Main Group Chemistry
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Lecture – 25
Chemistry of Group 13 elements

I once again welcome you to MSB lecture series on main group chemistry. This is my 25th lecture in this series on main group elements. Until the last lecture I had covered the classification of elements in the periodic table periodic, tense periodic properties and extensive and discussion on structure and bonding concepts and then chemistry of hydrogen and chemistry of group 1 and group 2 elements.

So, today let me begin my lecture with chemistry on p-block elements to begin with I will be considering a group 13 elements.

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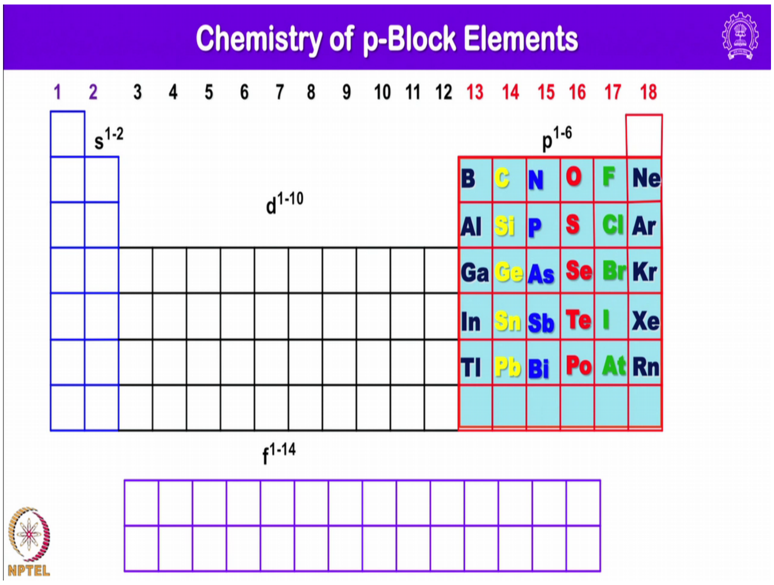

Chemistry of p-Block Elements

And of course, just if you look into the periodic table on right side we have 2 3 4 5 6 groups of totally 30 elements and of course, we have 31 elements including helium and here we have group 13 into group 18 having electronic configuration in there valence shell starting from s to p 1 in case of group thirty into s to p 6 in case of inert gases or inert elements.

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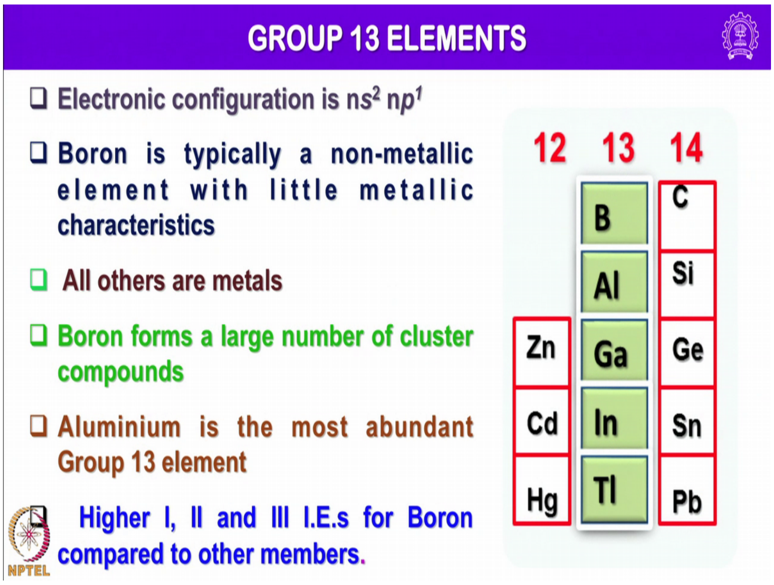

GROUP 13 ELEMENTS

- Electronic configuration is $ns^2 np^1$
- Boron is typically a non-metallic element with little metallic characteristics
- All others are metals
- Boron forms a large number of cluster compounds
- Aluminium is the most abundant Group 13 element
- Higher I, II and III I.E.s for Boron compared to other members.

12	13	14
	B	C
	Al	Si
Zn	Ga	Ge
Cd	In	Sn
Hg	Tl	Pb

So, let us discuss today on group 13 elements. Group 13 elements have valence shell electronic configuration of ns 2 np 1 that is s 2 p 1; that means, they have 3 electrons in their valence shell. So, boron is typically a non metallic element with little metallic characteristics and rest of the elements aluminium, gallium, indium and thallium all are metals boron forms a large number of cluster compounds known as boron hydrides. And also one can incorporate other p-block elements also.

I will be discussing all those things in more detail and also I will be talking about the structural aspects pertinent to boron hydrides using weights rules and aluminium is the most abundant group 13 element in the earth’s crust. So, all these group 13 elements show higher first second and third ionization energies for boron compared to other members of course, always there is some difference in their chemical reactivity when you compare the group one element with rest of the elements.

Here no exception. So, boron behaves little different than aluminium, gallium, indium and thallium because of its smaller size and high charge when it goes to trivalent form.

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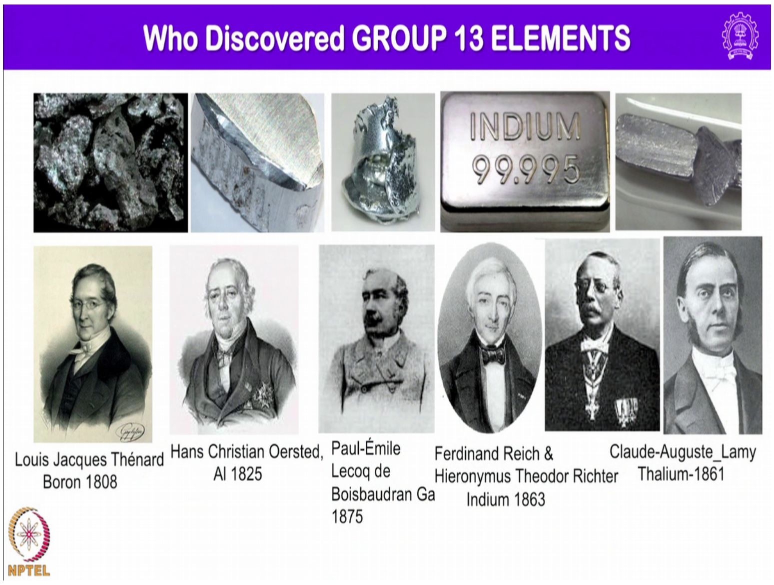

Who Discovered GROUP 13 ELEMENTS

Louis Jacques Thénard
Boron 1808

Hans Christian Oersted,
Al 1825

Paul-Émile
Lecoq de
Boisbaudran Ga
1875

Ferdinand Reich &
Hieronymus Theodor Richter
Indium 1863

Claude-Auguste_Lamy
Thalium-1861

And let us look into who discovered group 13 elements and boron was discovered by Louis Jacques Thenard of course, then it was isolated and in pure form by Humphrey Davy and aluminium was discovered in 1825 by Hans Christian Oersted and gallium was discovered initially by Paul-Emile Lecoq de in 1875. Indium was discovered by 2 chemist Ferdinand Reich and H T Richter in 1863 and the last element in the series thallium was discovered by Claude Auguste Lamy in 1861.

Of course, you can always go into Wikipedia to know more about these elements and the history of discovery and to know more about these chemist.

Let us start with boron. Boron is a fairly rare element with abundance is about 0.0001 percent by mass in the earth's crust. It exists in 2 isotopic forms are it shows to isotopes having 10 boron its abundance is about 19 percent and 11 boron it is about 81 percent.

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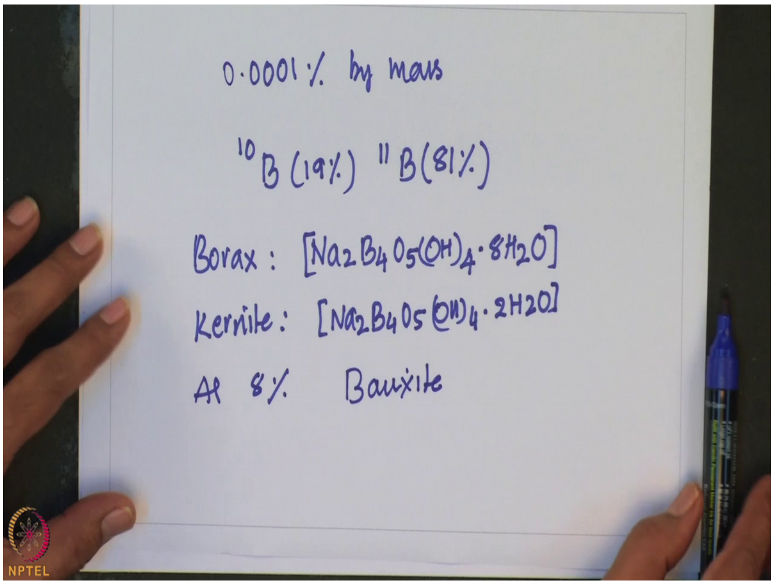

0.0001% by mass

^{10}B (19%) ^{11}B (81%)

Borax : [$Na_2B_4O_5(OH)_4 \cdot 8H_2O$]

Kernite : [$Na_2B_4O_5(OH)_4 \cdot 2H_2O$]

Al 8% Bauxite

The most common sources of boron or borax this is nothing but Na 2 B 4 O 5 OH 4 times having 8 H 2 O molecules and another one is kernite, it is also very similar to borax, but it only differs in the amount of solvent it is there hydrated water molecules solvated water molecules Na 2 B 4 O 5 OH 4 times, but it has only 2 molecules of water. There are essentially hydrated sodium borate hydroxide minerals.

Aluminium is the most abundant element in the earth's crust approximately it accounts for 8 percent, 8 percent by mass. It occurs in numerous clays and aluminium silicate minerals. But the commercially most important mineral is bauxite is a complex mixture of hydrated aluminium hydroxide and aluminium bauxite and in case of gallium, gallium oxide occurs as an impurity in oxide and is normally recovered as a byproduct of the manufacturer of aluminium.

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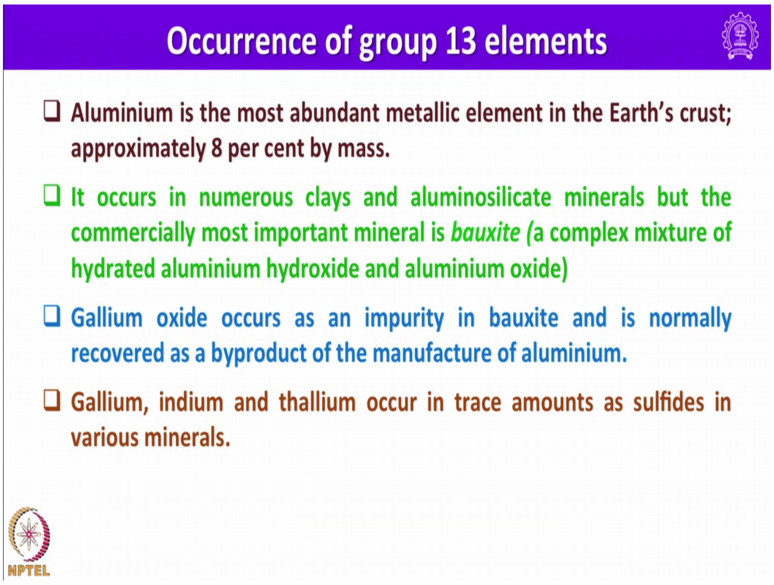

Occurrence of group 13 elements

☐ Aluminium is the most abundant metallic element in the Earth's crust; approximately 8 per cent by mass.

☐ It occurs in numerous clays and aluminosilicate minerals but the commercially most important mineral is *bauxite* (a complex mixture of hydrated aluminium hydroxide and aluminium oxide)

☐ Gallium oxide occurs as an impurity in bauxite and is normally recovered as a byproduct of the manufacture of aluminium.

☐ Gallium, indium and thallium occur in trace amounts as sulfides in various minerals.

So, when you are processing and extracting aluminium from bauxite essentially more and more gallium oxide will be concentrated and using inappropriate metallurgical process gallium oxide can be reduced to gallium. Gallium indium and thallium occur in trace amounts as sulfides in various other minerals.

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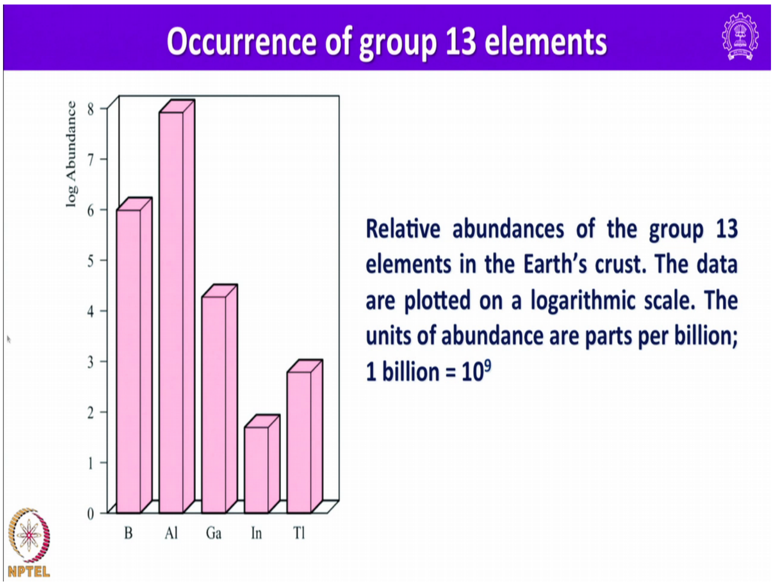

Occurrence of group 13 elements

Relative abundances of the group 13 elements in the Earth's crust. The data are plotted on a logarithmic scale. The units of abundance are parts per billion; 1 billion = 10^9

So, we can see here the relative abundance of group 13 elements is given here it shows the most abundant among them it is aluminium, next boron comes and next gallium comes and indium is in small quantity compared to thallium.

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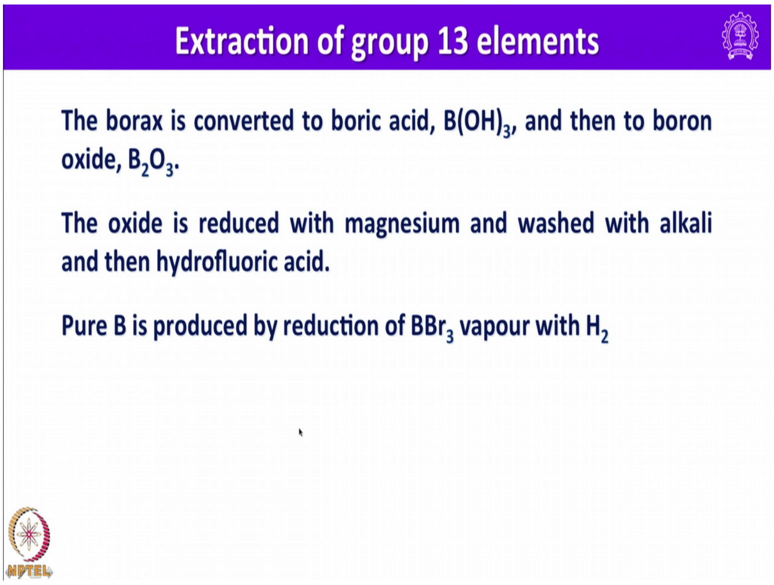

Extraction of group 13 elements

The borax is converted to boric acid, $B(OH)_3$, and then to boron oxide, B_2O_3.

The oxide is reduced with magnesium and washed with alkali and then hydrofluoric acid.

Pure B is produced by reduction of BBr_3 vapour with H_2

So, let us look into the extraction of this element to begin with let us consider boron. So, here the borax is convert into boric acid. So, the whatever the borax I showed that is first converted to boric acid by treating with sulphuric acid and then to boron oxide that is B 2 O 3 the oxide is reduced with magnesium and washed with alkali and then hydrofluoric acid and of course, if you want extra pure or ultra pure boron one can prepared by reducing boron tribromide use the hydrogen in vapor phase.

Take the vapors of boron tribromide and react this one with gas H 2 to get the pure boron. So, let me show this metallurgical process.

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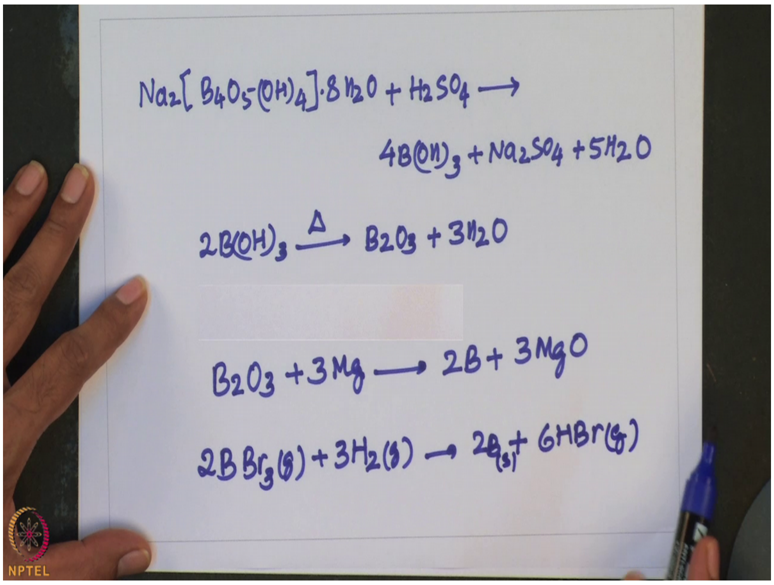

$Na_2[B_4O_5(OH)_4]\cdot 8H_2O + H_2SO_4 \longrightarrow$

$4B(OH)_3 + Na_2SO_4 + 5H_2O$

$2B(OH)_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$

$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$

$2BBr_3(g) + 3H_2(g) \longrightarrow 2B_{(s)} + 6HBr(g)$

So, of course, one can start with borax Na 2 B 4 O 5 OH 4 times can also write like this this is a better way of writing and treat this with sulphuric acid. So, what you get is 4 B OH thrice B OH thrice plus Na 2 SO 4 plus 5 H 2 O. So, this boh thrice on heating it gives B 2 O 3 plus 3 H 2 O. So, one can use magnesium as reducing agent. So, simply take B 2 O 3 plus 3 Mg it gives 2 B plus 3 MgO.

So, in case of boron tribromide one can use hydrogen. So, here in this case s plus 3 H 2 gives 2 B plus 6 HBr this is solid this is gas. So, this how one can get pure boron. So, boron crystallizes in a variety of forms all containing icosahedron B 12 unit ok. You can see here.

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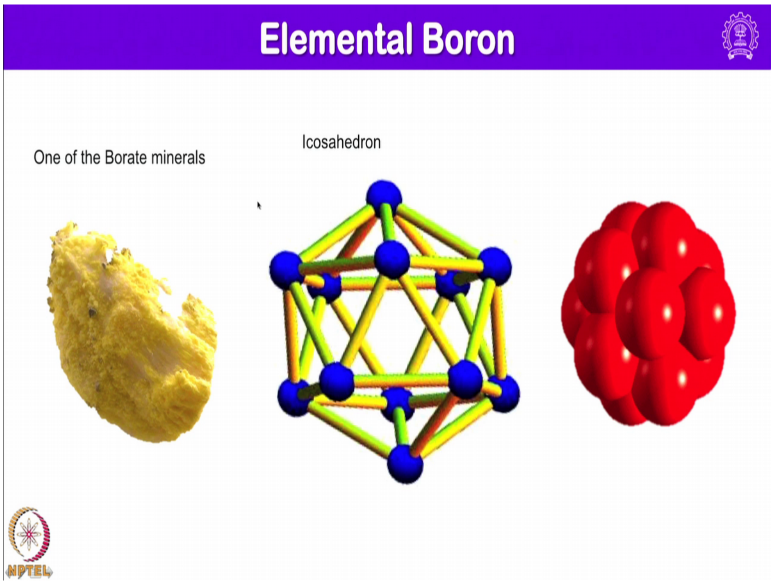

Elemental Boron

One of the Borate minerals

Icosahedron

This is how in the boron this is one of the boron minerals I have shown here. So, pure boron has a composition of B 12 and having in the geometry of icosahedron. So, we have essentially 12 vertices we have here, this is the other way of showing using a space filling model B 12.

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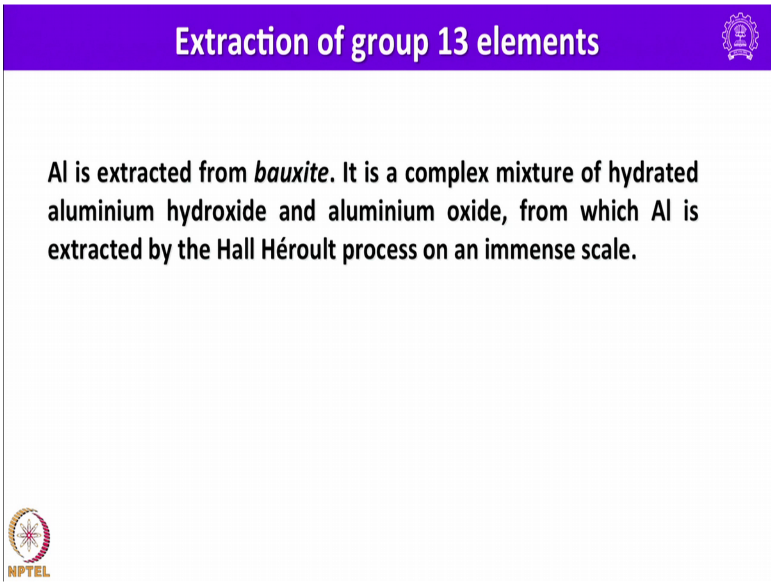

Extraction of group 13 elements

Al is extracted from *bauxite*. It is a complex mixture of hydrated aluminium hydroxide and aluminium oxide, from which Al is extracted by the Hall Héroult process on an immense scale.

So, let us look into aluminium. So, aluminium is extracted from bauxite as I said it is a complex mixture of hydrated aluminium hydroxide and aluminium oxide having all kind of impurities with the major impurity being iron oxide.

So, from which aluminium is extracted by a standard procedure introduced by one chemist called Hall Heroult his name is shown here and this is known as Hall Heroul’s process it has an. So, essentially in larger productions this, his method is used I will be elaborating on this method. So, bauxite essentially Al 2 O 3 - 2 H 2 O and another ore of bauxite is sodium hexafluoroaluminate. So, that is bauxite is essentially Al 2 O 3 - 2 H 2 O and another means cryolite cryolite is Na 3 Al F 6 sodium hexafluoroaluminate and of course, as I said bauxite contains a Fe 2 O 3 and silica, and other several other impurities are there.

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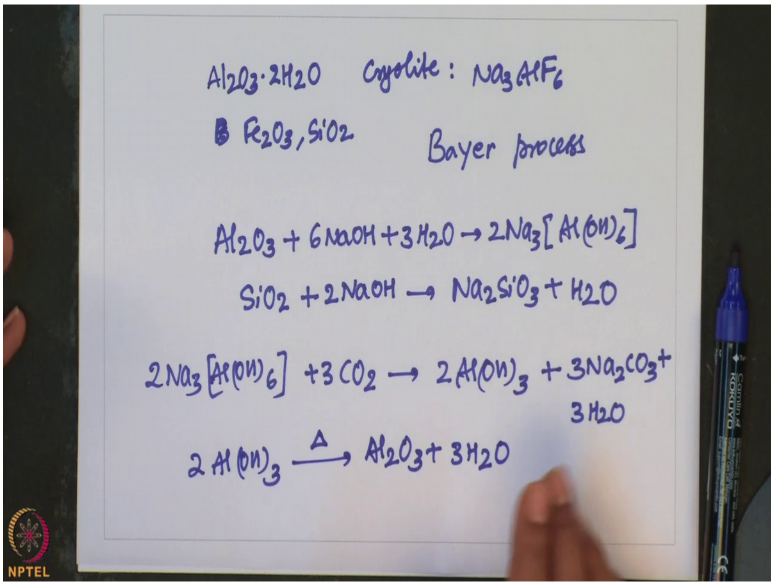

$Al_2O_3 \cdot 2H_2O$ Cryolite : Na_3AlF_6

Fe_2O_3, SiO_2 Bayer process

$$Al_2O_3 + 6NaOH + 3H_2O \rightarrow 2Na_3[Al(OH)_6]$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

$$2Na_3[Al(OH)_6] + 3CO_2 \rightarrow 2Al(OH)_3 + 3Na_2CO_3 + 3H_2O$$

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

So, in order to isolate pure aluminium these impurities must be removed this is done by a well known procedure known as Bayer’s process, Bayer process. So, in it involves treatment of bauxite with sodium hydroxide Al 2 O 3 plus 6 Na OH plus 3 H 2 O gives 2 Na 3 Al OH 6 times and of course, silica readily reacts with sodium hydroxide to form sodium silicate. So, bauxite treatment with sodium hydroxide solution results in sodium aluminate. So, this is sodium aluminate and also sodium silicate. So, iron part remains behind as a solid. So, now, we need not to worry about iron.

When CO 2 is blown through the resulting solution when carbon dioxide then sodium silicate stays in solution while aluminium is precipitated out as aluminium hydroxide, this hydroxide is insoluble it can be filtered off washed and heated to form pure alumina. So, this one on heating it forms aluminium oxide plus 3 H 2 O comes out. So, this insoluble aluminium hydroxide is filtered up and this is heated to form pure aluminium. So, the next stage involve the purification or reduction of aluminium oxide to get pure aluminium.

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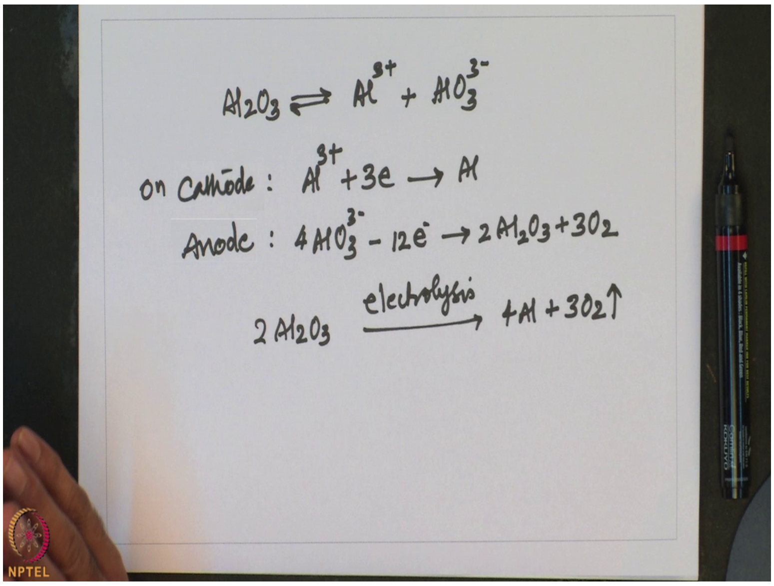

$$Al_2O_3 \rightleftharpoons Al^{3+} + AlO_3^{3-}$$

on Cathode : $Al^{3+} + 3e \rightarrow Al$

Anode : $4AlO_3^{3-} - 12e^- \rightarrow 2Al_2O_3 + 3O_2$

$$2Al_2O_3 \xrightarrow{electrolysis} 4Al + 3O_2\uparrow$$

It can be obtained by electrolytic method in aqueous solution aluminium oxide dissociates into ions minus cathode aluminium at, an anode. So, overall is 2 Al 2 O 3 electrolysis 4 Al plus 3 O 2. So, this is electrolysis is necessary as aluminium is very electropositive. So, these days electrolysis of the hot oxide in a carbon lined steel cell acting as the cathode with carbon anode is used in electrolysis.

So, the metal is obtained by electrolyzing the dried alumina in molten Na 3 l fc; that means, sodium hexafluoroaluminate. So, why it is done this way is essentially by adding sodium hexafluoroaluminate reduces the melting point of aluminium oxide. It is very similar to the down process we employ in case of the extraction of sodium from sodium chloride. So, elemental aluminium cannot be produced by the electrolysis of an aqueous aluminium salt because the hydronium ions that are generated readily oxidize elemental aluminium. So, although a molten aluminium salt could be used instead, but aluminium oxide has a melting point of 2072 degree centigrade.

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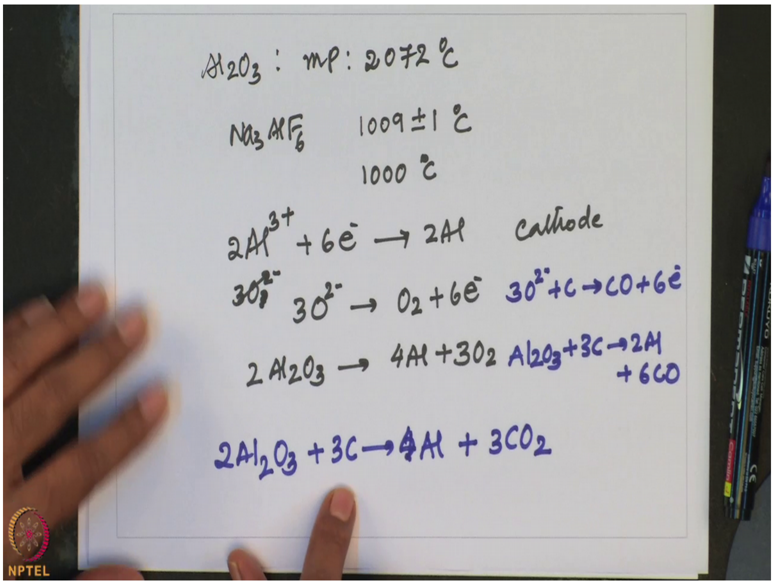

Al_2O_3 : mp: 2072 °C

Na_3AlF_6 1009 ± 1 °C

1000 °C

$2Al^{3+} + 6e^- \rightarrow 2Al$ cathode

$3O^{2-}$ $3O^{2-} \rightarrow O_2 + 6e^-$ $3O^{2-} + C \rightarrow CO + 6e^-$

$2Al_2O_3 \rightarrow 4Al + 3O_2$ $Al_2O_3 + 3C \rightarrow 2Al + 6CO$

$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$

If you just look into aluminium oxide melting point is, so this is because of high temperature, electrolyzing is impractical. So, in the Hall Heroult’s process aluminium that is Al 2 O 3 is dissolved in molten synthetic cryolite that is Na 3 Al F 6 and it essentially Na 3 Al F 6 is used to lower the melting point for easier electrolysis. Pure cryolite has a melting point of 1009 plus or minus 1 degree centigrade with a small percentage of alumina dissolved in it the melting temperature can drop to as low as 1000 degree centigrade. So, then at this temperature it is not a problem to do molten electrolysis. So, let me write the reactions involved in molten electrolysis.

So, aluminium is produced at cathode gives 2 Al this is cathode and oxygen gives O 2 plus 6 electrons. So, overall reaction can be written in this fashion of course, here we are using carbon. So, one should also write alternatively in a different way. So, here one can also write this one as 3 O 2 minus plus C gives CO plus 6 electrons and here Al 2 O 3 plus 3 C gives 2 Al plus 6 Co. So, in reality although it appears like CO is formed in fact, more carbon dioxide is formed at the anode than carbon monoxide. So, overall equation can be written in this way that is employed in the purification or isolation of aluminium starting from aluminium oxide using molten electrolysis.

So, this is the overall reaction that represents reduction of aluminium oxide using carbon to form aluminium to the formation of carbon dioxide. So, gallium as I mentioned is normally a byproduct of the manufacturer of aluminium from bauxite the purification of bauxite by the Bayer process results in concentration of gallium in its ratio from almost 5000 to 300 in the alkaline solution, from an aluminium electrolysis using a mercury electrode provides a further concentration and following electrolysis of the resulting sodium gallate using a stainless steel cathode one can get gallium metal. Gallium metal has a melting point of 29.76 degree centigrade one of the low melting metal.

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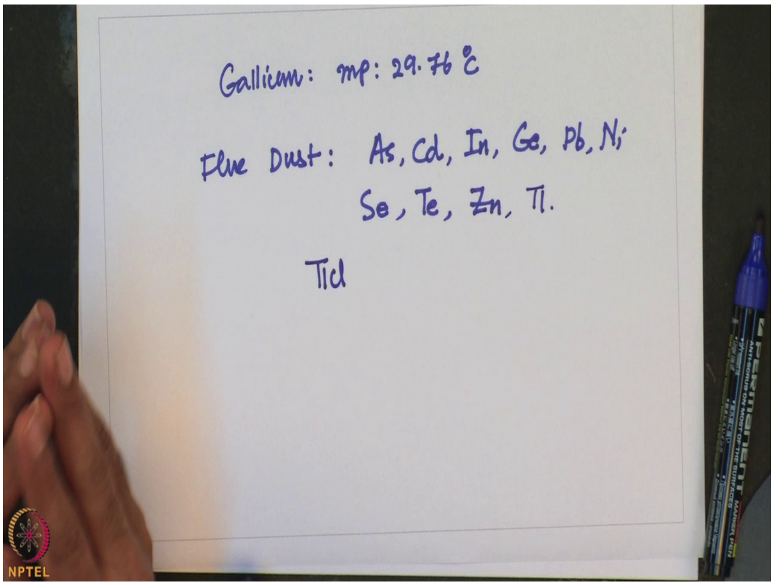

Gallium: mp: 29.76 °C

Flue Dust: As, Cd, In, Ge, Pb, Ni
Se, Te, Zn, Tl.

TlCl

So, preparation of pure gallium requires a number of further process ending with zone refining to make very pure gallium metal. So, I would tell you little bit more about zone refining when I discuss group 14 elements especially in the purification of silicon to get ultra pure silicon for semiconductor or electronic industries.

Crude thallium is present as a component in flue dust along with arsenic cadmium, indium, germanium and let the flue dust contains contain essentially arsenic, cadmium, indium, germanium, lead, nickel, selenium, tellurium, zinc. So, here thallium is also there in it.

So, so thallium is essentially prepared by dissolving of flue dust in dilute acid precipitating out lead sulphate and then adding HCl to precipitate thallium chloride TlCl. Further purification can be achieved by electrolysis of soluble thallium salts.

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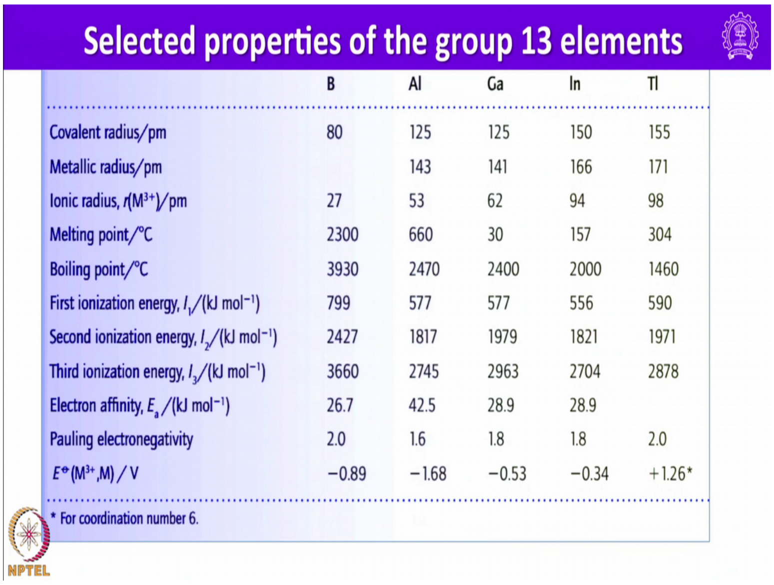

Selected properties of the group 13 elements

	B	Al	Ga	In	Tl
Covalent radius/pm	80	125	125	150	155
Metallic radius/pm		143	141	166	171
Ionic radius, $r(M^{3+})$/pm	27	53	62	94	98
Melting point/°C	2300	660	30	157	304
Boiling point/°C	3930	2470	2400	2000	1460
First ionization energy, I_1/(kJ mol^{-1})	799	577	577	556	590
Second ionization energy, I_2/(kJ mol^{-1})	2427	1817	1979	1821	1971
Third ionization energy, I_3/(kJ mol^{-1})	3660	2745	2963	2704	2878
Electron affinity, E_a/(kJ mol^{-1})	26.7	42.5	28.9	28.9	
Pauling electronegativity	2.0	1.6	1.8	1.8	2.0
$E^\ominus(M^{3+},M)$ / V	−0.89	−1.68	−0.53	−0.34	+1.26*

* For coordination number 6.

So, with this information about the extraction of group 13 elements let us look into the properties of group 13 elements. First let us focus on covalent radius. So, covalent radius is increasing down the group as expected and similarly metallic radius is also increasing down the group and ionic radius is also increasing as expected with boron having 27 picometer, whereas thallium has 98 picometer. Melting point is decreasing as expected again following strictly the periodic trends and boiling point is also decreasing and first ionization energy should decrease down the group and that is what the trend is observed.

So, here for boron first ionization enthalpy is 799 joules per mole whereas, for thallium it is 590 kilo joules per mole and of course, this is little higher compared to indium essentially the second ionization enthalpy if we take it is very high in case of boron and of course, second ionization position potential is our ionization enthalpy is relatively higher than the first one as expected for all group 13 elements and in this case in case of thallium its little higher compared to gallium and indium. Again it is because of inert pair effect. I will tell you what is inert pair effect later.

The third ionization energy is also expected to be decreasing down the group with borrowing showing highest value of 3660 kilo joules per mole and of course, this reduction potential also comes very handy in understanding their behaviour. In fact, thallium shows positive value 1.26.

Let us look into some similarities between boron and rest of the elements in the series.

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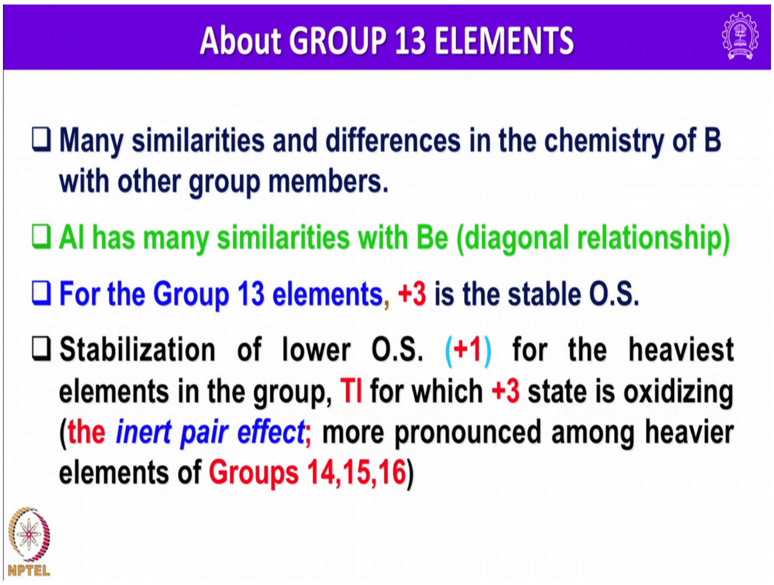

About GROUP 13 ELEMENTS

- Many similarities and differences in the chemistry of B with other group members.
- Al has many similarities with Be (diagonal relationship)
- For the Group 13 elements, +3 is the stable O.S.
- Stabilization of lower O.S. (+1) for the heaviest elements in the group, Tl for which +3 state is oxidizing (the *inert pair effect*; more pronounced among heavier elements of Groups 14,15,16)

Aluminium has many similarities with beryllium that we already discussed about diagonal relationship for a group 13 elements plus 3 is the most stable oxidant state and stabilization of lower oxidant state that is plus 1 for the heaviest elements in the group appears in the case of thallium for which in fact, plus 3 at state is oxidizing. So, here for the first time the term inert pair effect is introduced among the p-block elements.

Of course, more and more elements, heavier elements of group 14 15 and 16 show this inert pair effect its very interesting to understand and correlate inert pair effect with respect to their reactions are stabilization of lower coordination number that I am going to discuss in my next lecture.

Until then, thank you very much and have a pleasant reading of inorganic chemistry.