy also decreases here in this case and first ionization energy also decreases second ionization energy everything whether you consider first second third or fourth they all decrease down the group due to the increase in the size.

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Group 14 elements


Special features

- **The periodic changes among the chemistry of these elements**
- **The stability and abundance of C-C bonded compounds**
- **The importance of π -bonding in carbon compounds**

What are the special features of group 14 elements the periodic changes among the chemistry of these elements are strictly followed the stability and abundance of carbon; carbon bonded compounds the importance of pi bonding in carbon compounds very very important perhaps carbon forms largest number of catenated compounds essentially it is because of very strong pi bonding we come cross between carbon-carbon atoms between 2 carbon atoms.


They show major differences from the lightest element carbon to the heaviest element lead a typical main group element the similar trends are followed by almost most of the main group elements whether we consider group 1; group 2, 13, 14, 15, 16 or 17 and 18 and group of state is plus 4. It is very very important for carbon and silicon in hydrocarbons the oxidation is formerly minus 4 these compounds are thermodynamically unstable, but an extremely important class of compounds which have constituted the brands of organic chemistry; that means, essentially organic chemistry is essentially branch of one of the group 14 elements that is carbon.

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Group 14 elements 

Features

- **Ge** shows some stable **+2** compounds; **GeI₂**, although the **+4** state is predominant.
- **Tin (Sn)** shows both **+2** and **+4**; **+2** is reducing agent,
- whereas **Pb⁴⁺** is oxidizing and **Pb²⁺** is stable. **PbO₂** is a powerful oxidizing agent.



So, other features are germanium shows some stable plus 2 compounds like germanium iodide GeI_2 all though plus 4 state is still predominant and tin shows both plus 2 and plus 4 states plus 2 is reducing agent when it is in plus 2 state it is a reducing agent whereas, lead 4 plus is oxidising and Pb^{2+} is quite stable. In fact, PbO_2 with lead in plus 4 state is a very powerful oxidizing agent.

So, these elements in principle should show plus 2 of state using 2 P electrons. So, promotion of an electron from n s to n p requires energy, but the atom can now form 4 bonds; that means, essentially when the 2 bonds are formed by looking to the bonds strength and how much energy is released during the formation of the 2 bonds one can decide whether that compensates the energy required to promote n s 2 electron 2 the next n p orbital if that happens then in principle they can show higher of its state. So, essentially more energy is produced by bond formation in the case of carbon and silicon offsets the cost of promoting an s electron.

So, as a result tetravalent state is very stable for carbon and silicon. In fact, for the same reason they do not show inert pair effect; that means, I tell you again more energy produced by bond formation for carbon and silicon offsets the cost of promoting an s electron to P orbital. So, as a result what happens it shows stable plus 4 of oxi state and bond strength you should remember decreases down the group no matter which element we are considering for the bond formation whether we are taking hydrides oxides or halides bond strength decreases from carbon to lead.


That means, the energy that is liberated while formation of the bonds is not compensating the energy required to promote the n s 2 electrons to the n p in case of heavier elements as a result what happens? S electrons remain intact and paired as a result this inert pair effect comes into picture in case of heavier p block elements and in case of group 14. it is a tin and to a larger extent lead shows inert pair effect. So, important feature of group 14 elements is catenation which is less important down the group and of course, catenation is very important in case of carbon the next element that shows maximum catenation comes from group sixteen that is sulphur.

So, important source of carbon are essentially coal and crude oil and natural gas in natural gas the major component is methane C_2H_6 [vocalised-noise] carbon is known for showing allotropy graphite diamond and soot are important allotropes of carbon catenation is the formation of rings and chains by atoms of the same element after carbon sulphur forms the next largest number of catenated compounds.

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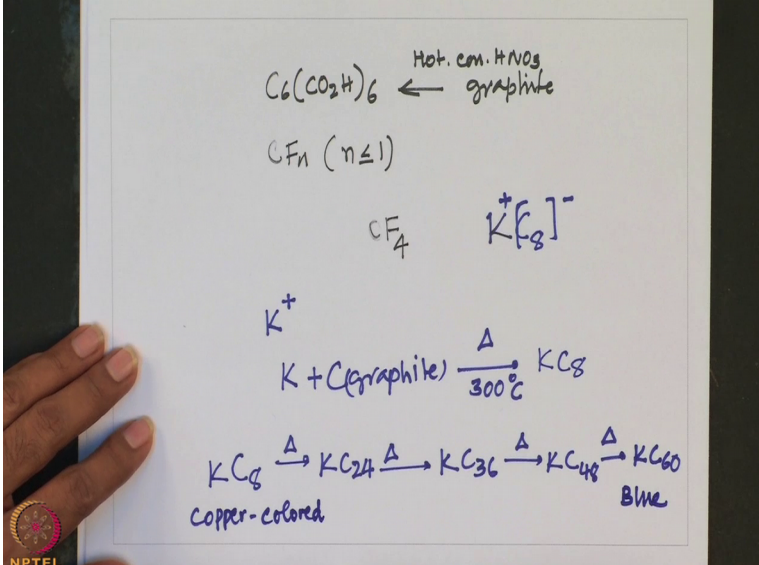
Allotropes of carbon: Graphite

- ❑ Graphite consists of stacked two-dimensional carbon sheets.
- ❑ Oxidizing agents or reducing agents may be intercalated between these sheets with concomitant electron transfer
- ❑ Graphite is more reactive than diamond
- ❑ It is oxidized by atmospheric O_2 above 970 K, whereas diamond burns at >1170 K
- ❑ Graphite reacts with hot, concentrated HNO_3 to give the aromatic compound $C_6(CO_2H)_6$



Let us look into the allotropes of carbon. The graphite is one of the important allotropes of carbon. Graphite consists of stacked 2 dimensional carbon sheets oxidizing agents or reducing agents may be intercalated between these sheets with concomitant electron transfer. Graphite is more reactive than diamond, it is oxidised by atmospheric oxygen above 970 Kelvin where as diamond burns at greater than 1170 Kelvin graphite reacts with hot concentrated nitric acid to give an aromatic compound having this composition.

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Handwritten chemical reactions on a whiteboard:

$C_6(CO_2H)_6 \xleftarrow{\text{Hot. con. } HNO_3} \text{graphite}$


$CF_n \ (n \leq 1)$

$CF_4 \quad K^+ [F_3]^-$

$K^+ \quad K + C(\text{graphite}) \xrightarrow[300^\circ C]{\Delta} KC_8$

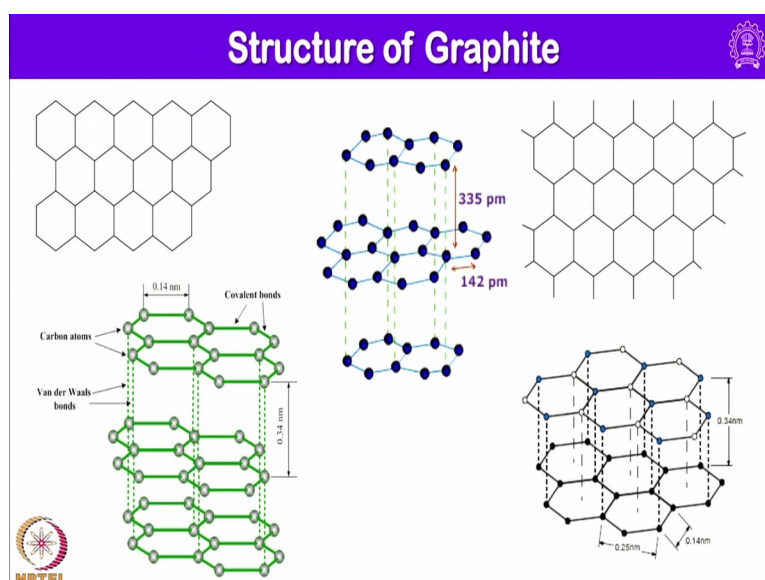
$KC_8 \xrightarrow{\Delta} KC_{24} \xrightarrow{\Delta} KC_{36} \xrightarrow{\Delta} KC_{48} \xrightarrow{\Delta} KC_{60}$

Copper-colored Blue



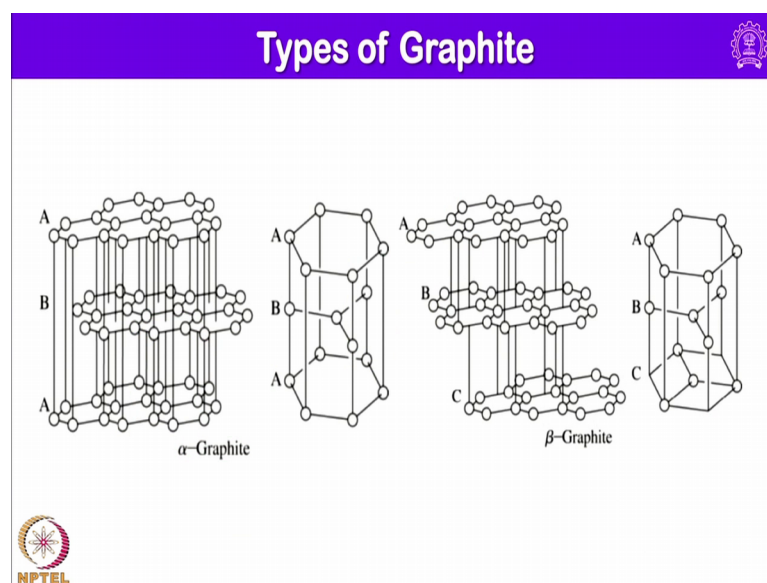
I am telling you graphite reacts with hot concentrated nitric acid to give the aromatic compound having this composition in graphite the carbon atoms form sheets of 6 membered rings very similar to benzene having each carbon undergone sp^2 hybridization in terms of n s bond theory the remaining p_z orbitals form extensive delocalised π system over the entire sheet. So, attraction between the adjacent sheets is weak. And so, the graphite layers can be slid over each other very easily graphite structure is unique for carbon among group 14 elements because the small p_z orbitals on carbon can overlap effectively to form the delocalised π system over the entire sheet of graphite you can see here.

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This is how the graphite looks like each layer is consists of 6 membered ring. It connected with adjacent carbon atoms and if you look into the separation between graphite layers this is about 335 picometre and CC bond distance in graphite is one forty 2 picometre and here weak π interactions hold them together. So, as a result, this graphite layers can slide very easily over the other.

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This is where the lubricating properties of graphite comes into the picture. This is alpha graphite and this is beta graphite you can just see the difference between the structural difference between alpha graphite and beta graphite.

And graphite can form interconnection compounds; that means, graphite can act as either an electron donor or an electron acceptor towards atoms and ions that penetrate between its sheets and give rise to an interconnection compound the formation of which involves movement apart of the carbon layers and the penetration of atoms are ions between them. So, there are 2 general types of compounds we come across the colourless non conductors of electricity in which the carbon layers becomes buckled owing to the saturation of the carbon atoms and loss of the pi systems when it is buckled the pi system is destroyed.

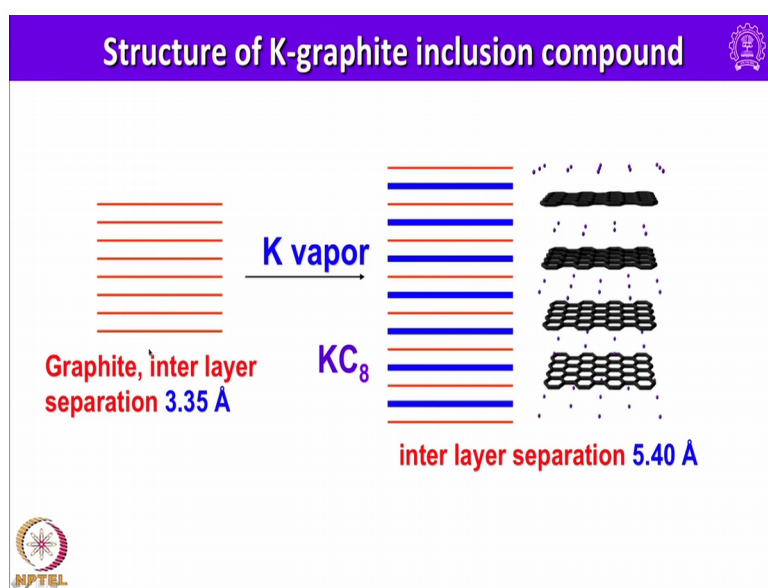
So, coloured electrical conductors in which the planarity and pi delocalisation of the layers are retained. So, these polymeric carbon mono fluorides; that means, $C F_n$. So, where n is greater than or equal to one is a widely studied example of the first type of compound it is formed when F_2 reacts with graphite at 720 Kelvin or at lower temperature in presence of hydrofluoric acid or hydrogen fluoride although at 970 Kelvin the product is monomeric; that means, if you take graphite and pause fluorine at 720. So, it gives $C F_4$.

The second class of interconnection compounds includes the blue graphite salts formed with strong acids in the presence of oxidizing agents and the metallic looking red or blue compounds are formed when graphite reacts with group one metals for example, when graphite is treated with an excess of potassium vapours a paramagnetic compound coloured material copper coloured material formulated as $K_c 8$ is formed $K_c 8$, of course, here something like this. So, the penetration of this K plus ions between the layers causes structural changes.

So, this potassium vapours when they are passed into the graphite. So, this potassium ions goes and sits in between the graphite layer as a result what happens that distance between the graphite layers increases from 3 thirty 5 picometre to 540 picometre the K plus ions lie above or below the centre of alternate $c 6$ rings by forming a layers of centred hexagonal motives for example, if we take potassium vapours and pass it into the graphite around 300 degree centigrade, we get $K_c 8$.

Heating $K_c 8$ leads to the formation of a series of decomposition products; there are 1, 2, 3, 4 or 5 carbon layers respectively between layers of K plus ions. For example, if we take $K_c 8$ and if you heat it, it can give $K_c 24$. If you heat further, it can give $K_c 36$ and further heating it can also form $K_c 48$ and it can give $K_c 60$. So, this is a copper coloured. So, this is essentially looks like copper coloured and this is blue. So, we have prepared $K_c 8$ in our laboratory; in my next lecture, I remember to show that $K_c 8$.

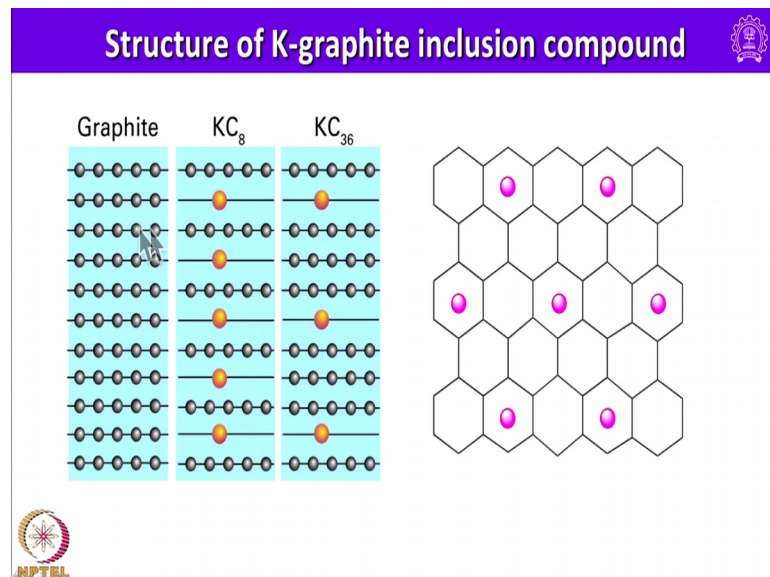
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You can see here how potassium vapours sits between the layers. For example, graphite layers if you consider this red lines represent graphite layers and the distance between graphite layers is 3.35 angstrom units or 335 picometre when potassium vapours are passed around 300 Kelvin; around 300 degree centigrade. So, these blue lines represent potassium ion sitting in between and ok.

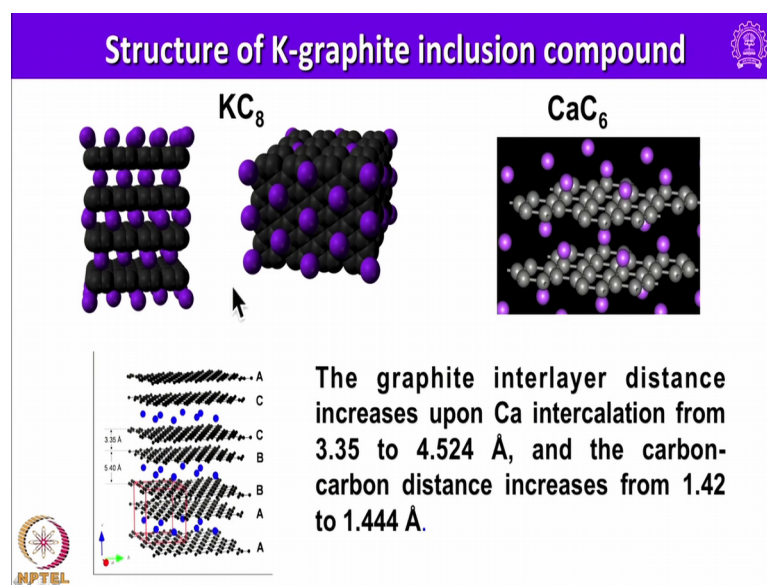
So, here the distance now increases from 335 to 540 picometre, you can see here graphite layers can be clearly seen here and also this small dots represent potassium atoms here ok.

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And this how one can also visualise how between graphite layers potassium is sitting here and also one can also see here.

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And this gives a clear picture of the potassium atom sitting between the graphite layers and this purple one represent potassium and in fact, if you just look into each potassium it is encapsulated by 8 carbon atoms 4 below and 4 above giving a square antiprismatic geometry for potassium atom; that means, potassium atom is at the centre of a square antiprismatic geometry with 8 corners are occupied by carbon atoms in this fashion you can see here yeah.

So, the graphite interlayer distance increases upon calcium interconnection similarly one can also include calcium by passing calcium vapours here the composition will be CSE 6; that means, here calcium sits in an octahedral cavity surrounded by 6 carbon atoms. So, in this case the distance increases from 335 picometre to 452 picometre and the carbon distance also increases from 1.42 initially graphite to 1.444 angstrom units ok.

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Allotropes of carbon: Graphene

- ❑ Graphite consists of multiple layers of carbon atoms. A single, isolated layer is called graphene.
- ❑ First prepared in 2004
- ❑ Graphene has been the center of considerable research, both to study its properties and to develop efficient ways to prepare graphene sheets
- ❑ Graphene is remarkably resistant to fracture and deformation, has a high thermal conductivity, and has a conduction band that touches its valence band



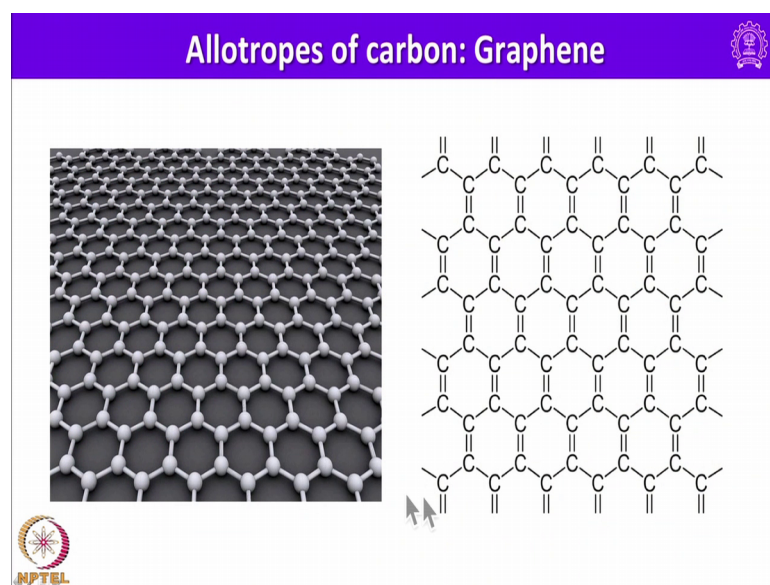
And graphite consists of multi layers of carbon atoms a single isolated layer is essentially called grapheme; for example, if you assume this entire is graphite if I just take out one sheet here this single sheet is essentially called as graphene.

First it was prepared in 2004, graphene has been the centre of considerable research both to study its properties and to develop efficient ways to prepare graphene sheets a graphene is remarkably resistant to fracture and deformation as a high thermal conductivity and has a conduction band that touches its valence band ok.

So, graphene has been prepared both by mechanically peeling away the layers of graphite they said mechanically peeling is essentially something like this take out this if it is there just if you take out this is called mechanical peeling away layers of graphite.

And by more specialised techniques including chemical vapour deposition on metal substances or metal substrates graphene represents an essentially 2 dimensional structure of a thickness approximately 340 picometre its honeycomb like surface has been imaged using scanning transmission microscopy that is s t m numerous applications of graphene have been proposed including their use in energy storage materials microsensor devices liquid crystal displays polymer composites and several other electronic devices.

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So, this is how a single sheet of graphene looks like; this essentially taking out a single layer effectively from graphite will constitute a graphene its a 2 dimensional single sheet. So, carbon nanotubes the structure of carbon nanotube can be imagined as a cylinder formed by rolling a graphene sheet and then closing it at both side it is something like this if is the graphene sheet if you just roll it and just clip it here this essentially represent carbon nanotube.

Graphene can be put into thin strips or nanoribbons by lithographic techniques this ribbons are described by their edges either zigzag or armchair one can join the edges of nanoribbons together to form such nanotubes in several ways it can also form multi layer carbon nanotubes in which one layer have pi interaction with another layer. So, one can play around once you know how to isolate a single sheet of graphite that is graphene you can play around and you come up with an interesting array of carbon nanotubes having very different shapes. So, let me continue discussing in my next lecture until then have a very pleasant reading of inorganic chemistry especially group 14 elements.

Thank you very much.