

good morning everybody today i'll start with electrochemistry it is a branch of chemistry that studies the relation between electricity and identifiable chemical changes where electricity can be cause or electricity can be output or effect now reactions involve electric char electric chain charge moving between electrodes or an electrolyte okay so it deals with electrical energy and chemical changes now production of electricity from spontaneous chemical reaction ah a large number of like metals uh chemicals like sodium hydroxide then chlorine etc are produced by electrochemical techniques batteries fuel cells etc here also electrochemistry is an integral part now ah reactions that are done with this electrochemical technique these these are basically you know in some cases these are eco-friendly and you know they don't generally produce pollutions now also the signal transmission in living system is also known to have this electrochemical or electrochemical in origin now ah when we talk about electrochemistry then the first thing that comes is you know conduction so conduction means conduction of electrical charge across some circuit now ah basically here you know whenever we talk about conduction then different type of conductors are to be considered one is like you know this metallic conductor another is a non-conductor or insulators another is a semiconductor and the fourth one is you know this electrolytic conductors now electrolytic conductors means you know whenever we measure resistance across those materials like electrolytic conductors then ah you know this resistance is arising as a result of something which is a little bit different from what is observed in case of say metallic conductors now in metallic conductors what is happening that suppose this is a conductor so you are applying some potential difference across this circuit so electrons are transported from this side to that side this is transported from this side to this side so ah so as such from outside there is no change in the material that is in the in the conductor now ah when it is the case of electrolyte conductor the situation is a little bit different that that you have a solution okay and you are emerging to electrodes so one is plus another is minus and when you measure resistance that means some current is flowing across these two ah these two electrodes then what is happening that in this case you know this ions which are there inside this solution these are

responsible for the for the carriage of charge from one place to another now
so so ah different type of types
of conductors like good conductor
so these are almost fully conducting almost fully conducting semiconductor this
is partially partially conducting insulator these are not conducting ok now
i have just talked about this conduction through metal and conduction
through electrolytic solution now what is the what are the typical
differences
in this metallic and electrolytic conductors
so so ah in case of metallic conductor the electrons electrons are transported
from once one position
to the other and in case of electrolytic electrolytic conductor ions are
responsible ions means
when we talk about ions that means ah the substances which when are
ah i mean dissolved in some solvent then they will produce ions and those ions
against
some applied potential difference they will you know move in a particular
direction depending
on the direction of the applied electric field okay
so in this case in in case of metallic
conductor
so no transport of matter no transport of matter is there matter
is there but in this case electrolyte or ions are transported these are
transported now third
difference can be like the resistance is almost proportional to temperature
and
in this case generally resistance resistance decreases with rise of
temperature this is
just a rough approximation i am not telling that exactly it is followed but
this is a rough
approximation and in this case no chemical change but in this case chemical
change
is there at the electrodes chemical change at the electrodes ok
so these are the few i mean these are the
differences between a metallic conductor and electrolytic conductor ok
so now let us move
on to another thing which is common that that whenever we talk about this
conductivity
then or conductivity or resistance that means when ah when you talk about this
conduction
of electricity then one thing which is very important one parameter which is
very important
is the resistance of this of the medium resistance now resistance its it is
basically proportional to length of the conductor and it is inversely
proportional to the area cross sectional area of the conductor
so for compound variation we can
say r is proportional to l by a or we can write is equal to ρl by a it is
 ρ is basically the
specific resistance or resistivity of the medium ok
so it is the resistance of one meter long you
know conductor and if the cross sectional area is ah unit then it it will be
called
as the corresponding resistivity now in in terms of conductance of a solution
the

generally used term is the conductance i mean i mean not it is not expressed in terms of resistance but it is expressed in terms of conductance

so conductance is nothing but inverse of resistance

so conductance is inverse of resistance ok so what you can write

so conductance is equal to $\frac{1}{\rho} \times \frac{a}{l}$ i mean from here we can write like this

so this is this was specific resistance or resistivity and this is specific conductance or conductivity

so unit of resistance is ohm and unit of conductance is inverse ohm and in si system it is siemens okay

so therefore we can write conductance is equal to specific or conductivity into $\frac{a}{l}$ or we can write from here we can write specific conductance is equal to conductance into $\frac{l}{a}$ which is basically a term which is given a new name sale constant why ah do we write sale constant i am coming to that

so specific conductance

so let us talk about unit of specific conductance specific conductance equal to conductance into cell constant conductance is siemens into sale constant is $\frac{l}{a}$ by a $\frac{l}{a}$ means length inverse okay

so that means centimeters if it is centimeter then centimeter inverse or if it is a meter then it is meter inverse ok

so it is if it is meter then centimeters meter inverse if it is expressed in meter but it is si system

so therefore it is better to use meter rather than centimeter okay

so specific conductance is given a symbol kappa

so kappa is equal to conductance into cell constant now let us come to the point why it is a cell constant now whenever we measure an unknown resistance okay whenever we measure an unknown resistance we generally use this celebrated wheat stone bridge principle now this wheatstone bridge principle is basically having this diagrammatic representation say this is your unknown resistance r_1 r_2 you have a device that which is in most of the cases the galvanometer source of electricity

so when the deflection is when it is there is no deflection means the bridge is balanced then ratio of these two this by this equal to this

by this

so $r_1 \times r_2$ is equal to $r_3 \times r_4$

so from this r_1 you can write $r_3 \times r_4$ into r_2

so if if this and this is a variable resistance

so you can you can have this balance of this galvanometer deflection there is balance of this bridge when i mean at at some appropriate value of r_2 then you can at the balance point balanced point okay

so this way you can find
out the unknown resistance r_1 okay
so now when it is solution
solution means you have an electrolytic conductor other than i mean it is not
ah common
this metallic conductor or some other kind of conductor then you have these
two electrodes and
you have you have to measure the resistance across these two electrodes
okay
so across
these two electrodes means you need to have one electrode over here another
electrode over
here and then this two wires are basically these two wires i mean you have to
connect this
this one this is represented like this your your electrolytic cell is
represented like
this okay
so this is one unknown resistance say r_1
so you place this over here okay
so your this diagram looks like this one
so you have to replace this with this one okay now
there is a little bit difficulty in measuring this this resistance or
conductance
of this electrolytic conductor this is because of the fact that as i
mentioned
to you earlier while discussing the difference between a metallic conductor
and an electrolytic
conductor that is there is a there is some chemical change at the electrodes
okay
so
so since there is a chemical change at the electrode then then during
measurement
of the resistance of this particular cell then this the characteristic of this
of
this material is getting affected ok
so therefore that is why you have to
construct a cell like this that you have your unknown solution kept over here
electrolytic
solution kept over here you dip two electrodes and then you measure resistance
but while measuring
resistance you have to be very careful that in this case in most in in most of
the cases when you
use the switch stone bridge then you supply a dc current okay in that case
there is no problem in
the measurement of the unknown resistance but the moment you use dc current
for this then there will
be electrolysis or various electrode processes so electrode is getting
affected and if the electrode
is getting affected then you are not going to get the right value of r_1
so in this case okay so
what you have to do you have to use you have to make use of a different
technique but but the
same hudson bridge principle but here in place of a dc supply you have to use
ac

so ac means

it is a cosine profile as a function of time in this case intensity of the field and this is your time

so what is happening that in the say first first positive half cycle if this electrode is positive then the other electrode is negative in the next half cycle over here the polarity is

reversed this becomes minus this becomes plus and if this alternation is symmetric that is area

under the curve over here and area under the curve over here these two match then then what

is happening ah then in the positive half cycle whatever is generated over here and also over

here the reverse is generated but the point is so therefore what is happening if a simple electrode

is used then the accumulation of various material is there especially when you use water as a

solvent then electrolysis product of water that is oxygen and hydrogen these are produced

in equivalent amount on each of the electrodes

so electrode will be affected electrode will be affected in the sense that it will be covered with those gases

so therefore characteristic of the electrode will be changed

so therefore in this case if you use a platinized platinum electrode platinized platinum electrode means it is a smooth platinum plate on which this finely divided

platinum metal particles are deposited on this and these are acting this can act as this can

act as a catalyst for the recombination of oxygen and hydrogen to produce water so

therefore electrode will be electrodes will be you know freed from these accumulating gases

so therefore electrode characteristics will not be changed and and as a result of which you can you can measure the actual resistance across these two electrodes

so basically you are putting putting this cell over here that is why the sale

constant is coming over here

so cell constant is nothing but it is the ratio of the length length with between these two electrodes this is your l and a means this is your a this is the area you

are talking about okay

so therefore l by a is the cell constant okay

so this way

so this way

you you make use of this ac supply to measure the resistance i mean the conductance of the of

the of the cell that means conductance of the cell which is containing your required material

now how do you how will you will you identify this balance point of this wheat stone bridge

this is done in a little different way
so here this frequency of ac is about say 500 to
say 1000 hertz or similar values are there and when the bridge is balanced
that means you
change your r_2 in or you you adjust your r_2 in such a way that that if you
put a headphone over
here then minimum sound will be will be you know will be there and therefore
therefore you
will be you will be confirmed you will get a confirmation that this bridge is
balanced and
at the balance point whatever values of these are there i mean r_3 r_4 and r_2
is there use
make use of this to find out the value of your unknown resistance that means
in turn you measure
the the conductance of your unknown solution okay
so ah
so therefore
so what is the expression
that you generally use is specific conductance is equal to conductance into cell
constant ok now let us have some idea about various
conductors various materials as far as their conductance value values are
concerned
so if you if you consider materials like materials and their conductance it is
in siemens meter inverse ok
so say for example copper copper metal its
value is about 6×10^3 silver its value is about say very
close
to this value i mean copper value ok glass its conductivity is very low it is
about
 1×10^{-16} pure water it is about about 4×10^{-5} for example if it is 0.
1 molar
hcl its value is close to four germanium it is about two
so you see that
if you think this think about these two and think about this metallic conductor
then it
is its value i mean this conductivity is very high in case of pure water it's
very low
but but it is much better than glass or some other non conducting material in
case of you know this point one molar hcl it is about 10^5 times
more than
that of pure water okay
so so why this is this is happening i mean i mean the clear cut answer
is that in point one molar hcl you have h plus and cl minus sign
so these are responsible
for the transport of electrical charge from one position to the other in case
of pure water it
is fibly ionized water is fibly ionized to h plus and which minus very fibly
ionized
so therefore since the ions present in water in pure water
so these are very
less in number therefore conductivity is quite low ok
so this gives you some idea about
the conductivity of of various materials next next we will will move on to

another

quantity which is called the molar conductivity molar molar conductance molar conductance is the

conductance of a solution which is having one molar substance dissolved in water and it is measured measured with two electrodes those are separated by those are these two electrodes are separated by unit distance one meter okay and whatever

conductance value you are getting it is called the molar conductance okay so uh

molar conductance is basically given in notation λ_m and

λ_m it is expressed as expressed as κ / c where λ_m is having unit siemens meter square mole inverse where κ is expressed in

meter inverse concentration is mole per meter cubed ok now ah if we would like to know why how this molar conductance will depend on concentration of the of the material but before that let us have

some idea of how simple conductance will will vary with concentration and other factors okay so

before that let us have some idea

so conductance as i mentioned that it is due to the due to the transport of transport of ions across the electrodes

so therefore ions means ions means things are to be considered are basically you know number of ions

so that means if more number of ions are there in the material then it is expected that that the amount of charge that will be

transported across the electrodes will be more

so number of ions is very important

it is an important factor then charge charge of the ion okay charge means

suppose you have you have say

m plus say m one plus say m two two plus and say m three three plus ok suppose you have m one

ion with uni positive charge say m two ion m one ion m two ion and m three ion with bi

positive charge and m three ion with tri-positive charge that means one ion contains three unit

charges this ion contains two unit charges and this ion contains only single charge then

suppose if this ion is transported across this two electrodes from here to here say m one plus

then only one unit of charge will be transported from here to here if m two plus is transported two

plus is transported from here to here then if the other factors are remaining same then you will

be saying you will be you can you can tell that that in the same time or in the same duration

suppose these two are reaching this this side in same time like t one time and here also

t one time then the amount of charge that is carry forwarded from here to here it

will be double for this it will be triple for this

so therefore charge of the iron is very important in the conduction process

so therefore conductance will also depend on the charge of the ions and next one is the speed of ions speed of ions suppose you have you have two ions see ion one and another is ion two say this is also uni positive this is also uni positive but the thing is that suppose that it can swim faster than this one that is its mobility is more than this one then in in same time interval the amount of charge effectively it will it will transport more charges than this one because it is it can move faster than this one so therefore that's why these are the three important parameters important factors that are needed to be considered while you know while discussing the conductance of a solution ok

so therefore therefore therefore when a solution is diluted what do you expect to have suppose you have one one molar suppose you have say for example ah one molar say nacl solution suppose you dilute to say ten to the power minus two molar and then you measure its conductance ok some value you can expect with the help of your device that is you know this using white stone bridge principle

so so some value you can expect that is maybe say for example x is the is the measured conductance now now you dilute it to say half into 10^{-2} molar ok initially it was this much now it is half into 10^{-2} molar then conductance is expected to be expected to be reduced why this is because of because of the fact that the number of ions ok number of ions that is present in a given volume it is now reduced okay number of ions is reduced and since number of ions is reduced therefore conductance is expected to be reduced so go back to the formula specific conductance equal to conductance into cell constant so cell constant is remaining same so what you are doing you are diluting the solution so what happens to specific conductance what is specific conductance it is the conductance of a solution which is placed between two electrodes unit distance apart say one meter apart and also the electrodes are having one meter square cross sectional area one meter square cross sectional area so so if you dilute it initially say for example x number of say ions say for example say x' number of ions were present in this unit cube now if you half dilute it then this becomes x' by 2 okay so x by 2 means your number of charge carrier is reduced reduced to half so number of ions is reduced then charge carried by ions charge on ions no change and

speed of ions this is also also all also you know you can consider this that this one is also remaining unchanged so therefore since the number of ions is reduced specific conductance decreases cell constant is fixed so therefore conductance is expected to be reduced okay so therefore therefore again come back to again come back to molar products so that that we we started to talk about and in between we wanted to you know learn about how conductance is dependent on various factors and we have you know explained to you that these are there are the major i mean three factors one is number of ions another is charge on the ions and speed of the ions so molar conductance is λ_m which is nothing but your specific conductance κ by c where c is mole per meter cube and κ is cements meter inverse now if you now plot if you now plot molar conductance that is λ_m with square root of concentration it has been found that for the it has been found that for the strong electrolyte the curve follows like this that is if you dilute it in this direction if you dilute it then molar conductivity increases so why is this so λ_m molar conductivity should ah should increase when you you know when you dilute the solution now now again λ_m is your κ it is your conductance okay then specific conductance and then inverse of cell constant ok that means $\frac{1}{l}$ ok so the idea is that you have to place your solution you have to place your solution against or in between two electrodes that are separated by unit length unit length l is equal to one ok so therefore if your volume of the solution volume of the solution is v then effectively area of the electrode is nothing but v is equal to e into 1 because a is the area because you have to place your entire solution in between two electrodes those are separate but separated by unit length and your there is no restriction of the of the area of the electrodes so therefore area is freely changeable depending on the dilution of the solution therefore you can write from here v is equal to a so therefore from here you can write λ_m is equal to κ into volume ok so therefore how does λ_m change as a function of dilution so when you dilute means volume is increasing okay and what is going to happen to κ very simple that as i already explained to you here that when you dilute then κ is reducing so therefore there are two opposing factors one is κ which is reducing as a result of dilution and volume which is increasing as

a result of dilution

so what is going to happen that your ultimately it has been found that the effect of change of well volume is much more than the effect of dilution of i mean

effect of lowering of c_{up}

so therefore in effect λ_m is found to increase

so therefore that's

why λ_m as a function of square root if you plot it it follows a trend like this but only

thing is that important point to note is that this type of linear dependence this type of linear

dependence is observed for strong electrolyte strong electrolyte strong electrolyte means the electrolyte which is which is completely ionized when you

dissolve it in water okay but the situation is not

so easy i mean it is not like that like a linear dependence for a weak electrolyte ok

so for weak electrolyte what is happening let me draw it again in a in another piece of paper for weak electrolyte for weak electrolyte ah the plot you know it is square root of c and this is λ_m it follows a trend like this whereas the strong electrolyte follows like this

so this is CH_3COOH and this is say for example KCl this is quite you know understandable i mean why this is increasing like this but in case of weak

electrode you see that as you dilute it there is not much perceptible change in the higher concentration range say for example if your concentration is in mole per liter and the value $\text{cm}^2 \text{mole}^{-1}$ then say for

example it is say about 200 and here it is say for example 0.

2 0.

4 these values are 0.

4 ok

and 0.

2 then you see that in higher concentration region it is almost flat okay it is it is

following the same trend as your you know this axis it is parallel to almost parallel to

x axis but when you decrease the concentration you know use it it follows a trend like this

and in very low concentration region it stiffly rises

so why is it happening this is

something strange ah why strange because it is unlike this strong electrolyte this is

following a different trend why it is like this now one thing that that you should take into

account that this CH_3COOH its a weak electrolyte

so it is not completely ionized

so if you dilute

it then its ionization increases

so that means CH_3COOH it is mostly in this form CH_3COOH minus

so degree of

dissociation if it is α then $1 - \alpha$ then α then α

so therefore degree of

dissociation since degree of dissociation is very small in moderate concentration range therefore you know number of charge carrier that is you know less in this region the moment you keep on i mean moment you increase the dilution that means if you add more of water then the degree of dissociation i mean the amount of dissociation increases and therefore therefore what happens that whatever factors were there like like you know λ_m is equal to κ into v so v factor is there v increases at the same time you know this κ is also increasing because if you dilute it then number of ions number of charge carrier increases so total number of charge carrier increases means your κ although there is a dilution effect but the effect of this increase of charge carrier is coming into action and as a result of which a non-linear dependence of you know non-linear dependence of this this λ_m versus \sqrt{c} plot is there so in case of strong electrolyte you know this for strong electrolyte λ_m that is the molar conductance follows a train like this $\lambda_m = \lambda_m^\infty + a\sqrt{c}$ where λ_m^∞ is a constant quantity and you can understand from here that that if if you go close to zero concentration that is infinitely dilute condition then then whatever λ_m value you are expecting that is nothing but λ_m^∞ .

so it is nothing but the value of λ_m extrapolated to ∞ concentration okay now

so therefore this is called the limiting molar conductance or molar conductance at infinite dilution molar conductance at infinite by infinite dilution one can understand like this that it is a state of dilution at which if you further dilute the solution there is no perceptible change or there is no further change in the conductance value of the solution

so that is called the that is called the state of infinite dilution

so therefore if you have a strong electrolyte if you plot like this then you have got certain points

so so these are all measurable thing

so you measure and then you extrapolate just because the trend is linear

so you extrapolate

so wherever it is extra wherever it is cutting the y axis is nothing but λ_m^∞

so so for for a strong electrolyte the job is easy easier

that you can measure the the value of λ_m at the infinite dilution condition but the problem

comes when you have you have this this weak electrolyte that like acetic acid then you cannot

apply you cannot apply this ah this extrapolation procedure to find out the
 find out the infinitely
 dilution condition this lambda value ok now
 so in that case what you can do
 so it was
 first proposed by kolras long time back that
 so coal russian long time back cholera's it
 is called the cholera's law of independent migration of ions
 so what was the observation
 observation was like if you measure like lambda m 0 for say kcl and then
 lambda m 0 for nacl
 and then again if you measure lambda m 0 kbr lambda m zero in a b r i mean if you
 if you ah take a difference of lambda m zero
 for kcl and nacl then kbr nabr or lambda m 0 k i 0 n a i it is found that its
 value is say close to 23 centimeter square mole inverse ok
 at some given temperature okay in the same way lambda m 0 n a b r minus lambda
 m 0 in a c l is
 equal to lambda m 0 kbr minus lambda m 0 kcl and that comes out to be close to
 2 centimeter square mole inverse that is your molar conductivity at infinite
 dilution if you take
 the difference it is found that this is following like this
 so this is very strange behavior that
 for electrolyte conductor electrolytic when you talk about the electrolyte
 conductance then then
 then it is ah it is very strange ah that kcl minus nacl k b r minus n a b r k
 i minus n a i
 so you
 see that here these co ions here also co ions you see we if we if we want to
 take the difference
 of this lambda m zero with same coins then this difference k plus n a plus
 this is k plus n
 a plus this is k plus n a plus this difference is almost same in the same way
 you know this
 coin sodium same this coin case potassium same
 so b r minus c l b r minus l
 they are follow in the same trend
 so this is a strange behavior
 so so it is proposed
 that that at infinite dilution something is happening what is exactly
 happening conceptually
 that i already have explained to you or discussed that that the conductivity
 of a
 solution is dependent on the number of ions charge carried by ions and speed
 of ions
 so when
 you have reached the state of infinite dilution condition then the number of
 ions present in unit
 cube it is also fixed then charge on the ion it is already fixed only thing is
 that the speed of ions
 now speed of ions is is an important factor for the transport of electricity
 from one position
 to the other now if the speed of ions is not changing any further due to
 dilution as

I mentioned to you that state of infinite dilution is nothing but that can be that can be stated in terms of conductance that if you further dilute the solution it does not bring in any change of the conductance of the solution therefore no further change is happening even if you dilute that means when you dilute solution a say a concentrated solution then suppose initially say there are there are two ions like this so they are interacting one with another and this is an that will be natural consequence because this one is charged this one is also charged so there will be charge charge interaction and many other factors may be solvation and other factors are also important so when you dilute means it is separate so interaction between this ion and that ion is expected to be reduced okay so therefore therefore if this ion is moving if they are in close proximity these two answer in close proximity then the movement of this ion is expected to be affected by the movement of this one and vice versa but if you keep on diluting then a situation will be reached when this ion and the other one they are so much separated that practically there is no effect of the inter ionic attraction or the influence of this ion on this one so therefore the ions can move freely so when ions can move freely that means they can freely contribute towards the conductance of the solution okay so that is why at infinitely dilute condition this one is independent this one is independent so their difference their difference in conductance or molar conductance is also independent I mean it is not also dependent on the co ion because coordinates are also separated from one I mean from from this one this ion or this ion separated a lot so that's why that's why the difference is nothing but the but the difference I mean here $\kappa_{Cl} - \kappa_{Na}$ where they are following the same trend so that is called the Λ^{∞} that is called the limiting molar conductance of independent migration upon and basically basically you can write at infinite dilution $\Lambda_m^{\infty} KCl$ is nothing but $\Lambda_m^{\infty} K + \Lambda_m^{\infty} Cl$ sorry $\Lambda_m^{\infty} Cl - \Lambda_m^{\infty} Na$ so in the same way if this this Λ_m^{∞} you know electrolyte is having more than one ion so accordingly you need to have some stoichiometric coefficient to be included over here okay so so therefore therefore therefore basically at infinite dilution condition each ion will contribute each ion

will contribute to a definite extent toward the total conductance of the solution toward the total conductance of the solution and let me write some numbers i mean some of these numbers for different ions few ions i have i will just write for you so λ_0 it is siemens centimeter square mole inverse for h plus it is 349. 6 for which minus it is 199.

1
k plus it is 73.
5 cl minus it is 76.
3

so you see that that for different ions this contribution this contribution is is different okay so therefore therefore see this independent ion migration this concept has to be applied in in finding out in finding out the ah the conductance ah conductance of the i mean μ_m in finding out the the λ_0 zero λ_m this λ_m zero for weak electrolytes i mean direct you know direct ah finding out of this ah λ_m zero for weak electrolyte is not possible is not possible although that is possible for strong nuclear in that case indirectly you have to find out the contribution of this ok contribution of these ah these ions individual ions and then you can find out you can find out this this λ_m

so this much for today so we will take up this issue i mean ah how to find out i mean how to make use of this λ_m zero for a weak electrolyte in finding out in finding out some important quantity important quantity important characteristic quantity of the weak electrode so what we have learnt today

so we started with this conductance ok now we have talked about this metallic conductor then some idea of the you know basically this insulator then the semiconductor we have just given some example that's it and then we have we have we entered into this electrolytic conductor because in electrochemistry this ah this is relevant in electrochemistry so electrolyte conductor we have we have entered into and the cause of this this conductance we ah discussed and then we we have used this the concept of simple chemistry concept to to know how this ah you know this conductance and specific conductance these ah this will will you know vary as a function of concentration so and and we we try to understand this this variation of molar conductance as a function of concentration for strong electrolyte and for electro weak electrolyte the direct determination of this ah λ_m by electr by this ah graphical

extrapolation is not possible

so in that case we need to find out this some some you know round about way in in in getting the value of λ_m^∞ for weak electrolytes and and will take up this

application of this λ_m^∞ measurement for for weak electrolyte in the next class so

till then thats all for today thank you you

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