Elementary Electrochemistry
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Lecture 35
Applications of EMF and Conductance Measurement

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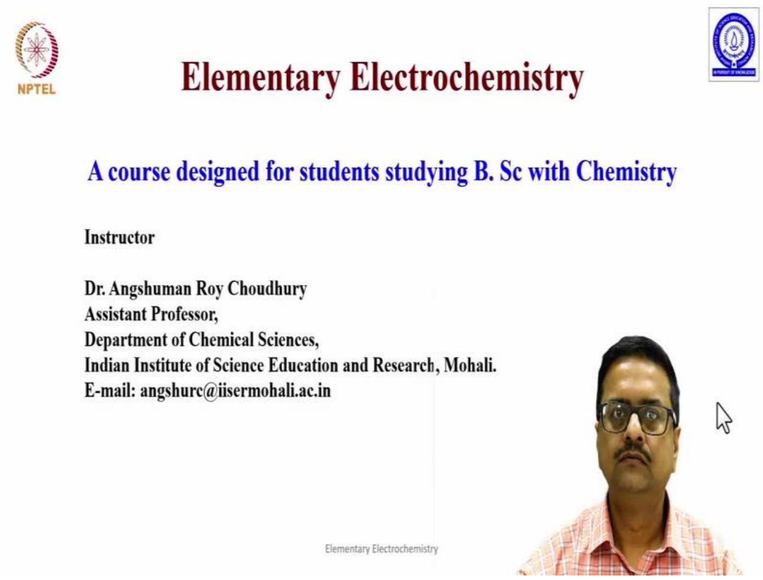

Elementary Electrochemistry

A course designed for students studying B. Sc with Chemistry

Instructor

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Welcome back to the course entitled Elementary Electrochemistry. In today's class, we are going to discuss some of the applications of conductance measurement and also the EMF measurements. We are now almost towards the end of this course, so I will just briefly discussed a couple of methods for determination of physical properties.

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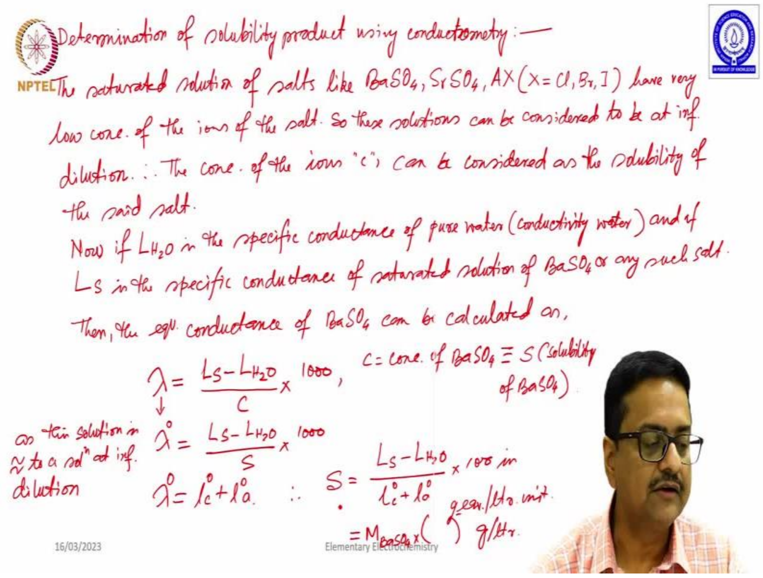

Determination of solubility product using conductometry:—

The saturated solution of salts like $BaSO_4$, $SrSO_4$, AX ($X = Cl, Br, I$) have very low conc. of the ions of the salt. So these solutions can be considered to be at inf. dilution. ∴ The conc. of the ions "c", can be considered as the solubility of the said salt.

Now if L_{H_2O} is the specific conductance of pure water (conductivity water) and if L_S is the specific conductance of saturated solution of $BaSO_4$ or any such salt. Then, the eqv. conductance of $BaSO_4$ can be calculated as,

$$\lambda = \frac{L_S - L_{H_2O}}{C} \times 1000, \quad C = \text{conc. of } BaSO_4 \equiv S \text{ (solubility of } BaSO_4)$$

$$\downarrow$$

as this solution is ≈ to a solⁿ at inf. dilution

$$\lambda^0 = \frac{L_S - L_{H_2O}}{S} \times 1000$$

$$\lambda^0 = l_c^0 + l_a^0 \quad \therefore \quad S = \frac{L_S - L_{H_2O}}{l_c^0 + l_a^0} \times 100 \text{ in g eqv./ltr. unit}$$

$$= M_{BaSO_4} \times (\quad) \text{ g/ltr.}$$

So, we want to talk today about the determination of solubility product using conductometry. So, what do we know about sparingly soluble salts? This sparingly soluble salts are technically immiscible or insoluble in water. So, when you try to mix something like barium sulphate or silver chloride or strontium sulphate etc. in water and star for a very-very long time, a very small amount of that salt will dissolve in water and make the solution conducting.

So, the saturated solution of salts like barium sulphate, strontium sulphate, silver halide like I would say I should write AX, where X equal to chlorine, bromine and iodine, de-saturated solution of salts like these compounds have very low concentration of the ions of the salt. So, these solutions can be considered to be at infinite dilutions therefore, the concentration of the ions which in general is written as C can be considered as the solubility of the said salt.

Now, if L H2O is the specific conductance of pure water, we have discussed about this water because this water is called also called conductivity water which is of course prepared by multiple times distillation of water and then passing that water through ion exchange columns to remove any residual ions so that you have very minimal ions dissociated from water which corresponds to the degree of dissociation of water. So, this L H2O is very small but it is a particular quantity this is a value of specific conductance for such a pure water can be determine.

And if Ls is the specific conductance of saturated solution of Ba SO 4 or any such salt. How do we make that saturated solution then, we first take a large quantity large excess of conductivity water and a pinch of solid barium sulphate or silver chloride or silver nitrate to that and start that suspension for a sufficiently long time maybe 24 hours, whatever amount of salt dissolves in that makes it a saturated solution of barium sulphate or silver chloride or silver hydride or strontium sulphate whatever it is. And then we let the salt precipitate whatever has undissolved and we use the supernatant liquid for further measurement.

So, then the equivalent conductance of Ba SO 4 can be calculated as lambda equal to L s minus L water divided by C into 1000, where C is the concentration of Ba SO 4 which is again equivalent to S the solubility of Ba SO 4. So, one can write lambda equal to L s minus L water by S into 1000 and this lambda also can be written as lambda 0 as the solution is equivalent to a solution at infinite dilution that is why lambda can be written equal to lambda 0.

So, now what do we know? We know that lambda 0 can be written as l0 c plus l0a therefore, the solubility the value of solubility can be calculated by Ls minus L water divided by lc0 plus la0 into 1000 in gram equivalent per liter unit. To this if you multiply by molecular weight of Ba SO 4 into this quantity then it becomes grams per liter unit in terms of solubility, solubility in terms of grams per liter unit.

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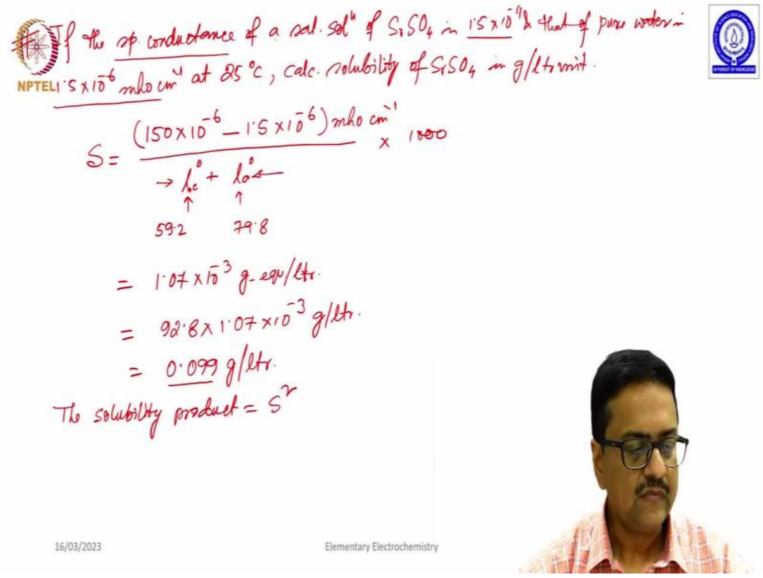

If the sp. conductance of a sat. sol^n of $SrSO_4$ is 1.5×10^{-4} & that of pure water is 1.5×10^{-6} mho cm^{-1} at 25 °C, calc. solubility of $SrSO_4$ in g/ltr unit.

$$S = \frac{(150\times10^{-6} - 1.5\times10^{-6})\text{ mho cm}^{-1}}{\rightarrow \underset{\underset{59.2}{\uparrow}}{l_c^0} + \underset{\underset{79.8}{\uparrow}}{l_a^0} \leftarrow} \times 1000$$

$= 1.07\times10^{-3}$ g-equ/ltr.

$= 92.8\times1.07\times10^{-3}$ g/ltr.

$= \underline{0.099}$ g/ltr.

The solubility product $= S^2$

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So, let us see this using a particular problem. If the specific conductance of a saturated solution of strontium sulphate is 1.5 into 10 to the power minus 4 and that of pure water is 1.5 into 10 to the power minus 6 mho centimeter inverse at 25 degrees centigrade calculate solubility of SiSO 4 in grams per liter unit. So, what we should do? We should do S equal to L s which is 1.5 into 10 to the power minus 4 which is 150 into 10 to the power minus 6 minus 1.5 into 10 to the power minus 6 mho centimeter inverse divided by the lambda 0 that is lc0 plus la0 into 1000.

So, now one has to find these values from the textbook in the table for the limiting ion conductances for strontium and sulphate and when you find those values, you will see that they are 59.2 and 79.8, and when you apply those values and do the calculation, you will end up getting 1.07 into 10 to the power minus 3 grams equivalent per liter.

So, now, this quantity has to be multiplied by the molecular weight of strontium sulphate. So, when you multiply this by m you end up getting 92 point sorry the molecular weight of strontium sulphate is 92.8 into 1.07 into 10 to the power minus 3 grams per liter, so that you can get is 0.099 grams per liter.

So, when this is the solubility of barium sulphate one can calculate the solubility product which in this case is S square. So, you can simply multiply this by this and get the value of solubility product for strontium sulphate. So, this is how one can use the method of conductometry measurements for determination of solubility product.

So, in this experiment what we need to do? We need to determine the specific conductance of a saturated solution of strontium sulphate, take the specific conductance of pure water from the standard table, take the values of lc and la0 from the standard table and calculate the solubility of strontium sulphate.

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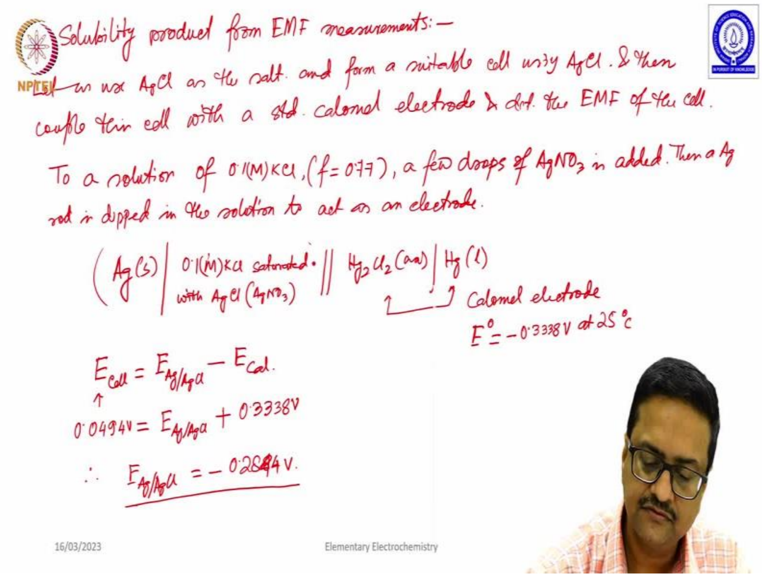

Solubility product from EMF measurements:-

Let us use AgCl as the salt and form a suitable cell using AgCl. & then couple this cell with a std. calomel electrode & det. the EMF of the cell.

To a solution of 0.1(M) KCl, ($f = 0.77$), a few drops of $AgNO_3$ is added. Then a Ag rod is dipped in the solution to act as an electrode.

$$\left(Ag(s) \,\middle|\, \begin{matrix} 0.1(M)\,KCl \text{ saturated} \\ \text{with } AgCl\ (AgNO_3) \end{matrix} \,\middle\|\, Hg_2Cl_2(aq) \,\middle|\, Hg(l) \right.$$

Calomel electrode

$E^0 = -0.3338\,V$ at 25 °C

$$E_{Cell} = E_{Ag/AgCl} - E_{Cal.}$$

$$0.0494V = E_{Ag/AgCl} + 0.3338V$$

$$\therefore \underline{E_{Ag/AgCl} = -0.2844\,V.}$$

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In the same way one can determine the solubility product from EMF measurements. So, here let us use Ag Cl as the sparingly soluble salt and form a suitable cell using Ag Cl and then couple this say cell with a standard calomel electrode and determine the EMF of the cell. So, what we do? We take a 0.1 molar K Cl solution, so to a solution of 0.1 molar K Cl for whom the value of f is 0.77, a few drops off Ag NO 3 is added.

What will happen when you have large excess of chloride ion in a solution like 0.1 molar K Cl you are adding one or 2 drops of silver nitrate solution almost all silver nitrate salt silver ions will form its chloride salt and get precipitated and very-very small amount of silver plus ion will remain in solution as we indicate it will indicate the solubility of that particular salt.

Then, a silver rod is dipped in the solution to act as an electrode. So, what we have is a silver electrode, silver solid as electrode in this chamber we have 0.1 molar K Cl which is saturated with AgCl which came from AgNO3, a couple of drops of AgNO3 and then this half-cell is coupled with the Hg2 Cl2 aqueous with Hg liquid which corresponds to the calomel electrode whose E0 value is 0.0494 volt at 25 degrees centigrade. So, now using our previous understanding of EMF of a cell one can write E cell equal to E Ag AgCl minus calomel I am sorry the EMF of calomel electrode is minus 0.3338 volt.

So, now when we have constructed this cell, one can determine the E cell using a potentiometer and suppose the E cell that we get from the potentiometer turns out to be 0.0494 volts. And E Ag is not known and E calomel which is a minus that when you write here it will become 0.3338, both in terms of volt. So, therefore, E Ag, AgCl will turn out to be minus 2884 0.288 sorry 0.2844 volts. So, this is the potential of that half-cell.

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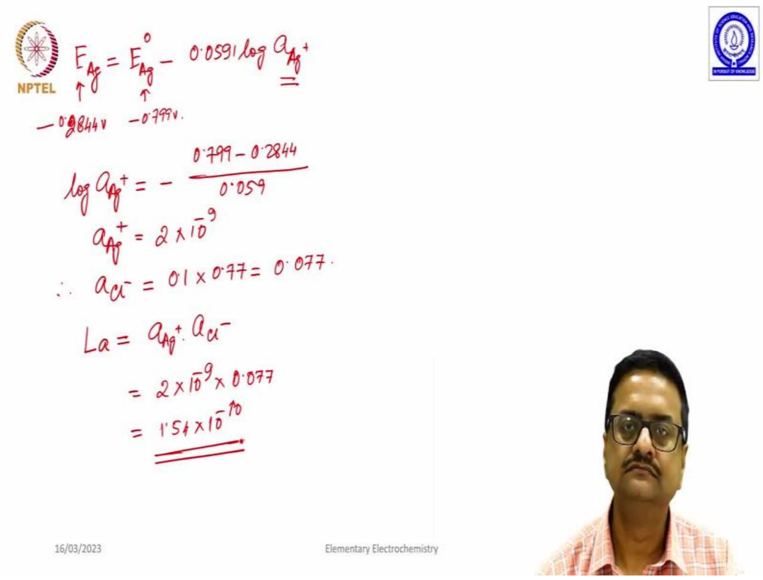

$$\underset{\underset{-0\cdot2844\,v}{\uparrow}}{E_{Ag}} = \underset{\underset{-0\cdot799\,v.}{\uparrow}}{E^{0}_{Ag}} - 0\cdot0591 \log \underline{\underline{a_{Ag^+}}}$$

$$\log a_{Ag^+} = -\frac{0\cdot799 - 0\cdot2844}{0\cdot059}$$

$$a_{Ag^+} = 2 \times 10^{-9}$$

$$\therefore\ a_{Cl^-} = 0\cdot1 \times 0\cdot77 = 0\cdot077.$$

$$L_a = a_{Ag^+} \cdot a_{Cl^-}$$

$$= 2 \times 10^{-9} \times 0\cdot077$$

$$= \underline{\underline{1\cdot54 \times 10^{-10}}}$$

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So, now when we write E Ag equal to E0 Ag minus 0.0591 log activity of Ag plus. So, now we have determined that E Ag as minus 0.02844 volts and this E Ag is again minus 0.799 volt. So, now, when you try to calculate the activity of Ag plus we write log activity of Ag plus is equal to we have a minus sign 0.799 minus 0.2844 divided by 0.059 which is equal to.

So, I do not have the value for this, does not matter. So, from this one can calculate activity of Ag plus as 2 into 10 to the power minus 9 therefore, activity of chloride will also be the concentration will be the concentration of K Cl that is 0.1 into the mean activity coefficient that is the value of f which is 0.77, so we get this value is 0.077.

So, here the activity solubility product l a is nothing but a of Ag plus into a of Cl minus which you can now do a simple multiplication 2 into 10 to the minus 9 into 0.077 which is equal to 1.54 into 10 to the power minus 10. So, this is the solubility product of silver chloride determined using the method of EMF measurement.

So, this is how one can easily determine the EMF of one can easily determine the solubility product of a sparingly soluble salt using 2 different methods conductometry method and a potentiometric method. So, we will continue from here in the next class and talk about how one can determine the dissociation constant of weak acids weak di-basic acids like oxalic acid. Thank you.