and fine in my previous lectures i had discussed
about the chemistry of s block elements   that is alkali metals and alkaline earth metals
today i would like to draw your attention to the   chemistry of p block elements as you all know
ah main group elements are classified into   two categories one is s block consists of two
groups and p block consists of 6 groups with   regular addition of electrons from p 1 to
p 6 that means group 13 14 15 16 17 and 18   in the group thirteen we have this is the p block
about thirty elements are there excluding helium   and in the group thirteen we have five elements
are there start with boron and aluminium gallium   indium and thallium and in the group 14 we
have carbon silicon germanium tin and lead   and in group 15 also called neutrogen series
we have nitrogen to begin with and then we   have phosphorus arsenic antimony and bismuth in
the group 15 oxygen series also called chalcogen   series we have oxygen sulphur selenium and
tellurium and in the group seventeen we have   halogens fluorine chlorine bromine and iodine and
lastly we have inert gas elements such as neon   argon krypton xenon and redone in group 18 along
with helium and these thirty elements dominant   p block chemistry and let us discuss
one group at a time to begin with   let us start discussing the chemistry
of p block elements such as group 13 in the group 13 we have boron which is
typically a non metallic element with   little metallic characteristics and rest
of the metals such as aluminium gallium   indium and thallium all our metals and
all group 13 elements show little higher   ionization energies or ionization enthalpies
compared to alkaline earth metals however   higher ionization energy for removal of three
electrons is anticipated in case of boron compared   to the rest of the elements because of the
smaller size and similarly there is some chemist   the difference in the chemical properties also one
can see between boron and rest of the elements and   aluminium has many similarities with beryllium
that i discussed while discussing the chemistry of   alkaline earth metal elements for the group
thirteen elements group of state is plus three   that is a stable oxy state ah because they have
s two p one electron configuration all the three   electrons can be removed to generate a trivalent
cation and hence the group shows plus three as   the most stable oxygen state and stabilization
of lower state for the heaviest elements is not   possible that is only thallium in this case and
plus three state compounds of thallium are highly   oxidizing that means it has

a tendency to getting
reduced to thallium plus one state to retain those   s electron in its place and this is called inert
pair effect and i would elaborate more about inert   pair effect later however this inert pair effect
is more pronounced among other elements of group   fourteen fifteen sixteen in case of group
fourteen it is tin and lead in case of group   fifteen it is bismuth and in the case of group
sixteen it is tellurium these five elements have   little tendency to unpair the s electrons
to promote to p orbital to show the group of   state and whenever such oxidations are possible
those compounds are highly oxidizing in nature   ok
 so boron is a fairly rare element and abundance
is 0.
001 percent by mass in the earth's crust that   is it is the 34th most abundant element in the
earth's crust and it has two isotopes one is 10 boron this is about 19 percent abundant   and other one is 11 boron this is about 81 percent
abundant of course when we look into nucleus   nuclear spin for ten boron is i equals three
and in case of lemon boron i equals three by two the most common sources of boron
are tormeline that is boron oxide   are borax that has the composition n a two b four o five o h four times and eight equivalence of water
this is called tourmaline there is also another more mineral called carnite its composition is more or less same
but differs in the water of hydration
 so just if you look into this one they are nothing
but hydrated sodium borate hydroxide minerals   it is not very easy to purify boron and one method
that is used ah for purification or reduction of   boron is using magnesium one can
say boron trioxide pure borin   boron trioxide and subjected
to reduction using magnesium it gives pure boron along with magnesium oxide
the oxide is made by melting boric acid   one can heat boric acid and ah to get rid
of hydrogen in the and get b two o three   and then high purity boron can also be obtained
by thermal decomposition of boron trichloride   or boron tribromide combining
with hydrogen and passing through   a heated tantalum wire for example one can
consider boron trichloride or boron tri bromide along with hydrogen it has to be
passed over a heated tantalum wire of course ah results are better when the hot wire temperature reaches 1000 degree centigrade
 so boron crystallizes in a variety of forms all
containing aecosahedral b-12 unit you can see here   ah this is one of the borate minerals this how
it looks this is how the icosahedron looks like   and i have a model to show you here and this is
icosahedron it has 12 vertices you can see here   5 are here 1 2 3 4 5 6 7 8 9 ten and one axial
here one axial here

so we have twelve vertices are there and then we have five ten fifteen plus five
twenty triangular faces are there and 30 edges are there that means a icosahedron has 12 vertices 20
triangular faces and then 30 edges
 so this is how crystalline boron looks like and it has several
forms all of them have this icosahedral structure and you can see other space filling
model is shown here in this one it shows the arrangement of twelve boron atoms in the psychosihetral fashion ok
 so aluminum is third most abundant element in
the earth's crust that is about eight point three percent we know the most abundant one
in the earth's crust is oxygen next one is silicon and third one is the aluminum and the the
common or most common war of aluminium is bauxite and there is one more war of
aluminum that is called cryolite this is nothing but hydrated aluminum oxide
 so another more is called cryolite this is nothing but hexafluorosodium
aluminate sodium hexafluoroaluminate ok and bauxite contains ah mainly
iron oxides such as fe two o three silicon dioxide or silica
and several other impurities in order to isolate pure aluminum these impurities must be removed this is
done by a method called bias process
 so in this process what they do is initially
this bauxite is treated with sodium hydroxide to eliminate sodium silicate
and form sodium aluminate it forms sodium aluminate of course silica also reacts
with sodium hydroxide to form sodium silicate
 so bauxite treatment with sodium
hydroxide gives these two which results in the formation of sodium aluminate and sodium silicate
 so iron remains as a solid and when c o
two is blown through the resulting solution sodium silicate stays in solution while the
aluminum is precipitated out as aluminium hydroxide
 so second step is the blowing carbon
dioxide through the
 so this sodium aluminate reacts with carbon dioxide to form aluminum hydroxide ok
 so the hydroxide can be filtered off
washed and heated to form pure alumina
 so this aluminum hydroxide on heating forms alumina
 so the next stage is the formation of pure
alumina from aluminum oxide
 so it is performed by electrolytic method
 so in aqueous
solution aluminum oxide dissociates into ions they are a l three plus and
a l o three three minus
 so in in solution in aqueous medium aluminium
oxide dissociates into aluminum three plus and aluminium three minus such as a l three
plus and a l o three three minus
 so on anode one can anticipate this reaction l three plus plus three electrons are

added to give aluminum metal on cathode aluminum a l o three three minus releases twelve
electrons to form again a l two o three and again   this process starts ah the dissociation
of this one happens again
 so that it   it it continuously it goes until all the
aluminium oxide is exhausted and overall   electrolysis process can be represented through this equation
 so this is how aluminum is extracted and
purified using base process starting from   bauxite and electrolysis is necessary
as aluminium is very electro positive   these days electrolysis of the hot oxide in a
carbon lined steel cell acting as the cathode   with carbon anode is used the metal is obtained
by electrolyzing the dry alumina in molten   sodium hexafluoroaluminate also one can also do this electrolysis   ok
 so next one is gallium it is normally
a byproduct of the manufacture of aluminum   that means in the bauxite it is present
in trace quantities the purification of   bauxite by the bayer process results in the
concentration of gallium in its ratio from 5000   to 300 in the alkaline solution from an aluminum
that means to start with the ratio of gallium   to aluminum is about 1 is to 5000 on concentration
it increases to 300
 so once after the bauxite   turns into more and more aluminum oxide through
a series of process that i had described   it leads to the concentration of gallium so
later electrolysis using mercury electrode   is used for the concentrated ah gallium and
this electrolysis will give sodium gallate   once gallium is concentrated electrolysis
using a mercury electrode provides a further   concentration and following electrolysis
of the resulting sodium gallate   using a stainless steel cathode offers liquid gallium metal because gallium is a low melting   element and its melting point is 29.
76 degree
centigrade
 so at room temperature it is liquid   similar to mercury
 so preparation of very pure
gallium requires a number of further processes   ending with zone refining to make pure gallium
metal and about zone refining method i would   explain when i discussed the chemistry
of group 14 elements and especially while   purification of silicon and its ultra
purification for semiconductor purposes one uses   zone refining method that time i give more
information about zone refining technique ok
 so the other element is indium
its also a byproduct of formation of   lead and zinc that means lead sulfide

and zinc sulphide warts do contain   a small amount of indium and indium metal is
isolated by the electrolysis of indium salts   in water further process are required to make
very pure indium for electronic purposes so   crude thallium is present as a component in fluid
dust along with several other elements of p block   such as arsenic cadmium indium germanium lead
nickel selenium tellurium and zinc and also in   zinc sulphide it is present in very trace amount
thallium is prepared by dissolving the flu dust   in dilute acid such as sulfuric acid and
prospecting out lead sulphate and then it   is treated with hydrochloric acid to precipitate
thallium chloride that is thallium monochloride   tlcl further purification can be achieved by
subjecting thallium chloride to electrolysis let us look into the reactivity of boron and aluminum ok
 so element b are elemental
boron combines with oxygen   halogens sulfur and nitrogen and with many metals
it is resistant to acids and only reacts with   molten sodium hydroxide above 500 degree
centigrade that indicates its inertness   at normal circumstances towards acids aluminium
being very reactive metal usually made unreactive   by a thin coating of aluminium oxide so
freshly if you see manufactured aluminum on   exposure to atmosphere for few days will
readily form a a thin coating of aluminium oxide   and this is called passivation process actually
this passivation process is remarkably helpful   in preventing the further corrosion of aluminum
so that way when whenever aluminum is not used   ah if it forms a thin coating it is actually
good for its life it should not be disturbed   only when we have to use it for some purpose then
only this oxide coating can be removed through a   proper acid treatment
 so aluminium dissolves in
hydrochloric acid to give hexa aqua aluminum three   plus ion and hydrogen gas will be liberated and in
strong hydroxide solutions giving aluminates and   hydrogen for example if you take
aluminum and trade with sodium hydroxide initially it gives insoluble aluminium
hydroxide but on treatment with excess it forms n a a l o h four times with
the liberation of hydrogen gas   similarly indium reacts with
hcl to form indium trichloride with the liberation of hydrogen gas
same thing is to in case of thallium thallium on treatment with nitric
acid it forms thallium nitrate plus h2 comes out when boron is heated with
most metals ah metal borates are formed very   similar to carbon and silicon interacting
with the metals to give ah corresponding   carbides and selenides in the same way
 so these
borides can also be made by heating with metals   compounds with these the

different composition
can be formed the structure of these borides are   dependent on the metal to boron ratio and contain
either single boron atom or a pair of boron atoms   or a chain of boron atoms or double chains
or sheets or even clusters of boron atoms   for example compounds with composition
say m two b this these are all borides if the composition is say m two b
 so example   f e to b ok
 so you have single boron atoms are
there single boron atoms are there in the lattice   and while those with one is to
one ratio for example in f e b m b
 so here have a single chain boron atom chain ok and in m b 2 b sheet will be there boron atom sheet will
be there ok between the 2 layers of metal   and in case of m b 6 a 6 boron atoms
arranged in the octagonal fashion   in an octahedral fashion will be there in the
lattice
 so here essentially eight boron atoms   make a cube and at the center this b6 octahedra
will be placed and similar to c s c l type   structure in case of m b 12 this indicates the
type of borides we come across ah with metals   example aluminium b12
 so here ah the boron
atoms form a network of link icosahedral ah   clusters similar to free crystalline boron
atom that means like this ah boron clusters   containing 12 boron atoms will be included in the
lattice i can show you some of those things here   you can see the structure of this one is a chain
where the ratio is one is to one you can see here   clearly this the gray ones are
the metals and here boron chain is   there like this here one can see the ratio
overall ratio or composition will be one is to one   and in this one sheet case here you can
see a metal sheet is there and below that a   boron sheet will be there
 so they are
alternately they are arranged in this fashion   and for example if you just look into
zirconium bromide you can see here the green   one is zirconium layer and the next one beneath
that one is boron layer is there and below that   you have again zirconium layer
it continues in this fashion and in case of ah borides of the type m b
six as i mentioned you can see this cuban   consists of metals at eight corners
and that is ok encapsulating this   boron cluster with boron atoms are arranged in
octahedral fashion
 so now let us look into the   reactions of boron and aluminum with halides
or halogens and all give trivalent halides
 so that means all combination of all elements
of group 13 with all elements of groups 17   are possible to generate trivalent

highlights
of the type m x 3 where m is a group thirteen   element and x is group seventeen halogen and
except thallium triiodide
 so if you just look   into thallium triadic one is highly oxidizing and
one is highly reducing and it is very difficult to   bring two entities which is one is highly
oxidizing and one is highly reducing difficult as   a result tl i3 thallium triad is bit difficult to
make and also it is highly unstable and all these   group 13 element halides can
be seen and among them this bx3   boron halide trihalide is a planar
molecule and it appears like this   you can see here a typical boron trihalide can be
represented in this fashion it is trigonal planar   and in this one ah one p orbital is left
so that is perpendicular to the plane
 so it is something like this we have this if you
assume this is p orbital this is perpendicular   and of course ah yeah this is the ah p orbital
m t p orbital
 so in case of b f three and also   to an extent in case of b c l three pi back
donation can be anticipated from fluorine or as   they also have filled p orbitals in this fashion
if you recall the lewis dot structure we wrote it can be c l r ah f
 so here ah what it is
expected is these lone pairs can interact with m t p orbital coming here ah to have some sort of
p pi p pi interaction through which some of the   electrons can move from halides to boron
 so that
its electron deficiency can be compensated ok and   and of course although one can
think of this kind of arrangement   ah it is little less pronounced in case of boron
trichlorides whereas it is more in case of boron   trifluoride as a result what happens boron
trichloride is more or strong lewis acid   compared to boron trifluoride despite fluorine
is the most electronegative element for bcl three   overlapping of orbital is poorer
 so the boron
is more electron deficient
 so that means when we   consider fluorine another thing one should
remember is if you take here ah fluorine both are   essentially two p orbital and two p orbital
here here overlapping can be more efficient   because of the similar size on the other end when
you consider chlorine you are considering three   p orbitals the three p orbitals are lit larger
in size as a result what happens interaction of   three p orbitals with two p orbitals are not very
efficient as a result what happens electrons are   not readily moved from chlorine to boron atom as a

result what happens the electron deficiency still remains intact at boron atom as a result b c l
three is much more lewis acidic in nature compared to boron trifluoride
 so you can see here ah in
the picture you can see that boron m t p orbital and field p orbitals of fluorine can be seen and
the size is essentially same you can anticipate some sort of interactions here and through
which and also another important aspect one should remember is fluorine being the smaller
one when you have eight electrons in the f minus due to the inter electron repulsion it has a tendency to reduce its density by giving some electrons towards the boron m t p orbital as a result what happens it carries it to multiple bond
character and as a result what happens it is less lewis acidic in nature compared to b c l three
and same thing you can see here in case of ah b c l three you can see the size of p orbitals
are little larger compared to the boron p orbital boron p orbital
 so here your the
interaction is not very effective
 so boron atom still has more electron deficiency
and making b c l three much stronger lewis acid
 so essentially we call this as a
mismatch of orbital for the same reason when we go to higher elements in the p block multiple
bonding is not possible and multiple bonding is only effective in case of first row elements where
we involve two p orbitals for such pi bonding ok
 so ah b x three are boron
trihalides are monomeric in nature where the structure of aluminum trihalide depends
on the type of halides we are considering aluminum trifluoride is a high melting polymeric solid
built from fluoride bridge alf six octahedra
 so here the structure of aluminum trichloride
in the solid state has six coordinate aluminum centers with chloride bridges that means both
aluminum trifluoride and aluminum trichloride show octahedral geometry in solid state however
in the liquid state and also in gas phase ah aluminium has a dimeric structure that means a
dative bond exists between aluminium and chloride in the bridging unit and aluminum tri bromide
and aluminum tri iodide are dimeric in all states
 so you can see the structure
of aluminum tri halides here if you take aluminium trichloride one can write and if you assume aluminium has undergone s p
three hybridization
 so here what we have is s two p one and they combine together to form four s p
three hybrid orbitals having three electrons one is empty and now three sp three orbitals with one
electron will interact with chlorine to form three alcl bonds other one is

empty
 so now similarly i
can write another one here in opposite direction
 so now here this lone pair of chlorine can be
given here and this day two bond forms this   stabilizes ah the structure as a result
aluminum trichloride will exist as a dimer   having a 2 cl 6 formula and you can see that
structure given here and inner angles are about   86 degree and outer angle is 90 degree it is a
aluminum is in a typical tetrahedral arrangement   and also because of dative bond you can see
the tlcl bond is little longer 234 picometer   whereas the terminal bonds are shorter because
they are covalent the distance is two twenty four   pico meter you can also see aluminum fluoride
giving a three dimensional structure and here   another reason why it it goes for tetrameric
structure or octahedra structure is very simple   if you just look into the size
of aluminum and size of chloride
 so the size of fluorine is much smaller
compared to the chloride
 so as a result   when fluorine makes an attempt to have a dimeric
structure ah the angle here does not permit ah two aluminum atoms to come very close to each
other
 so in this case if both the aluminum come   very close to each other they repel because
of both are positively charged because of   this repulsion what happens this bend structure is
not possible if the bend structure is not possible   one can think of a linear structure
if linear structure is there then   dimeric structure is not possible you can
possibly think of a tetrameric structure this is what exactly happens
ah and if you just look into   ah each unit in aluminum fluoride in the solid
state you have a tetrameric structure like this   is there and and in most of the
cases when fluoride reacts with   several elements from p block r d block and always
they have a linear structure to keep this angle   close to 180 and in those cases obviously you
cannot have dimeric structure it has to be either   trimeric or a comfortable strain free tetrameric
structure all the trihalides are powerful lewis   acids forming adducts of the type m x three
l that means if you take any lewis base   close to trihalides they readily form adduct of
this type for example if you take and if you bring   ammonia it readily forms an adduct of this type
often bf3 is used as an adduct of diethyl ether so   bf3 is actually sold and also stored in this
fashion by making an adduct with diethyl ether
 so the formation of anions of the type m x

four minus is also because of the lewis acidic   properties of boron trihalides of group boron
triharits or trihalides of group thirteen elements   and this is essentially nothing
but the acid base complex formation ok
 so ah for example b f three plus n
eif if you take it forms n a b f four
 so it it happens all aluminum   and heavier group members are also ah show
a maximum of six coordination and that means   ah in case of boron we can because of presence of
only s and p orbitals one can think of a maximum   coordination of four whereas in case of aluminum
ah one can use d orbitals and aluminum and heavier group thirteen elements one can use d orbital
to increase its coordination number as a result   they will show up to a maximum of six
coordination number
 so ah we saw now   ah all group thirteen elements form
tri halides of the type m x three
 so all group thirteen elements
also form diatomic halides   of ah type m x ok with element in plus one oxy
state however except thallium or are unstable   towards disproportionation to the metal and
the trivalent halide only in case of thallium   chloride or thallium halides plus one state
oxygen state is very stable
 so even gaseous   thallium chloride for example is unstable
to disproportionation and aluminium chloride and gallium chloride can be readily formed
by the reaction of aluminum or gallium metal   with hcl at high temperature and low pressure
giving red colored aluminum trichloride   or gallium trichloride   ok which are condensed at low temperature of
seventy seven kelvin ok
 so on warming this gives undergo disproportionation to
form the corresponding tri halides of this type
 so that means ah this is called
disproportionation reaction plus one is giving   plus three and zero valence metal in case of boron
boron trichloride when it is treated with mercury   it is reduced to b two c l
four that is plus two state   boron dichloride with the
formation of mercury chloride one can also use copper
atoms instead of mercury here
 so some atoms of the same element are oxidized
and some other reducer in the same reaction can   be described as the disproportionation
reaction for example in case of   ah this one i showed you here so
this one ah since it is unstable   it readily undergoes disproportionation to form m
c l three plus two m
 so reverse of this reaction   is called con proportionation reaction that means
the reversing of disproportionation reaction   is called count proportionation reaction that

means when m c l three is treated with excess of two m it gives three m c l so opposite
reaction is called con proportionation reaction ok and b two c l four decomposes at room
temperature to form progressively b eight c l eight
 so that means except for trivalent boron
trihalide others are unstable and b two c l four even at room temperature it dissociates or
decomposes to give higher series halides such as b8cl 8 b9 cl 9 and also higher clusters such
as b ten c l ten b eleven c l eleven and up to p twelve c l twelve
 so in case of b twelve c l
twelve ah boron retains icosahedral structure with each boron having one chlorine atom
and gallium two occurs in the species
 so in this species anionic halide g a to x six
gallium is in plus two state and here where x equals c l bromine or iodine ok formed by
electrolysis of gallium metal in strong acid and these essentially contain gallium gallium bond
and that accounts for oxidized oxygen state of plus two but are readily oxidized by halogens on
addition of halogens they readily form g a x four minus very similar to a l c l four minus r b f
four minus ok
 so let us look into the interaction of boron with hydrogen boron forms more hydrides
than any other element in group 13 series and these essential electron deficient compounds have
both two center two electron and three center two electron bonds these compounds can be classified
into two groups having b n h n plus four series is one type of boron hydrides
another one is b n h n plus six series the simplest boron
hydride is b h three and this is never been isolated and this one has a tendency to
undergo dimerization to form b two h six and and that means the smallest boron hydride is
diborane or b two h six formed by the reduction of boron trifluoride with lithium aluminium hydride one can conveniently prepare by treating boron
trifluoride with lithium aluminium hydride the simplest boring is diborane and higher boron hydrides can contain the same
structural features as b two h six that means ah three centered two electron or two center
two electron bonds with one or more boron to boron bonds and these higher boron hydrides
can be prepared starting from diborane itself for example when diborane is heated
to 100 to 120 degree centigrade it forms b four h ten and h two is liberated similarly when diborane is heated to about one eight to one
eighty to two hundred twenty degree centigrade it forms b five h nine plus six h two and one can see
here the the diborane structure is shown here and it is very easy to understand the three
standard two electron or electron deficient bonds we can again use valence

bond
theory here ah if you take b h three   to start with to the formation of b h three
one can look for ah again hybridization of   ah s and p
 so this one essentially what happens
before the bond formation they are distributed in this fashion
 so that means
s electron is promoted to p   to have a situation like this we
have now four s p three orbitals one electron one electron one electron here no electron
 so now b h three what it does is one s   electron of three hydrogen will utilize
these three s p three hybrid orbitals to form three b h covalent bonds and now
one of the empty orbits will be like here   and similarly one can write
for another one in this fashion now essentially this ah interacts with this
one and here this one to form a diborane
 so here two electrons are there here two
electrons are there here no electron is   there here no electron is there
 so now if you
overall count the electrons present between b   h and b it is three centers are there
and two electrons are there and same   thing is true in this case whereas
here we have two electrons no issues
 so we have ah one three centered bond here and another one three   center two electron bond here
 so that
means in this one we have a total of two three centered two electron bonds and one two
three four four two center two electron bonds so   this is how diborane x can be explained
 so here
essentially two electrons are delocalized between   these three atoms to form a three center to
electron bond this is also referred to as banana   bond
 so boron hydro you can see in the structure i
have shown here
 so boron ah the s p three orbitals   of boron ah here this one i have shown as m t
red one is empty and here one electron is there   and here one electron is coming from hydrogen and
this is empty
 so total we have two electrons here   and three centers are there
 so this is how the
bonding can be explained using valence bond theory   in case of boron hydride especially b two h
six ok and other boron series as i mentioned   you can see we have two series b n h n plus four
series and b n h n plus six series ah they give   very interesting ah structural types and all these
structural types can be explained using wades rule   ah at appropriate juncture i would introduce
weights rule to explain the bonding and geometry   in case of boron hydrides and for example you can
see here i have shown the structures for two type   of two higher boron hydrides

one is b four h ten
and one is b four h nine here you can see we have   one two three four five six ah terminal b
h bonds and one two three four bridging b   h are there
 so overall it is b four h ten in
this case it appears like a square pyramidal   structure that means probably from an octahedral
structure one axial boron atom is taken out and   hence it appears like a square pyramidal structure
having nine hydrogen atoms in this fashion we have   four bridging hydrogen atoms and five terminal
hydrogen atoms sitting on one boron atom each
 so ah i stop ah at this stage
today and i will discuss tomorrow   in my next class about some
reactions of boron hydrides