Elementary Electrochemistry

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Lecture 32

Ionic Strength of an Electrolyte and its Importance

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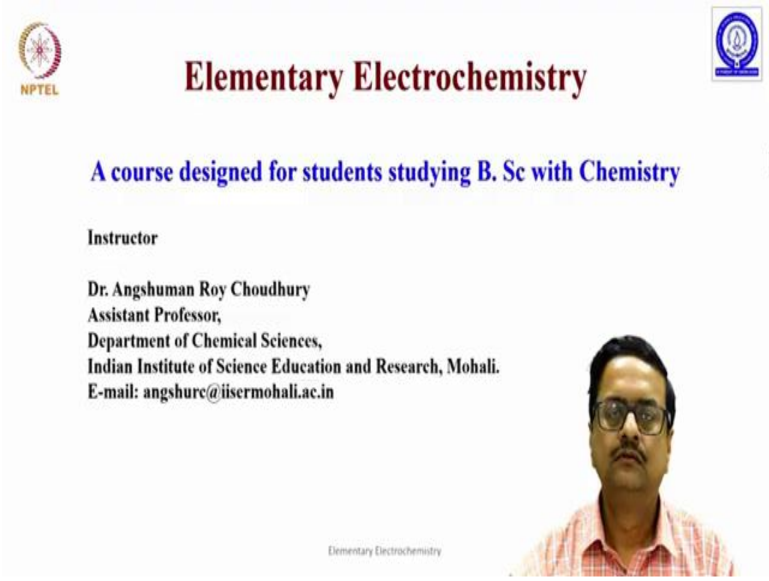

Welcome back to the course Elementary Electrochemistry, we have now started our week 7.

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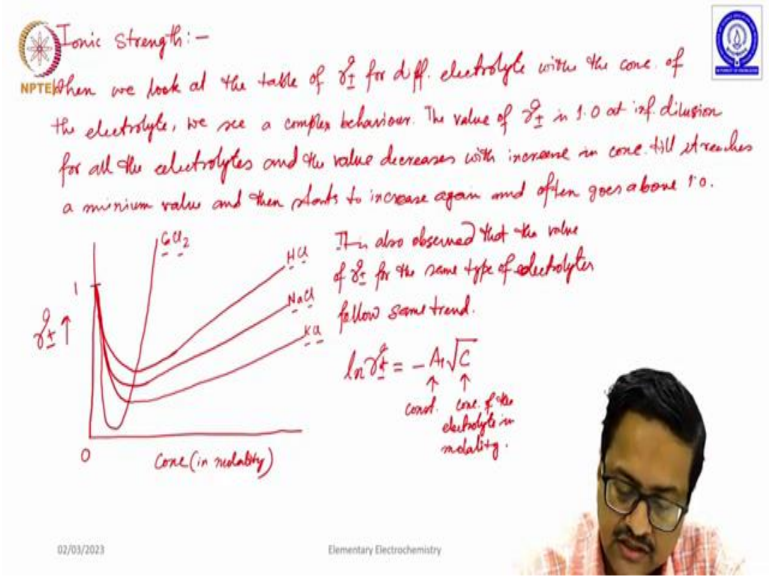

And in this week, we are going to start discussing about the Ionic strength of an electrolyte and its importance. So, when we look at the table in a textbook, if you look at a table in a textbook of the values of gamma plus minus for different electrolyte with the concentration of the electrolyte, we see a complex behaviour. The value of gamma plus minus is 1 at infinite dilution for all the electrolytes and the value decreases with increase in concentration till it reaches a minimum value and then starts to increase again and often goes above 1.0. So, when we plot these values of gamma plus minus versus concentration in molality for various electrolytes, we see a plot like this what I am going to draw here, concentration in molality versus gamma plus minus on Y axis with a value of 1 for this concentration 0.

So, what we see for solutions like for what we see is for HCL what we see is like this, for NaCl it follows nearly the same like HCL to certain value and then it deviates from the value of HCL, so this is for NaCl, HCl trend is observed for KCl, but then at some point it again deviates from NaCl as well and we see a pique layer behaviour for calcium chloride which goes further down and increases sharp and goes high above 1 even at a very low concentration.

So, this indicates something about the dependence of gamma plus minus on the nature of cation or specifically the charge of that cation. So, if it is also observed that the value of gamma plus minus for the same type of electrolytes follow same trend that is here you have Uni univalent they follow a similar trend where you have bivalent was univalent electrolyte the nature that you see is different.

And most of them are very similar at low concentration. So, an empirical relation for gamma plus minus versus concentration also was derived based on the experimental values that were observed and that empirical relationship is Ln gamma plus minus is equal to minus A1 into square root of C where A1 is a constant quantity and C is the concentration of the electrolyte in molality, this is again an empirical relation that was derived based on the experimental observations of gamma plus minus.

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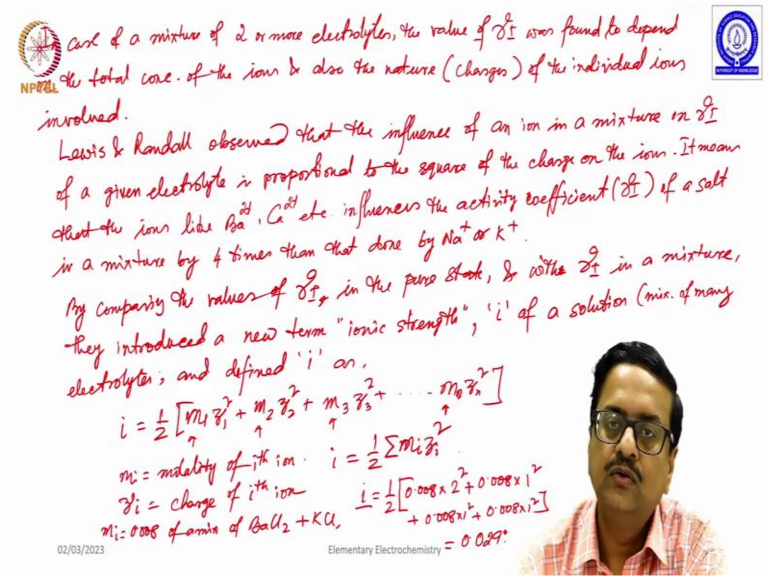

In case of a mixture of 2 or more electrolytes the value of gamma plus minus was found to depend on the total concentration of the ions and also the nature that is the charges of the individual ions involved. So, based on many several experiments on strong electrolytes Lewis and Randall observed that the influence of an ion in a mixture on gamma plus minus of a given electrolyte is proportional to the square of the charge on the ions. It means that the ions like barium 2 plus calcium 2 plus etcetera influences the activity or the other activity coefficient that is gamma plus minus of a salt in a mixture by 4 times then that done by Na plus or K plus which are monovalent cations.

So, by comparing the values of gamma plus minus in the pure state and with the gamma plus minus in a mixture, they introduced a new term called the ionic strength which is written as small i of a solution which is essentially a mixture of many electrolytes and defined i that is the i strength as i equal to half of m1 z1 square plus m2 z2 square plus m3 z3 square plus dot dot mn zn square that means there are n number of ions may be cation anion it does not matter and m terms are the corresponding concentration of those ions in terms of molality.

So, mi is molality of ith ion and zi is molality of the ith sorry the charge of the charge of ith ion. So, i is equal to nothing but half of sum over mi zi square, so just to give you an an idea of the ionic strength if mi for all the ions is 0.008 of a mixture of BaCl2 plus KCl, so then you should calculate i equal to half of 0.008 into 2 square, 2 square plus 0.008 into 1 square that is for barium chloride plus 0.008 into 1 square plus 0.008 into 1 square for KCl.

So, when you do this calculation the value of i turns out to be 0.029. So, this is the ionic strength of this solution which turns out to be a mixture of two different strong electrolytes.

So, this is an important parameter to identify how, what is the strength of a solution of two or more electrolytes.

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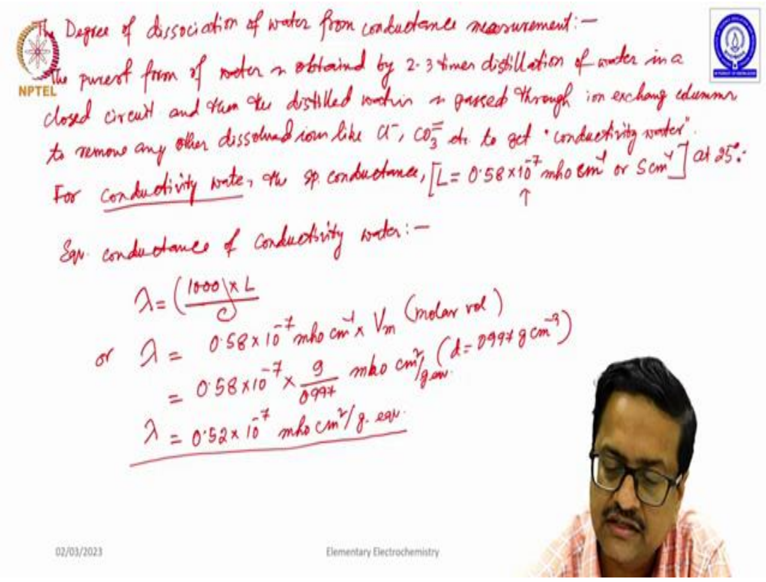

So, now let us try to see how can we estimate the degree of dissociation of water from conductance measurement, see for conductance measurement we need to get a very high-quality water which essentially should not be dissociated and should not be conducting electricity but that is practically impossible.

So, the purest form of water is obtained by 2 to 3 times distillation of water in a closed circuit which essentially means that you distilled water from first container collect it in a second container which is isolated from the environment and then use the second container as a boiler boil that water again collect the water vapour in a third container and do the same again, so you do a three times distillation in a closed system and collect that fresh water.

And then the distilled water is passed through ion exchange columns to remove any other dissolved ions, like sometimes you may have still have a dissolved chloride, carbonate, etcetera, to get something called a conductivity water. So, we use this conductivity water for all our practical experimental applications.

So, this the for this conductivity water, the much specific conductance that is L is determined to be 0.58 into 10 to the power minus 7 mho centimetre inverse or that is Siemens centimetre inverse, you see that the value is in 10 to the power minus 7 that means the resistance of this solution is extremely high.

So, for this solution one for this water conductivity water one can calculate the equivalent conductance that is lambda equal to 1000 into L by C or lambda is equal to this L is 0.58 sorry 0.05 no, the value of L is 0.58 into 10 to the power minus 7 mho centimetre inverse into this term is nothing but the molar volume of water.

So, now you can do this calculation easily 0.58 into 10 to the power minus 7 molar volume of water is nothing but 9 by 0.997 and the unit becomes mho centimetre square where density of water is 0.997 gram per C 3. So, you can calculate this value as 0.52 into 10 to the power minus 7 per gram equivalent in meter, so mho centimetre square per gram equivalent. So, this is the equivalent conductance for water and this value is at 25 degree centigrade as usual.

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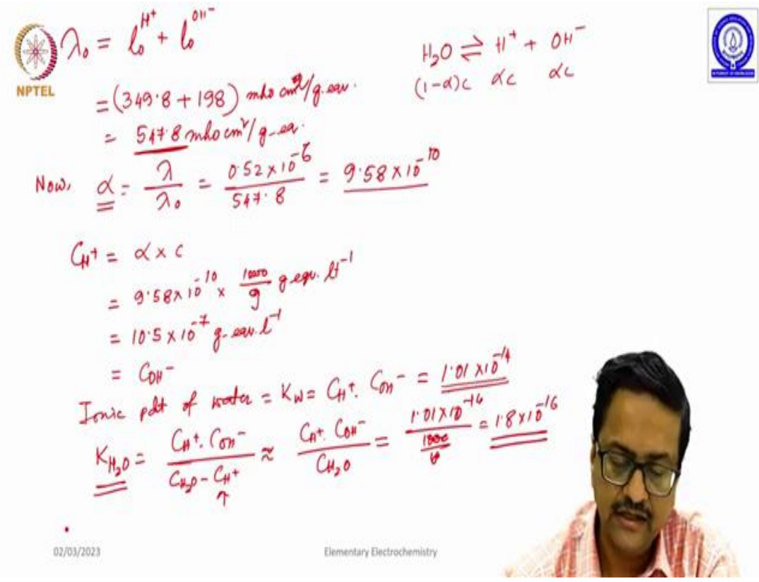

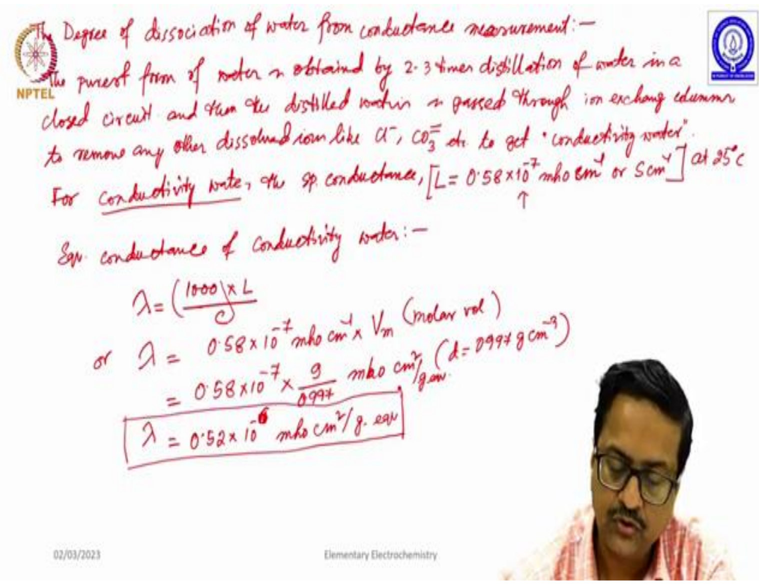

So, now if you look the values for the lambda 0 that is the equivalent conductance at infinite dilution for water if I want to calculate I need the value for L 0 for H plus plus L 0 of OH minus. So, one can look at the corresponding table in the textbook and find the values for L 0 for H plus which happens to be 349.8 and the other one happens to be 198, so when you add these two of course the unit is mho centimetre square per gram equivalent which is equal to 547.8 mho centimetre square per gram equivalent.

Now, we can easily calculate the value of degree of dissociation that is alpha as lambda by lambda 0 which we have discussed in the previous class, so you can calculate it as 0.52 into 10 to the power minus 6, let me check whether I wrote 6 or 7 here it should be 6 please correct it, by 547.8 the unit gets cancelled, so the degree of dissociation of water is nothing but 9.58 into 10 to the power minus 10.

So, now from this if we want to calculate the concentration of H plus in this conductivity water it is nothing but the degree of dissociation alpha into concentration of water that is alpha is 9.58 into 10 to the power minus 10 and concentration of water is again 1000 by 9 gram equivalent per litre or you can calculate it as 10.5 into 10 to the power minus 7 gram equivalent per litre, which is also same as C OH minus because both H plus and OH minus are dissociated from water. So, if the degree of dissociation is alpha in terms of concentration it is alpha into sorry it is 1 minus alpha, alpha and Alpha, so in terms of concentration it is multiplied by C.

So, then one can calculate the ionic product of water as equal to k w which is CH plus into C OH minus, if you do this product it turns out to be 1.01 into 10 to the power minus 14 and equilibrium constant of this dissociation of water that is K water is nothing but CH plus into C OH minus divided by CH2 O minus CH plus which is sort of equal to CH plus into C OH minus divided by CH2 O, because CH plus is extremely small compared to the overall concentration of un-dissociated water.

Now, if you do this calculation you will get the value as 1.01 into 10 to the power minus 14 for this product and concentration of water is 1000 by 18 which is equal to 1.8 into 10 to the power minus 16. So, these are the two very important physical quantities for water that is the ionic product of water and the equilibrium constant for the dissociation of water obtained from the value of alpha that is the degree of dissociation of water and this value of degree of dissociation of water is obtained from the limiting conductivities of the cation and anion and also the equivalent conductance of very pure water which is the conductivity water. So, along with this we I am going to conclude today's lecture and I will give you some of the problems in the next class on these topics. Thank you.