so hello good morning everybody
so we are
still continuing with d and a block elements and today we will start our discussion from ionization enthalpies where we just want to see how a typical ionization process can be helpful in assigning the corresponding states what we are discussing
so far for the formation of the metal atoms from the m which is present in bulk quantity
say iron as iron rod iron as iron powder to its atomic state then to its different ionic
states where we don't know what are the typical values for n how many electron transfer can take
place and the different oxidation states what you can get and obviously these will all form in
solution that means in aqueous medium how we can think about the formation of the
corresponding different metal ions and as we are discussing everything related to the metals
so we at one time will just reach to the different metal ions also and
the properties what we are talking about for the different metal atoms and now we will
see how the different cases of ionization can think of from the corresponding charges the
nuclear charges residing on the nucleus of the metal atom
so what we see that these changes that
means this ionization enthalpies it can change from and left to right where due to an increase
in nuclear charge how we can change the nuclear charge by going from scandium to copper we are
able to fill the different orbitals and most of these cases these are inner orbital because
if we talk about the corresponding 3d orbitals the forest level is there
so we'll have to
knock out the electrons from the corresponding d level which are inner orbitals and we see as
we move from scandium to titanium to vanadium to ultimately say copper and zinc the
nuclear charge what we have seen
so far in our previous classes that the nuclear
charge will be increasing very much and with that increase the ionization enthalpies what
we now see the ie values the ionization enthalpy values will also increase and what is that
particular trend if we just simply compare the corresponding metals or the metal atoms for the
3d series for the 4d series and for the 5d series we will see that for each of these
series they change along the series of these transition elements from left to right
and the important thing is that why we should change these values because the nuclear charge
is increasing and their attraction on those electrons by those nuclear charges which
are positively charged will be higher so it would be difficult to knock out

the electron
from those d orbitals
so what we see that the successive enthalpies successive enthalpies mean
successive enthalpies for each and every element
so if we just consider when we consider the
knocking out of the first electron
so if we have scandium then titanium vanadium
and chromium etc what we see that due to this corresponding process of
atomization we get the corresponding metal atoms then the electron transfer
so if we go for
the first level of electron transfer the first electron transponder and all of
them are
taking place in the gaseous state is not that we are having some aqueous
solution
or the water medium or some other solvent medium
so if we just consider that
the first electron transfer giving rise to for this species like say chromium
from the right
chromium we are getting as the monovalent state
so the thing what is going on there for
the transfer of this first electron to get the unipositive chromium is related
to
the corresponding ionization enthalpy for first electron transfer and we call
these as the
first ionization enthalpy
so the first ionization enthalpy is there we can theoretically also
calculate it out or we can find out experimentally that what is the
corresponding magnitude of this
ionization enthalpy then the problem comes or what we can compare if we find
that for all these
transition elements already we have discussed that we can have variable
oxidation states
so one of
the important criterion for all these species is that they are having variable
oxidation states
so what does it mean that means if we can have a particular metal center or a
metal
atom such as chromium and in solution or in gaseous state they have some
stability
stability for not only the uni positive or the monovalent species but also the
di positive
or the bivalent species or chromium three plus
so the second electron transfer
the third electron transfer gives us the chromium in plus two oxidation
state and chromium in plus three oxidation state
so these will also involve some other ionization
enthalpy values
so what we see here that the bulk metal its conversion to the atomic state
and
then the electron transfer for its ionic states
so these ionization enthalpies will have some
parameters which will also be related to the enthalpy of atomization because
this
we see from the chromium bulk metal

so chromium metal we have and during that
process we see some other enthalpy term
so enthalpy of atomization
so this is the process where from the bulk metal if we just consider or
if we can think of in such a way that we have the corresponding atomization
process and which
we all know that a different thing we will also if time permits will also at
some point of
time will discuss something related very much to experimental in organic
chemistry or the
laboratory in organic chemistry is our flame test and the flame test is very
much dependent on
what we just looking for something testing the corresponding metal atoms that
flame tests are
very useful to know that the sample any unknown sample whether it contains
sodium or potassium
or any other characteristics metal center which can give rise to color within
the flame of bunsen
burner or any other burner
so sodium and potassium since they are very easily atomized that means the
atomization process for this alkali and alkaline earth metals are very easy
so starting from the
identification of say our common table salt sodium chloride or potassium
chloride we all know that
both of them are white in color and white powder is tough but if i want to
distinguish that which
one is sodium chloride and which one is potassium chloride we have to do
something that means
we can get these as the solid and the solid if from that and do the injection
within the flame
so that solid from the sodium chloride which is n a plus c l minus this is
also k plus c l minus so
large number of electrons because we are burning hydrocarbons we are burning
some gases or lpg
gases in the flame
so the burning of hydrocarbon process will give us some idea that the flames
are all rich with electron free electrons because burning process which is
also sometime the
flames are also we call is a reducing flame
so these electrons basically will be helpful for
giving you sodium zero from those sodium plus inside the flame
so similarly we can
have potassium as the potassium zero
so these are the corresponding atoms
sodium atom and the potassium atom
so these are typically the corresponding
atomized state but we are doing something we are thinking of this
corresponding
atomization process in a reverse direction or the opposite direction there
have been ions
we are having we are putting electron and we are getting this corresponding
atomic state
because this atomic state when it is excited within the flame also it will be
in a zero in

the excited level in a zero star still present as   atom in a zero it is getting excited
 so when we
excited by the flame also the energy is getting   from the flame the system is getting energy
from the flame
 so when it is excited it is   reaching some excited state then when it is coming
back to the ground state again that means nh 0   it emits some characteristic flame which is
a differently color for different element   in this particular case for sodium it is a golden yellow flame
 so the atom the atomic state of the sodium when
it is excited
 so in the excited state it basically   give rise to some characteristic radiation
and the color it is giving
 so his lambra is in   589 nanometer which is characteristic
for its golden yellow flame
 so when it emits
 so basically this
is a corresponding emission process and this emission process what we can see that
this particular emission process is solely   dependent on the excited state of the atoms but we
are getting these as the corresponding free atoms
 so this atomization term which is very important
and which we can apply in different places so   enthalpy of atomization also contributes
something that how quickly or how easily   ah with the expense of very little energy how
we can get the corresponding atomic state from   the bulk metal of chromium to chromium zero
so if we see that the ionization enthalpy for   the first electron transfer the ionization
enthalpy for the second electron transfer   and the ionization enthalpy for the third electron
transfer and if we want to compare these values   what will be the trend because we know that in
solution it some process that means these atoms   will be also hydrated
 so the hydration
energy will also contribute to the thing
 so the contribution for the hydration also
will tell us that whether this chromium three   plus will be stable in the solution or not and
ultimately we know that it can go from chromium   three to four to five to ultimately chromium
six which is also the reality the group number   group number is something and related to the
group that thing and where we can knock out all   the possible electrons which is there from the d
cell of chromium giving rise to a d zero system
 so this d zero system what we will see also
afterward that the stabilization of these   other oxidation states

so that will also tell us that though we are having the different oxidation states that mean the existence of variable oxidation states we if we just consider that ok ah the different oxidation states are there ah but the depending upon the nature how we get it so if we can just simply compare the first ionization enthalpy to the second to the third what you see that this particular change in all these enthalpy values for the 3d elements for the transition elements or the d block metals are completely different compared to the main group thing that means for the main group elements what we see that the successive enthalpies of these elements do not increase as abruptly so the change is not very much or change is not so abrupt that means that one step to the other is not so abrupt as in the main group elements that means the main group elements which we call as the s block elements or the p block elements their change is more abrupt but in case of transition metal ions the change is not so abrupt in terms of the corresponding ionization enthalpies and if we just see that the successive enthalpies that means the first ionization enthalpy to the second ionization enthalpy to the third ionization enthalpy because we know that they exist in different oxidation states and by getting that oxidation state at one point of time we can knock out all the electrons so knocking out of all the d electrons will give you something where like that of your chromium chromium can go up to chromium six or hexavalent chromium where no d electron is present but if we just simply compare for this successive one as well as for a particular triad we know now what are those triads so for these triads basically as we have just compared in our previous class the triad for say chromium molybdenum and tungsten this is one particular triad then we can have nickel palladium and platinum so the d electron configurations are all same for a particular oxidation state only thing is that the nuclear charge is increasing their corresponding size is also increasing so how quickly we can reach basically for a hexavalent chromium extravagant molybdenum and hexavalent tungsten so within this triad basically if we consider now the ie values the same the first ionization enthalpy the first ionization enthalpy if we compare what is the corresponding trend so this within a particular triad that's why we are saying that within a triad the first ionization energy is generally higher

for the third then for the first and second metals   that means if we just see for the triad like
chromium molybdenum and tungsten what is the third   one the third one is the tungsten
 so the first
ionization energy for tungsten would be higher   than that of the first and the second metal
atoms first is chromium second is molybdenum
 so what we see basically that the first ionization
energy values for these metal atoms have a trend   but when we consider that a different
proposition that first ionization will give you   the only that monovalent species that
means the uni negat any positive chromium   molybdenum also in a positive that means m o
one plus chromium one plus and tungsten one plus
 so all these are there and we just compare
for the first ionization energies the first   ionization energies for the formation of chromium
in chromium one plus molybdenum in molybdenum one   plus and tungsten in tungsten one plus
 so there is
a trend
 so these physical parameters are physical   quantities is some interesting role to play
because whenever you have some data related to   all these electron transfer values or the enthalpy
values or the ah corresponding thermal energies so   we can have always some good trend like the way we
compare the melting points and the boiling points
 so how they basically related to the corresponding
properties of all these metal atoms that we can   see
 so this is for the first one and if we
go for the second ionization enthalpy and the   third ionization enthalpy we get chromium 2 plus
molybdenum 2 plus tungsten 2 plus similarly we get   chromium three plus for the third molybdenum
three plus and tungsten three plus since   size is changing and all these cases whatever
trend we see for the first electron transfer   for the first electron transfer we see that the
statement what we made therefore is the first   ionization is generally higher for the third than
for the first and the second
 so this is higher for   tungsten only to get some contribution
that whether we are able to knock out   the first electron from the tungsten to get a
tungsten in one plus condition
 so compared to   chromium and molybdenum the tungsten we
know that is the post lanthanoid element
 so the post lanthanoid element
 so there is a
lanthanide contraction the size is little bit less   and the nuclear charge has increased

anonymously particularly the 14 unit addition of those lanthanide elements
so the nuclear
charge effectively contracting the size only difference and only thing is that the
5d orbitals are little bit specially exposed compared to 4d orbital or the 3d orbital
so the
exposure of these in space that means the spatial exposure of d orbitals are little bit different
and if these are bigger in case of tungsten compared to molybdenum but removal of this first
electron is very difficult
so that's why for this removal of this first electron for the first
ionization thing that means if we just compare for these that means the first ie
so the first
ie for this will be the tungsten will be higher than that of molybdenum and that of chromium but
if we go for the successive removal of electrons the successive removal of electrons will give
rise to the other oxidation states
so once you get the highest possible element in this particular
triad that means the tungsten in the mono positive state it would be easier now to remove the second
electron or the third electron because we are removing that electron from that that particular
5d level already which one has lost is electron from this particular s level either s level
because always we have the s2 electron centered
so s211 and the d-level and during that particular
removal basically what we see that always we have the s2 and dn electronic configuration this s2 and
dn electronic configuration is very interesting to compare because what we see that ground state
electronic configuration we just compare then at one point we are just comparing the
corresponding electronic configuration for the ionic state what we are present or we are
getting in solution
so once this first electron is removed for the first ionization energy
that means it is s 1 and d n and the relative ordering of these levels suppose this is 4 s for
chromium if we are considering this for chromium this is 3d
so the electrons what we are trying
to move from there is that we are removing this electron
so we are having this electron in
the forest level
so we knocked out these and at the same time when initially in the
ground state we have some energy gap between these two levels if we say and after removal of
these your this energy gap may not be the same there is some change in this particular relative
or energy levels for this 3d and 4s level and that's why when we move this particular electron

from this level that means s level to s1
so these two are basically these two energy levels are
going very close to each other and this particular removal if they are very close and if they are
merging to each other this s electron can go to the d level because there is no s therefore so
s will be therefore 0 and d will be d n plus one
so the successive removal of all these electrons
from the first to the second and to the third once we remove the first one which is removed from
the s level but the subsequent electrons if the reorganization can take place we can have some ah
gain in energy through the reorganization energy and that reorganization energy will help us to say
that whether we have the s level is empty only the d electrons we can have for getting the second
ionization energy and the third ionization energy
so the second electron the third electron and so
on are going from this particular d level only
so d level are there
so not only the organization
energy
so we can have some d orbitals more number of d electrons in these levels we can have
we know that the starting point we have the six electrons are there
so we also consider the
corresponding in contribution for exchange energy
so exchange energies are there
so that is
why the what trend we are getting for the first ionization enthalpy is not true and
its sometimes it is river and often true for removal of the subsequent electrons so
these are the removal of for the subsequent electrons and the trend would be different
and it is reversed also
so what we see there therefore that if we move from there that means
once we get this the removal of these electrons what will be getting will be getting some
oxidation states whether it is in the gaseous state or in the ah corresponding solution
state or the aqua state
so oxidation states how we get those oxidation states
so this
is definitely related to the corresponding group member and those group members are there and
depending upon the group level that whether this a particular group level we know from the periodic
table and this is the corresponding group number
so all these things that means the chromium
molybdenum tungsten like that of our nickel palladium and platinum
so we get all these things
that means the group numbers for all these things and the oxidation states
so we can something we

can assign to them as the group oxidation states   that means the highest
possible oxidation states
whether we are able to achieve that or not   that we can find it out that means
the hexavalent chromium formation
so we can go up to the removal of all the
electrons giving rise to a 3d zero system
so that will see here that is related also to
the corresponding oxidation states just we are   also discussing all these
things simultaneously
so by looking at the corresponding metal atoms   this particular table is also
there in your
crt book and it has been taken from that book   also because it's easier to
discuss from that
book if you open up that particular book you   can think of what we are talking
about over
here for this particular type of table only
so we just we are here
so something what is
written in the bold is plus three and plus   six that means these two are more
stable oxidation
states
so if we just simply compare for chromium   and if we just see the chromium
with
molybdenum down and the tungsten more down that   we see that if we just remove
more
number of electrons from there   that means more number of ionization energies
are
involved but the stabilization of these how we   can compare the stabilization
of chromium in hexa
balance state chromium in six plus molybdenum and   stix pass and tungsten in
six plus also
so these
are all very much important related to that of   your group oxidation states
so group oxidation
states is is the maximum one
so whether we get   that particular group oxidation states which is
the maximum one and we see that the corresponding   species what we are getting
that means we are just
taking all the electrons from its corresponding   influence of the nuclear
charge and the middle
line center will remaining as the hexavalent one
so it will also be electron greedy that means
it would be highly correspondingly it have the   electron greediness and it will
basically reducing
but what about the corresponding other one so   the nature basically
so this one that the
corresponding nature that is goes for the electron   ah corresponding electrons
what we are getting
from there that the number of oxidation states   as we move that for scandium it
has one electron
in the d level
so if we remove all three together   for the four s two and three d one
electron we get
the trivalent

so that's why scandium has only one   oxidation state which is whether we call it as a more stable one or the   ah not
so stable one is there does not matter
because we are not able to have some chance to   compare with the other oxidation state similarly
that is true for zinc and in case of jing it   is written in bold and is not written in bed so
the scandium in trivalent state is not
so stable   compared to the corresponding oxidation state
for zinc as zinc 2 plus because the situation is   also very much similar for zinc 2 plus where
only two electrons you can remove from the   uh d s cell for a cell and leaving behind with a
three d ten electronic configuration and three d   ten electronic configuration is the stable one so
for all these cases like that of our manganese we   have seen that in kmno4 the potassium
manganate 7 or potassium permanganate   again we can remove all the electrons from
its sphere of attraction of the nuclear charge   the manganese can go up to a hepta balance state
that means the plus seven oxidation state and in   case of manganese also we just write that the plus
two and plus seven are stable
so when you see that   the manganese and the different redox reactions we
if we just consider the different redox reactions
so for these redox reactions now we just
slowly moving to the ionic reactions
so these redox reactions if we just comparing the
corresponding properties of k amino 4 in solution   whether we are comparing it in the acid medium or
in the basic medium or in the neutral condition
so whatever solution we are handling that is
important for the electron transfer reactions   but since this is a species where your manganese
is in the heptavalent state manganese is in the   plus seven oxidation state
so definitely it will
be reducing
so it will just basically just go go   for the just it will the center will be reduced
rather and it will just accept ah corresponding   electrons
so this is a typical oxidizing agent
so the for the redox titrations the permanometry   also we have seen in the redox titrations we use
this manganese as the manganese seven
so it has   the corresponding thing that where you can reduce
so it can reduce for all these oxidation states
so just now we have seen that you can have an
oxidation state from plus seven to plus two
so this is plus seven
so plus seven it can
go to plus six plus five plus four two plus   2
so when you reduce it
so manganese in acidic

medium in this particular medium when you have h plus plenty of h plus is there that means this species which is corresponding the aqua species and if we have all the water molecules and the most common one is the six water molecules bound to this manganese center when we do it in aqueous medium in the water medium so this binding so in the acidic medium only it can supply these water molecules so that's why this particular species is present that means the plus two oxidation state for manganese is stable in acidic medium but in the neutral condition or in the basic medium before that in absence of a large amount of h plus or plenty of h plus what we will have will have either h2o or the self dissociation of h2o also can sometimes give hydroxide and because we all know when we have water we have both h plus and oh minus so when manganese is reducing stepwise and at one point as going to say plus 4 oxidation state so when it is in plus 4 oxidation state more electron transfer can take place to reach 2 plus 2 but we are reducing that particular center that means the and mangan is in a stepwise manner so one electron is putting two plus six another electron to plus five and the third electron to plus four so once plus four is forming that means manganese in plus four oxidation state that means the tetravalent manganese is there and in the system has more number of hydroxide ions and all these things so immediately what we think that the species will slowly attract these hydroxide ions because this is positively charged and the positively charge is not that much that means seven plus for the heptavalent manganese so this particular assembly will also try to gather there and if basically it has some species that means the manganese four hydroxide that means mn this we can write very quickly or very easily but this particular species related to its existence its solubility and all these things so if it is not there that means the hydrated hydroxide in the tetravalent state so similarly similarly immediately it can just go for not giving you this particular species because you can have further depotonation from this h o minus so what we have earlier we have water molecules in hand that is getting or giving you h o minus to removal of one proton and the removal of the second proton will give you o two minus so at one point of time if you have bound hydroxide two manganese force center the tetravalent manganese center and this o h bond this o h bond because this manganese is bound to this particular tetravalent manganese

through
these lone pair of electron there are more number of lone pair of electrons on the hydroxide ion
so the more number of electron pairs it has
so it will basically attract more this electron density
because it is already manganese is in not in plus two oxidation state it is in the tetravalent
oxidation state
so it basically pulling towards that particular site
so the pulling of this
electron density to the manganese center will give rise to some unique uh observation that is your
pka of for this what removal of the second proton that means the pka of this is going down and
this lone pair which is responsible for the this particular bond keeping of this
particular bond is moving towards this o
so you have the chance
so the p k is lowering
and your this h is removed from here as h plus and o will stay there as o2 minus
so this is the
particular situation which is arising even in the bound form of manganese if we are thinking that
the theoretically possible species is manganese ah four in the hydroxide which is not
physically observable only thing that from there immediately within the same oxidation
state the manganese will be removed as mno2 because it has less amount of proton because it
is not acidic medium it is alkaline medium or the neutral medium
so protons are not there so
we are not forcing to protonate these oxides which is bound to the manganese center and
the manganese oxygen bond is very strong now and we are leaving behind with the corresponding
separation of this manganese dioxide or the manganese precipitation is there that means
manganese dioxide will be precipitated from that particular medium
so we see that a particular
redox reaction what we will be talking about whether the condition is acidic or basic we
get that we will just at one point we just stabilize this particular reduced form
of manganese in the bivalent state in other case we will just simply stay at the tetravalent state of manganese dioxide
so we just see that this is also true for all
other cases like that of our iron iron we all know that the two oxidation states the two plus and
three plus the ferrous state and the ferric state we always have even in the mineralized condition
the nature is also giving us this particular form in ah corresponding hematite and magnetites
so these oxide or arts are there similarly for cobalt also the plus two and

plus three
so we see that most of these cases starting from manganese to nickel to zinc we have
the stability which are written in the bold
so they are all in by valence state so
this particularly which is also true for copper copper is also in the bivalent state but
the copper can also be reduced to copper one plus which we also know the q plus oxides u two o so
this basically go for something where we see that the elements which give the greatest number of
oxidation state occur in or near the middle of the series why this particular area that means
chromium to iron basically
so the chromium to iron we have more number of variable oxidation states
so which are very much true for the corresponding property of transition metals
that they have variable oxidation states so variable oxidation states in terms of
the large number of oxidation states which is aptly fitting with that of our chromium
molybdenum and iron which are close to the middle of that particular series
so that is why they are
giving these all these different oxidation states
so as we move for electron transfer for the
atomic state or the gaseous atomic state we also can talk about the corresponding
electropositivity that means when we move for the corresponding increasing ionization energies
so as we move for increasing ionization energies there is decline in electro positive character
since the analgesian enthalpy is very less for alkali and alkaline metal atoms like sodium and
potassium they are well known for us that they are the electropositive metals
so we see therefore
that what about these that's why as we move as we go down that means for considering the second
ionization enthalpy and the third ionization enthalpy we see that though we are getting this
chromium will be getting when we go for the typical examples for these chromium centers
in chromats as well as in dichromates which are highly oxidizing and we use for the redox
titrations titrametric analysis of some reductants but what about this molybdenum and tungsten
because of their large size we see that these are very much stable and the stability of these
things will be there that these later elements they are also from the elemental state also what
we know that that the noble metal atoms or the coinage metal atoms those are the heavier metal
atoms also
so similarly in the ionic states also

so these ionic elements which are in the
latter part also basically
so they are not so reactive in terms of the reactivity
pattern or the redox potential value for the chromium six because the chromium
six is
there you know that is the chromium six is the stable oxidation state and the
chromium three
when you settle between this trivalent and hexavalent state we know the
corresponding e
0 for chromium
so if we are just thinking of something where we have the corresponding e 0
value the potential for the electron transfer for molybdenum as well as tongue
strain
which is also very simple to understand that we will discuss in detail in our
next chapter
where we talk about the corresponding coordination compounds but the example
what we can take very
simple just now we have discussed for manganese that if we go for some
stabilization
of manganese in the tetravalent state compared to manganese in the bivalent
state that
means this manganese is the manganese 2 plus
so this manganese has manganese
2 plus which is stable in acid
so in acidic medium this mn 2 plus is stable but
this mno2 is stable in basic or neutral condition basic or neutral medium
so what
we see that if we just compare these two that means the by valence state and
the tetravalent
state and in our previous class what we have commented somewhere that the
stability of these
that means the stability of these can take place in the higher oxidation
states for harder anions
so o2 minus we have classified as an harder anion like that of our fluoride
chloride itself but o has a charge o two minus as a charge higher
amount of charge and size is also less which is more harder than the other
species which is
uni negative like fluoride chloride bromide and iodide
so this particular one which can be
stabilized
so harder anions can stabilize the higher oxidation state higher oxidation
state in
terms of the oxidation state what we are comparing with that of our bivalent
state of manganese
so the binding of this o that means o two minus will stabilize this particular
manganese in the
plus four oxidation state which is not available to stabilize this particular
manganese
because simply from manganese four plus to reduction plus one electron to
manganese
three plus two manganese two plus is taking place very quickly to ultimately
reach
this m n two plus in acidic condition
so this is not getting to bind this particular

one even if you have some interaction like these what we just now i have shown you that if
you have a discrete m n o h bond that will discuss again in detail in our ah coordination
compound classes
so this is there and if we just see that the medium is acidic
so you can go
for the corresponding protonation is not that this particular species that the hydroxide
ion with this lone pair of electron is binding to this manganese
so lone pair of electrons
are still available to bind h plus what happens then
so if this lone pair
of electron is available for binding this h plus
so in acidic condition this manganese
will be mno back to mnoh 2 that means the water molecule
so water molecule as it bounced
to the manganese two one
so it has no extra power of stabilizing the higher oxidation state so
this is four this is four
so this will just simply remove it has no extra stabilization power for stabilizing the manganese in the tetravalent state
so this water molecule will be removed from there
and we get manganese 2 plus what we are writing over here by sequential electron transfer
now two electron transfer
so we are having a species which is very much stable that means
the manganese two plus in acidic conditions so we see that the thing what we have defined earlier
that the stabilization of these manganese by oxide is feasible
so when we are just now we are seeing
the comparison of chromium in hexavalent state molybdenum in hexavalent state and tungsten
in hexa valence state
so all these three and these two are more stable compared to chromium
so we you should not confuse
with the stabilization to that of your electron transfer this chromium is highly oxidizing that
will discuss when we talk about the corresponding standard electrode potential or the potential
for electron transfer from the manganese as manganese zero or any other lower oxidation
state
so e zero is higher for this but for these two cases the 0 is lower but the stabilization is
something different
so stabilization that means the higher oxidation states are stabilized
all together for the higher member of that particular group the way we have discussed earlier
the series of iron ruthenium and osmium and what are the different oxides which can be stabilized
for that
so this particular one but what effect we are just trying to explain over here is that the

effect of this o 2 minus
so once you just see that this particular species what we will be getting
that in the stabilization of this molybdenum in the hexa valence state and the
tungsten in the
hexavalent state and if we do all our reactions in the aqueous medium in the
water medium or some
mixed solvent medium or the water alcohol medium what we see that this
particular one like same
thing the thing what we are now discussing we are concentrating our attention
on the particular
type of bond which we all the time getting from coordination of water molecule
also because the mo
bond is there mo bond is always there if you have bound water molecules we all
discuss all these in
detail again that if you have a typical metal sort like that of our nickel
chloride or copper
chloride we dissolve it in water and immediately the corresponding echo
species are forming the
aqua species are forming in solution and all these aqua species why they are
forming they
are forming the corresponding coordinate bonds and those coordinate bonds why
they are forming
because you have a typical or a definite structure definite geometry for a
particular arrangement
where you have m and o bond
so m o bond is there similarly in this particular situation what we
have seen just now over here that means m n o h
so metal is there it can be chromium it can be
molybdenum it can be tungsten
so for hydroxide also you have mo bond and for oxide also you
have mo bond but the nature is always different
so this particular one is the longest one because you have this water
so the neutral
species the species is typically neutral no advantage from the charge only the
lone pair is
interacting with the metal center and obviously the metal charge is also play
an important role
how good that particular center to attract the lone pair from the water
molecule because
these water molecules are getting polarized because the polarization is there
so is a
covalent molecule these water molecules are typically covalent molecules but
there will be a
charge separation
so hypothetically you can have initially you can have delta delta minus
charge
separation from this delta plus and delta plus charge separation but finally
what we can see the
full charge separation for the oxide formation and this will be remaining as h
plus h
plus and o will be going for o2 minus
so the charge advantage will be there
and due to that charge advantage when this is going from m o h 2 to m o h to
m

o
so this will be the shortest the very simple logic you can have you can also yourself you
can establish that particular logic or think of you satisfy you can satisfy yourself also that mo
bond distances are decreasing
so the decrease in these m o bond distances will tell you something
that you can have other lone pair of electrons and is not that this particular condition
or the situation is very much similar to that of our mononuclear entity it can be by
nuclear it can be trinuclear or it can be a corresponding polynuclear type of thing the
way we get that means the oxide what we are talking about this mno2 we all know because
the metal goes for the metallurgy and the metallurgical people are also talking about
is basically a subject which dealt by the metallurgists and these metallurgists
can think of in such a way that the same oxide bond formation
can take place and this we all know is a mineral or ore for manganese which is pyrulocyte
so what we are getting from the solution as this manganese in the tetra balance
state from the solution we are producing from kmn 4 is the same type of thing
so nature
is also doing whenever the nature is getting manganese into the system
so you see that this
is not
so unusual oxidation state of manganese
so nature is stabilizing that manganese in
the plus four oxidation state like that of the stabilization of iron oxidation state in the
ferric state for fe3o4
so this one but this is not a mononuclear entity that you can have one
manganese and two oxide groups are attached to that manganese center
so is a polynuclear
matrix type of arrangement and you can have more number of bridging groups
so this oxygen
so this oxide
so this oxide we can have and that particular oxide can give rise to
something where we can have the initial shearing of this lone pair can bind two of these
metal center the same metal center one is m one another is m two also we can have
another as m three
so this entity which is very interesting to know that this
particular entity for a trinuclear system this is there due to the same
o which is your oxide only
so oxide can hold three metal centers
together that is why the networking the matrix which is also possible for other
oxide minerals because the large number of oxide minerals we can have
so this oxide can give

rise to
so instead of getting one single mo bond   we are getting three mo bonds
so when if you have
some discrete mo bond for this
so that particular   discrete mo bond you know that that corresponding
m o bond character is completely different
so if we have the terminal and the discrete amo
bond that particular m o bond we can consider at   as m o double bond
so m o double bond is
there because this this distance is very   short and the shortest for multiple
bonding also
because for water you cannot have a double bond   hydroxide also you cannot have
immediately the
double bond but for the oxide we can have a double   bond because it is a very
compact arrangement and
most of these cases when we go from these that   through the removal of this h
as the h plus what
we get that the oxide and this particular one if   the orbitals are available on
this particular
metal center or the metal ion center depending   upon its charge or the
oxidation state we can
have the corresponding double bond corrector
so two things we are discussing over here that how
we can stabilize using the harder donor atoms the   higher oxidation states and
the corresponding
binding of the oxide ion
so oxide ion binding   is pretty important to stabilize this particular
center such as if it is molybdenum and tungsten   we have the corresponding
oxidation state as
the stabilization of the hexavalent manganese   center
so what we get there basically
therefore that we just commented over here   that molybdenum 6 and tungsten 6
are
found to be more stable than chromium 6.

so how we can just simply explain this
particular line this particular statement   that chromium we all know that the
chromium is 6 is in chromium oxide also   we know that this is stabilized by
oxide only
and this is the chromium hexavalent state so   there also you can have some
multiple bonds around
this chromium and its stability in the solid state   but once we go and once we
produce this as in
the solution state we know that cro4 2 minus   which is also again a hexavalent
chromium center
so that hexavalent chromium center we can have   and this chromium has four this
is the
mononuclear species well non-mononuclear species   has four chromium oxygen
bonds
so we cannot have
some network or we cannot have some corresponding   matrix formation for the
corresponding oxide type
of thing and we at the same time depending upon   the chromium oxygen distance
we know that there is

no chance of getting you or giving you or putting you to a corresponding chromium oxygen multiple
bond
so chromium oxygen multiple bond is not the thing what is forming over there but
as we move down we move down to molybdenum and tungsten again in the hexa valence
state molybdenum 6 and tungsten 6 now we see the proposition what we are discussing
just now that for that 3 dimensional system or a matrix type of system what we can have for these
so molybdenum always will have some affinity that means even the free condition also that this is
particular species is very much stable instead of talking in terms of the stabilization of m n
plus in presence of say water or some aquas medium there is no necessity to give you an alkaline
medium or the supply of the hydroxide ion if the system is greedy or the system
is stabilized using hydroxide ions it can generate those hydroxide ions which are
required for stabilizing this particular species from the water molecules itself
so getting those
from water molecule itself as the hydroxide ions and finally what we get that this molybdenum
if it has the hydroxide groups attached to it and this particular pka value is changing say
again like that what we have discussed for manganese is very simple to apply
over here also that you get that you go for the corresponding deponentian and this
molybdenum center can have a molybdenum oxobond
so this particular stabilization is that
so instead of talking the same molybdenum center where n value is equal to 6 we say so
this is also a hexavalent molybdenum center
so is not that the molybdenum size of
molybdenum as well as the tungsten also the size is little bit bigger
so there is no
competition or the steric crowding for putting one ox over here and opposite to
that center as another that means trans to each other
so these two are
trans to each other 180 degree apart can be utilized
so this particular unit
similarly for molybdenum also it can be trans or it can be cis also of 90 degree ah
90 degree separation
so this can be cis also
so the same entity what we are trying to
say over here is that the same entity what we have discussed earlier in the previous
slide that the stabilization of mno2 so what is not discrete is not that it is the

mononuclear manganese dioxide is giving you   like this
so this particular matrix for large
number of oxides and the large number of species   what we can have and even in the complex chemistry
the coordination complex formation will see also   that very quickly we can stabilize this manganese
or the tungsten in hexavalent state by putting   one oxide or another oxide is this particular
species
so getting this molybdenum
so instead   of talking in terms of the corresponding
say molybdenum in hexavalent state tungsten   in hexavalent state similarly for other species
like vanadium also will be talking about vanadium   4 plus as well as the non transition
elements also that if we can we know that   is the laboratory reality also in the laboratory
experiments we use sodium bismuth n a b i o three   at one point we have discussed during our redox
reactions that n a b i o three is there
so again   large number of oxides around bismuth
so all
these things can very nicely be stabilized   because these are not their lower oxidation
state stable lower oxidation states
so simply this particular one can be stabilized
by their corresponding oxo bonds
so like this
so we consider that this particular entity is
stabilized as the corresponding molybdenum species   this particular part is stabilized as the vanadium
species similarly the tungsten double bond oxygen   and the bismuth double bond oxygen is also a
reality
so this entity is
so stable that means the   molybdenum oxygen bond or the tungsten oxygen bond is stable is
so stable that even in the strong   acidic condition it is very difficult to kick out
this particular oxygen or this particular oxygen   from their corresponding species which is
molybdenal or vanadel
so the bare thing   we wont get
so instead of getting that we
get this oxygen
so very quickly we get this
so this particular
so if we have any other species
that means the charge neutralization the four   charges due to this o2 minus and this o2 minus is
balanced only the overall charge remaining will be   two plus
so some other group or some other ligand
can come and bound to this particular species   and effectively what will be getting

effectively what we are getting as that of the   corresponding species is a bigger
size but the charge is small   like that of our nickel ah manganese
two plus nickel two plus or copper   two plus
so we will just continue from here in our
next class that how the different oxidation states   and assigning the oxidation state to the species
but we should not forget at any point of time   where we are in the periodic table because the
size and their position in the periodic table will   guide us where we can go from manganese to any
other species manganese to any other species as   well as the chromium to any other species and the
different oxidation states ok thank you very much you