welcome ah to the class of electrochemistry
in our last lecture we started discussing this   electrolytic cell now if you recall this slide
 so this is a daniel cell in normal case
but if the you know applied potential   difference is greater than 1.
1 that means
if this one is biased in reverse sense   then then what will happen that the reverse
reaction will take place that copper will dissolve   and copper zero to copper sulphate and zinc metal
i mean zinc two plus sign will will return to   zinc metal ok
 so ah basically electrolysis will
take place now normal ah this natural direction of   the reaction is this and in that case delta g is
negative but if you make i mean if you make this   delta g in the reverse sense negative that you apply a reverse   potential drop against this electrode
 so that here
you know this reverse reaction will take place   now typically what is the difference between
i mean in that case it will be it will be   an electrolytic cell where electrolysis will
take place now what is the difference between   a galvanic cell and an electrolytic
cell
 so electrons are
 so galvanic cell and electrolytic cells
 so here in galvanic cell electrons
are generated at the anode electrons are generated at the anode and they are consumed at the cathode and naturally
they will it will be consumed at the cathode means   in the other electrode that is which is
plus and in electrolytic cell electrons   come from an external power source
that's why i was telling that if you   supply an external current such that
the cell is rev i mean reverse biased   ok
 so which supplies to the
cathode i mean electron is supplied   to the cathode and and removes them from the
anode that is cathode in that case it is minus cathode in this case is minus anode is in in this case   is plus
 so you are supplying electron from
outside to the cathode okay
 so so ah typically   this is the difference that the electrons are
generated from within the cell as a result of   some chemical transformation here electrons are
supplied from outside that is it the electrons   are feed from from outside to this cell and the
chemical reaction is taking place over there   ok as for example you know in case of
electrolytic cell the classical classic   example will be you know electrolysis of molten
alkali halide
 so in in it is
 so electrolysis of liqulasis of molten alkali halides like say sodium chloride it is in molten state ok

so it is   it is the method of industrial method for
preparation of sodium metal sodium metal ok now ah
 so what happens for in in
this case
 so cathode at cathode
 so ah   reactions are taking place both at the both at the
anode and cathode
 so therefore cathode reaction cathode reaction it is reduction that gets you in
a liquid and corresponding
potential is equal to minus 2.
71   volt anode reaction anode reaction is c
l minus gates of half c l two in gas form   plus electron and corresponding
potential is equal
to minus one point three six volt that gets you   um as a total of four for the
net
reaction net reaction is sodium plus   plus c l minus giving rise to n a zero in
liquid
form plus half c l two in gas form
 so therefore   the net e for the for this process is e zero
for this process minus four point one volt ok now
 so it is it is in molten
state remember this is in molten   molten salt it is not an equas solution okay
now think about another example where you are   using where you are using this
aqueous solution of
some salt like say for example equal solution of of say nickel chloride
 so in that case one thing that you should remember   that here when you do the
electrolysis you
need to have you know one i mean you need   to use inert electrode
 so in this case carbon
electrodes are generally used
 so carbon electrodes are generally used for the
electrolysis of molten sodium chloride next is for aqueous solution of nickel
chloride
in this case ah platinum electrodes are used
 so platinum electrodes are
used this cathode reaction cathode reaction is like nickel two plus   plus twice
electron that is
reduction that gets you nickel zero solid and corresponding e naught is equal
to minus zero point two four volt anode anode is 2 cell minus cl minus that gets
you cl2 gas
plus twice electron e naught is   equal to minus one point three six volt
 so net
reaction is net reaction is nickel two plus   plus two c l minus gets you nickel
solid
plus two nickel solid plus c l two gas   and the net 0 is equal to 1.
6
with a negative value 1.
6 volt   okay next is electrolysis of ah say aqua solution
equal solution means it is a echo solution of   ah you know something ok some
some you know
electrolyte
 so in case of electrolysis i mean   when you think talk about electrolysis of
water
then what what is happening at anode electrolysis electrolysis of water ok

so anode anode reaction h2o that gets you half o2 gas plus two ice h plus plus twice electron where   e naught is equal to minus one point two three volt cathode cathode reaction is   two h two plus twice electron gets you h two gas plus two o h minus e naught   is equal to minus zero point eight three volt so
these are the things that happen
 so there will be   a competition between the above reactions i mean these reactions i have mentioned this reactions ah and i mean this reaction will be there say for
example ah there may be a competition between   above reaction means this reaction with this
reaction or ah there may be ah suppose in   place of nickel something else is dissolved
 so ah
possibility is also there i mean the competition   ah between between this reaction and the reaction
involving the electrolyte that is dissolved   in in water that is there now the question is why
do we need to dissolve dissolve an electrolyte ah   electrolyte in water because ah pure water for
pure water its resistance is very high ok so   therefore electricity will face a huge resistance
to you know when it is passing through just pure   water
 so therefore in order to reduce that you
need to add something some electrolytes
 so that   the electro electricity can pass through and the
and the required reaction may take place ok now   say for example suppose you have you have ah say
sodium chloride ok
 so equal sodium chloride what   is ah going to happen suppose you have aqueous sodium chloride
 so equaus solution of of initial ok
 so what is going to happen so
cathode reaction cathode means reduction   cathode reaction will be the favored reaction
will be like two h two plus twice electron   giving you h two gas plus two h minus where
ah you know this potential will be will be   like potential will be like e is equal to
0.
41 volt when the concentration of h minus is around ten to the power minus seven molar
otherwise it it would have been like this   and anode reaction anode reaction will be chloride minus
plus water that gets you half cl2 half cl2 plus electron in this case your e naught is minus zero point nine five volt ok
 so therefore see you have a competition over
here ok you have a competition over here that   that this is one reaction anode reaction
and there could be another anode reaction   as a whole as a whole
 so therefore in this case
in this case you see that it is less negative   than this one
 so this one this reaction is
expected to be favored over over this one   and also there is another reaction

what
you can think of in the cathode case that   cathode reaction could be like reduction of
sodium plus plus electron that gets to sodium   sodium ah liquid but its potential is potential
is e naught is minus two point seven volt okay
 so therefore therefore therefore this
is this is much you know larger in negative   sense
 so therefore this reaction will not be
favored but this reaction will be followed
 so therefore
 so net reaction will be will be
c l minus plus water that gets you two h two gas or h two s plus half half c l two plus 2 o h minus ok
 so you can appropriately balance it that's
not a problem anyway
 so in this side you have   two h minus ok
 so therefore
 so basically you
have ah three h two right here three h two ok anyway
 so you can balance it appropriately
so in this case your in this case this e is minus 0.
95 volt anyway these numbers are not
that important but anyway i just wanted to   tell you that when there is a competition
then you need to consider these numbers okay
 so that will decide which one will
be favored over over the other   ok
 so for electrolysis of pure water as i
mentioned to you that it has got you know high   resistance
 so therefore it is difficult to
undergo electrolysis
 so electrolysis of water of water pure water high resistance high resistance so
that means difficult to undergo difficult to undergo electrolysis ok
 so in that case little bit
of acid if you add little bit of of acid then it becomes conducting and
then reaction is taking place ok so   if you add little bit of acid
then cathode reaction may be cathode reaction if you use a platinum ah
pair of platinum electrodes then cathode   direction will be two h two plus two is
electron that gets you h two gas plus two h   minus e naught is equal to minus zero
point eight three volt anode reaction anode reaction is water to get you half o two
o two gas plus two h plus plus twice electron   and here e naught is equal to minus one point two
three volt
 so net is net reaction is three water   liquid that gets you h to gas that gets you h2
gas plus half o2 plus other ok and net e e is e   naught is equal to minus two point zero six volt
ok next we will move on to one important thing   ah which ah which which are basically laws

of electrolysis it is called the faradays michael faraday faraday's law of electrolysis it is by michael faraday michael faraday in 1832 ok
 so so
 so laws are like this first law first law
of electrolysis the weight of substance formed at   the electrode
 so law one faraday's law number one
so weight of substance formed at the electrode weight of substance weight of substance means the substance which is
formed out of this electrolysis substance formed at the electrode electrode during electrolysis during electrolysis is directly proportional to to the quantity of elect to the quantity of electricity that that that passes through through through the electrolyte through of course through a pair of electrodes
 so mass is is proportional to q   or or you can write mass is equal to z into q where z is the electrochemical equivalence electrochemical equivalence ok what is
electrochemical equivalence
 so when q is equal   to one then m is equal to z
 so so when when one
coulomb of electricity has been passed through the   electrolyte then whatever mass of the concerned
electrolyte i mean concerned material has you know   formed has been formed at the electrode
is called the electrochemical equivalence   of that particular material number two there is ah
law number two the weight of different substances weight of different substances substances means this
electroactive substances formed by formed by the passage of by the passage of of same quantity of electricity of same quantity of electricity electricity are are proportional to proportional to the equivalent weight with equivalent weight of each substance of each substance that means that means your
w1 by by w 2 m 1 by m 2 w or mass whatever   is equal to u 1 by e 2 or or which is equal
to can write since q is q is equal to i t you can write you can write z 1 i t divided by
z 2 i t is equal to e 1 by e 2 or you can write   z 1 by z two is equal to u one
by e two that is ratio of the   electrochemical equivalence equal
to ratio of the chemical equivalence   ok now now let us you know focus our attention focus our attention again back to   back to some industrial process industrial process
means you know electrolysis of brine solution of brine solution   solution brine means sodium chloride
solution okay
 so in this case anode reaction we can write two anode reactions like
two c l minus giving rise to c l two gas   plus twice electron its corresponding e naught
is equal to minus one point three six volt   and four o h four which minus o two gas plus
two water plus four electron here e naught   is equal to minus zero point four volt okay
so thermodynamically this reaction should be   favored but the point is that this is very slow
kinetically very slow

so therefore if it is slow then it is a problem but at the same time the other reaction is kinetically fast
 so therefore therefore what will happen that this reaction
will be i mean effective i mean this reaction will be prominent ok
 so therefore this reaction
although this is thermodynamically favored but but kinetically this
 so therefore kinetics will
take over thermodynamics
 so kinetically controlled as a kinetically controlled product this one
will be major
 so this reaction will take place
 so so and and for the cathode cathode reaction it is ah again two reactions
in a plus plus electron that gets to n a liquid it is e naught is equal to minus two
point seven volt and anode reaction it is water plus twice electron that gets you that gets you
h two gas plus two which minus where e naught is uh plus 0.
41 volt
 so therefore this reaction
will be favored over the other reaction
 so net reaction will be your nacl plus
water giving rise to nh at the cathode plus h2 gas that is that is also at the cathode and plus c l two gas at the anode ok
 so this way this way you
know what is happening that you put brine solution in and
basically the diagram looks like this you have a sodium ion selective membrane over here it looks like this
 so h2 is coming out here chlorine it is coming out this is minus this is plus okay
 so there this basically you are
you are doing electrolysis over here it is no it is basically you are supplying you
know um this current from you know outside ok
 so therefore these two are cathode reactions ok so
therefore therefore what is happening that you have sodium hydroxide coming out and water is put in here sodium chloride is fed and here spent brine spent brine is taken out okay
 so this is an sodium ion selective
membrane in a plus selective membrane membrane and sodium ion will move this direction n a plus will move this direction
 so this is precisely precisely what is happening
you know when when electrolysis is carried out on on the brine solution okay
 so what can be
the other application of electrolysis other application of electrolysis can be electrolytic
refining of some metals impure metals so you can you can you know refine like like suppose
you have say for example ah two silver electrodes ok
 so one is say ah the one which is at the
anode is ah say for example it is impure and the other one in the cathode is a pure form
so what will happen when you electrolyze it then then the then the impure ah silver will be
will be dissolving and the pure silver will be deposited to the other in this

way you can you
can you know purify this impure metal to to ah   you know pure metal
 so another application can
be electrolytic refining of aluminium next is storage battery i mean storage
like primary
storage battery or a primary storage cell primary storage cell or secondary
storage cell ok
 so ah the thing is that this
one is capable of being recharged of being recharge okay and electrode reaction
can proceed in both
either direction i mean whether it is it is a   it is a electrolysis or maybe
normal electricity
production
 so during charging the electrical you   know work is done on the cell
 so when you
charge it electrical work done on the cell and as a result of which the   the
free energy required to force the
reaction
 so this will provide the free energy the free energy to force the reaction in
the in the
backward or in the in the reverse direction ok now in case of primary storage
cell see
ordinary flashlight cells or battery ordinary flashlight battery ok cannot be
recharged with
efficiency you cannot recharge cannot be recharged it is not better to recharge
this because
maybe some accident can take place because   it is d it is designed to to i mean
designed in
such a way that you will get electricity once   ok in a single use but you
cannot reuse
it by by charging it like a secondary cell   ok and the amount of energy it can
deliver the amount of electrical energy that it
can deliver will depend on the amount of   you know chemical substance that is
there while it
is you know manufactured once that stored chemical   is exhausted the battery
life is gone or battery
dies okay
 so so these are the typical i mean   differences between a secondary storage
cell and
a primary ah primary storage cell that you can   store electricity but the point
is that you cannot
store electricity for in finite period of time but   i mean it is some some
finite period for for
some finite period of time now let us turn our   attention to the secondary
storage cell secondary
storage cell is a is a lead acid storage cell lead acid storage cell lead acid
storage cell it is ah gaston plantae
it is done by a glaston ah plateau in 1859 okay the cell is like this pb solid
pbso4 then h2so4 that's why it is
lead acid aquas then pbso4 then pbo2
 so that is this
 so net cell
reaction is net cell reaction is p b plus p b o two plus two h two s o four
equals that gets you two p b s o four plus two

h two
 so when the discharge is taking place that is you take out electricity out of it this is
the normal direction of the reaction when you charge it then the reaction has been driven in
the backward direction i mean
 so it is charging and the other one is discharging okay and what happens that after it is discharged you
see that some amount of water is generated
 so generally ah density of sulphuric acid h2so4
rho h2so4 is approximately twice rho water
 so when discharge is taking place you know
your this ah sulphuric acid solution which is the electrolyte of the of this ah an active
electrolyte of this cell it is diluted ok
 so generally concentration of h2so4 that is used
in this secondary storage cell it is about 6 mol per decimeter cube ok and normal cell voltages cell voltage is about 2.
1 volt at 298 eight kelvin ok now
ah what is what are the problems with this ah this ah lead acid cell problem could be
 so problem problems may be like it is its weight is
ah you know high
 so weight is a problem because you need to have this large amount of
blade involved over there along with salpus so weight is a problem
 so during
winter time the viscosity viscosity of sulphuric acid increases
increases during during ah during winter and as a result of which ah flow of ions from
one plate to another it is it is you know big it becomes a sluggish and as a result
of which that reduces the current
 so reduces reduces current that is why there
may be problem during winter time you know starting of car ah you know there
there may be some problem ah happens when during winter time and also since it has some
internal resistance
 so slowly it may discharge now number four could be if it is
charged very fast
 so for fast charging
 so h 2 evolution is
 so much that it is
it is you know it will happen you know um on the i mean the bubbles
of h 2 will will be there on the lead surface and
 so therefore lead
when coated with lead lead oxide that forms one electrode
 so lead oxide will be removed
from lead and as a result of which the electrode is modified
 so so ultimately it will damage
the the cell
 so typical diagram is like this series of you know electrodes are there
and one is inserted in between the other
 so this is your p plus cathode this is p b cathode cathode plate plate with p b
with pb o2 coating and this is basically your pb anode plate right and the whole

thing is immersed
whole thing is immersed in sulphuric acid H_2SO_4 with H_2SO_4 with given
specification   ok
 so that is an example of a storage
battery net next we will come to dry cell dry cell it is lake lance's dry cell
la clances dry cell it is in ah it is this was invented in 1866 ok
so basically the electrode reactions are like reactions are like this at anode
you have zinc to zinc two plus plus twice electron ok and
you have a carbon cathode with a brass cap that is you perhaps you have seen
in the market that you know this double a battery   or triple a battery
 so the technology
is like this you have a zinc   you know cup or zinc container and you have this
like one cover and then you
have this carbon electrode and you have on top of this there is
a metal cap
 so that connects i mean   that makes the electrical connection
ok
 so ah
 so you have here paste of of NH_4Cl and you have MnO_2 over there   and MnO_2
manganese dioxide is also there so
so carbon cathode cathode reaction is two m n   o two plus two h plus that is
coming from ammonium
ion ok plus twice electron that gets
 so m n two o   three plus h two o okay
 so or if you write
in the form of NH_4Cl then or NH_4 plus then   you should have written NH_3 over
here like like
if it is if you replace this with NH_4 plus then two n h four plus then you will
have to write plus two n h three   ok
 so therefore it has a limited shelf life
due to self self discharge because it has   got some internal resistance to
which this
this electricity is discharged
 so voltage is voltage is 1.
5 volt and the cell reaction
cell reaction we can write like this zinc zinc plus 2 mn o2 solid plus
two nh4 cl aqueous that gets you   zinc chloride plus mn2 o3
solid plus two nh3 plus water or it may proceed further as follows or i
mean beyond this it may happen this reaction may proceed further as follows as
follows zinc solid plus two m n o two solid
plus two nh four c l equals plus two h two   liquid that gets you zinc chloride
plus
mn oh whole to solid plus two nh3 gas ok
 so this is the typical reaction and it it is
marketed like giving an outside jacket with some   you know some material maybe
some
plastic or some some other material   paper paper packaging may be there
 so so this is
the this is the older version oldest version of   this dry cell that is known as
electricity
cell now modern version of alkali cell modern version of alkali cell modern
version of alkali or or this type
of cell modern version of this primary storage storage it is invented
in 1949 that koh has been used koh has been used has been used in place of in

place of this ammonium chloride in place of ammonium chloride which is
basically corrosive to this zinc metal corrosive to zinc metal this
one is corrosive to zinc metal
 so here what is happening
you use koh and zinc powder zinc powder and it gets a higher current gets higher
current rating higher current rating and voltage is about voltage is about 1.
5 to 1.
65 okay and the net reaction is reaction can be zinc plus 2 mno2 that gets you
zinc oxide
plus mn two o three
 so this is uh this is   the this is called the alkaline cell which is
the modern version of this lake lance's cell   ok
 so so this is basically you know that completes our discussion with respect to
this dry cell and this dry cell and this or the   primary storage and the
secondary storage so
this completes your discussion about primary or secondary storage okay
 so while summing up
 so what we have learnt in this
particular piece of lecture that is we started our discussion
with with difference between   basic difference between this galvanic cell cell
and electrolytic cell in one case we are getting electricity out of
it that is chemical energy has been converted   to the electrical energy in this
case you you
apply electricity from outside
 so that the   natural reaction in some cases you may
require to reverse the direction of the   natural across natural reaction ok
 so you
if you bias the cell in appropriate fashion   then the natural direction of the
reaction
will be reversed and as a result of which   you know electrolysis may take place
 so as an as
an application i mean as an example as examples   of electric electrolysis we
discussed this molten
salt electrolysis or may be electrolysis of equas   solution of different
electrolytes and also we
discussed if there are a there are a com a number   of competing reactions then
which reaction will
predominate over the other and that is decided by   by the value of the
potential that is value of
the potential means the magnitude of the potential   and also the in some cases
the kinetics
of the process or maybe in some cases   you know thermodynamics of the process
is
also important next we talked about this   faraday's law of electro electrolysis
there are
two laws
 so we discussed these laws and then we ah   moved our attention to we we talked
about
this primary storage and secondary storage as   an as example of primary storage
we talked about
this ah this lake lance's cell and lead acid cell   as example of the secondary
storage
 so ah this
completes ah i mean today's uh discussion on   you know on electrochemistry

so in next day i mean
next class will take up this fuel cell that that   is a that is an important
important concept
 so we
will take off the basic idea of fuel cell and then   we will move on to this
another important issue
which is called corrosion
 so till then thank you you