Elementary Electrochemistry
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Lecture 34
Solubility and Activity Product

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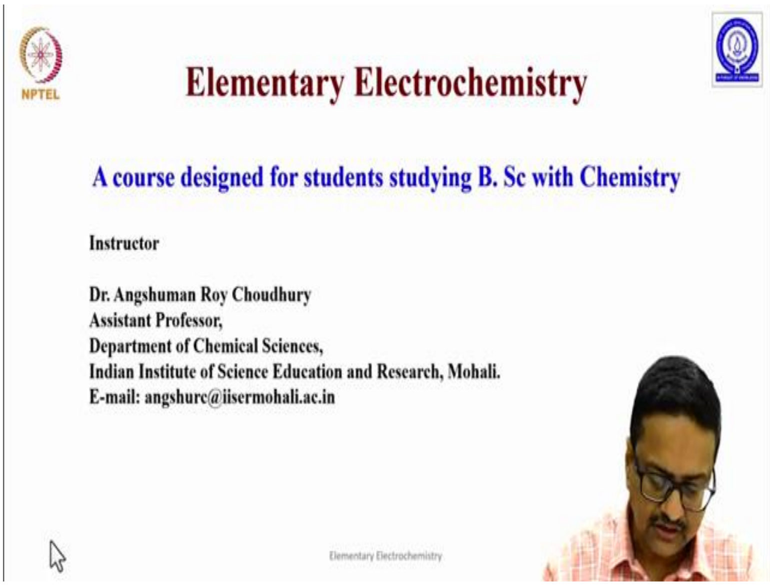

Welcome back to the course entitled Elementary Electrochemistry we are in the seventh week of this course and we are almost towards the end of the contents.So, today we are going to discuss how one can calculate or determine the ionic product or the other the solubility product or activity solubility product of a sparingly soluble electrolyte using the concepts that we have learned.

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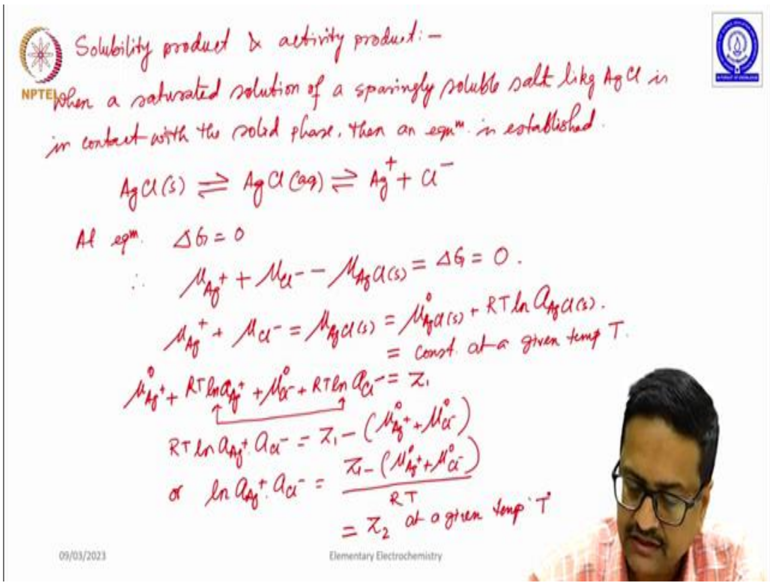

So, we will discuss today the determination of solubility product and activity product. So, when a saturated solution of a sparingly soluble salt like AgCl is in contact with the solid phase then and equilibrium is established. So, what is that equilibrium? The equilibrium is AgCl solid is in equilibrium with AgCl aquatic and further there is an equilibrium between the dissociated Ag plus and Cl minus.

So, at equilibrium delta G for this reaction is 0, so then one can write that mu Ag plus mu Cl minus minus mu AgCl solid is equal to delta G is equal to 0. So, now we rewrite this equation as mu Ag plus plus mu Cl minus is equal to mu of AgCl solid which then can be written as mu 0 AgCl solid plus RT ln activity of AgCl solid, this quantity on the right-hand side is a constant quantity at a given temperature t. So, suppose we write this constant as Z 1 and the left-hand side we can rewrite as mu 0 Ag plus plus RT ln activity of Ag plus mu 0 Cl minus plus RT ln activity of Cl minus.

So, now we can further rewrite by taking these two quantities together we can write RT ln activity of Ag plus activity of Cl minus equal to Z 1 minus mu 0 of Ag plus plus mu 0 of Cl minus or ln activity of Ag plus and to activity of Cl minus equal to Z 1 minus mu 0 Ag plus mu 0 Cl minus divided by RT which is again another constant say Z 2 at a given temperature t.

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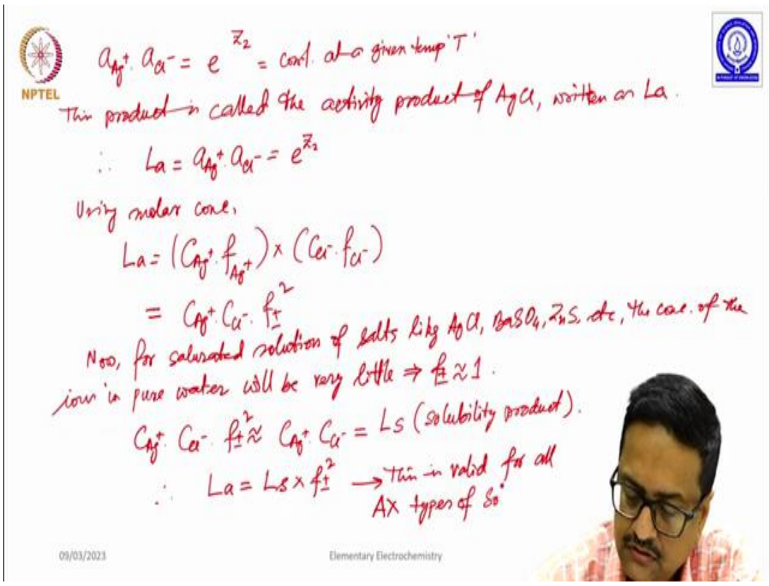

Therefore, one can further write that activity of Ag plus and to activity of Cl minus equal to e to the power minus Z 2 sorry e to the power Z 2, this is a constant at a given temperature T, because Z 2 is constant at a given temperature T, this product is called the activity product of AgCl, which is written as la.

So, we write la equal to activity of Ag plus activity of Cl minus which is equal to e to the power of Z 2. Using molar concentrations one can rewrite this la equal to concentration of Ag plus into activity coefficient of Ag plus into concentration of Cl minus into activity of Cl minus which is nothing but concentration of Ag plus into concentration of Cl minus into f plus minus square.

So, now for saturated solutions of salts like AgCl BaSo4, zinc sulphide etcetera the concentration of the ions in pure water will be very little which indicates that one can assume f plus minus to be very close to 1. So, one can assume its ideal behaviour and you can assume that the mean activity coefficient for both cation and anion will be close to 1.

So, concentration of Ag plus multiplied by concentration of Cl minus into f plus minus square can be equated to concentration of Ag plus into concentration of Cl minus which is equal to Ls that is the solubility product. So, then one can write for all other solutions La equal to Ls into f plus minus squared and this is valid for all Ax types of solids or salts.

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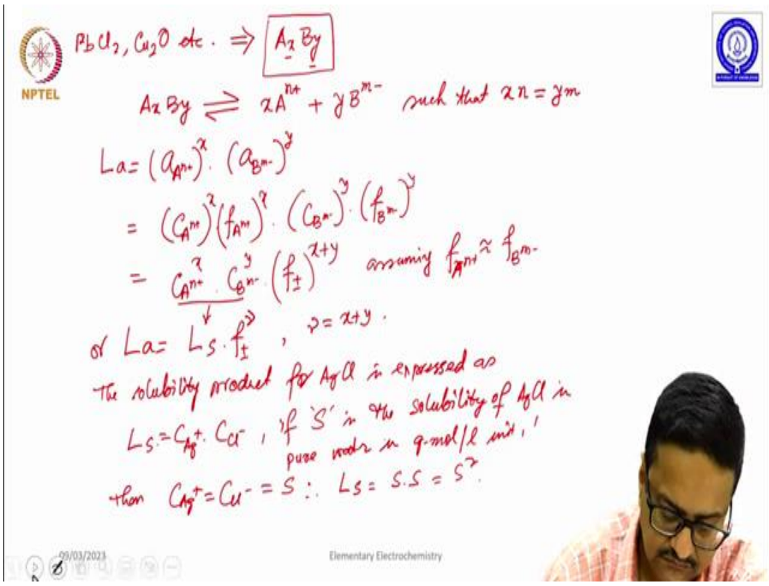

But then all these solids or salts are not like Ax type, say for example there are salts like PbCl2, Fe3, CO2 O etc which are very sparingly soluble in water. So, for those we assume the formula to be Ax By where A and B have different oxidation states different charges as a result this stoichiometric coefficients are not same. So, when we consider this salt Ax By in water it dissociates as xA n plus plus yB m minus such that xn equal to ym to maintain electro neutrality of the solution.

So, using this equation La one can write La equal to activity of An plus to the power x into activity of B m minus to the power y and now when you replace the activity terms with concentration you can write concentration of An plus to the power x into f An plus to the power x into concentration of B m minus to the power y into f B m minus to the power y.

Further one can write that C An plus to the power x C B m minus to the power y into f plus minus to the power x plus y assuming f An plus is same as f Bm minus or La is equal to Ls which is this quantity multiplied by f plus minus to the power Nu, where Nu is nothing but the sum of these two isometric coefficients x plus y.

So, now the solubility product for AgCl is expressed as S, sorry expressed as LS into is equal to concentration of Ag plus into concentration of Cl minus, if S is the solubility of AgCl in pure water in gram moles per litre unit then concentration of Ag plus is equal to concentration of Cl minus is equal to S, therefore Ls equal to S into S that is S square, this is for one is to one salt like silver chloride.

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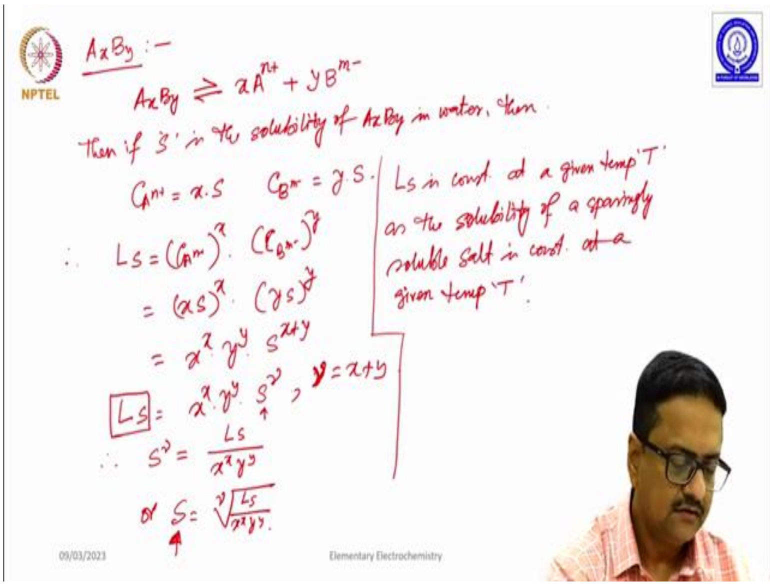

But then if we have a salt like this if we have a salt where the stoichiometric coefficients are different what will be the expression for the corresponding solubility product, as we have already written Ax By we will dissociate as x into An plus plus y into B m minus then if S is the solubility of Ax By in water, then concentration of An plus is nothing but x into S similarly concentration of B m minus is y into S.

Therefore, to calculate Ls we need C An plus to the power x C concentration of B m minus to the power y, so we have x S to the power x, y S to the power y which is equal to x to the power x, y to the power y and S to the power x plus y which one can write as x to the power x y to the power y, S to the power Nu where Nu is equal to which we have already written Nu is equal to x plus y. Therefore, S to the power Nu is equal to Ls by x to the power x, y to the power y or S equal to Nu at root of Ls by x to the power x, y to the power y.

So, if you know the soluble you can determine if you know the solubility you can determine the solubility product, if you can determine the solubility product by some titrimetric method or by a conductor metric method then you can determine the solubility of a sparingly soluble salt, what we see here is that Ls is constant at a given temperature T as the solubility of a sparingly soluble salt is constant at a giving temperature.

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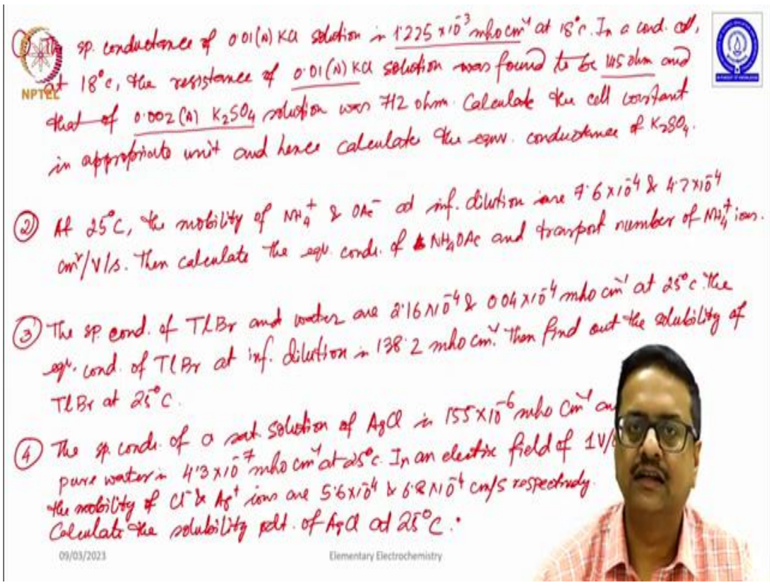

So, now I would like to give a few problems to you to solve based on the concepts that you have learned in using conductivity and conductivity measurements. The specific conductance of 0.01 normal KCl solution is 1.225 into 10 to the power minus 3 mho centimetre inverse at 18 degree centigrade in a conductivity cell at 18 degree C the resistance of 0.01 normal KCl solution was found to be 145 ohm and that of 0.002 normal K2So4 solution was 712 ohm calculate the cell constant in appropriate unit and hence calculate the equivalent conductance of K2So4.

So, here what we have given is the specific conductance using this value for specific conductance and the corresponding resistance one can determine the value of cell constant and once you have determined the value of cell constant then it should not be a difficulty to find out the specific conductance of this particular solution using the same expression and then you can calculate the equivalent conductance which is nothing but 1000 by C into specific conductance.

Question number 2, at 25 degree Centigrade the mobility of NH4 plus and OAc minus at infinite dilution is dilution R 7.6 into 10 to the power minus 4 and 4.2 into 10 to the power minus 4-centimetre square per volt per second. Then calculate the equivalent conductance of NH4 OAc that is ammonium acetate and transport number of NH4 plus ions. So, we have already discussed about the relationship between ionic mobility and ion conductivity from that you should be able to calculate the equivalent conductance and then one can easily calculate the corresponding transport numbers.

Question number 3 is the specific conductance of thallium bromide and water are 2.16 into 10 to the power minus 4 and 0.04 into 10 to the power minus 4 mho per centimetre at 25 degree centigrade, the equivalent conductance of thallium bromide at infinite dilution is 138.2 mho centimetre square. Then find out the solubility of thallium bromide at 25 degree centigrade.

And the 4th question is this one the specific conductance of a saturated solution of AgCl is 155 that sorry 1.55 into 10 to the power minus 6 mho centimetre inverse and that of pure water is 4.3 into 10 to the power minus 7 mho centimetre inverse at 25 degree centigrade in an electric field of 1 volt per centimetre the mobility of Cl minus and Ag plus ions are 5.6 into 10 to the power minus 4 and 6.8 into 10 to the minus 4 centimetre per second respectively. Calculate the solubility product of AgCl at 25 degree centigrade.

So, we will have another theory class in the next session and after that you will have the last week which will be the demonstration of conductometry related experiments followed by one more lecture where we will discuss about the solution or how to do the graph plotting out from those experimental data. Thank you very much.