Elementary Electrochemistry
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Lecture 31
Activities in Electrolytic Solutions

Welcome back to the course entitled Elementary Electrochemistry. In the previous lecture, we were discussing about various applications of conductance measurement and we discussed how one can perform those experiments, we will demonstrate those experiments in the following week.

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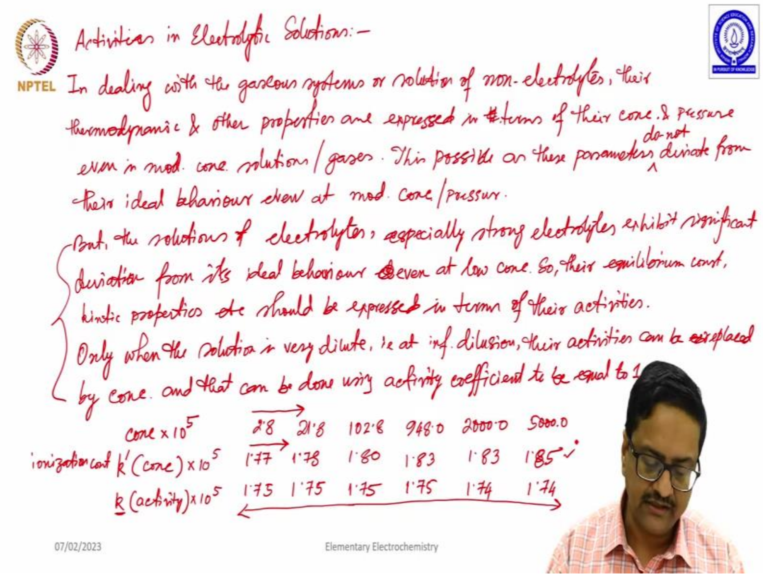

Activities in Electrolytic Solutions:-

In dealing with the gaseous systems or solution of non-electrolytes, their thermodynamic & other properties are expressed in terms of their conc. & pressure even in mod. conc. solutions / gases. This possible as these parameters do not deviate from their ideal behaviour even at mod. conc / pressure.

But, the solutions of electrolytes, especially strong electrolytes exhibit significant deviation from its ideal behaviour even at low conc. So, their equilibrium const, kinetic properties etc should be expressed in terms of their activities.

Only when the solution is very dilute, ie at inf. dilusion, their activities can be replaced by conc. and that can be done using activity coefficient to be equal to 1

conc $\times 10^5$	2.8	21.8	102.8	948.0	2000.0	5000.0
ionization const k'(conc) $\times 10^5$	1.77	1.78	1.80	1.83	1.83	1.85 ✓
$\underline{k}$(activity) $\times 10^5$	1.75	1.75	1.75	1.75	1.74	1.74

07/02/2023 Elementary Electrochemistry

In this lecture, we are going to discuss about the activities in electrolytic solutions. As we know in dealing with the gaseous systems or solutions of non-electrolytes their power dynamic and other properties are expressed in terms of their concentration and pressure even in moderately concentrated solutions or gases gas mixtures. And this is possible as these parameters deviate from their ideal behavior, these parameters do not deviate from their ideal behavior even at moderate concentration or pressure.

But the solutions of electrolytes especially strong electrolytes exhibit significant deviations from its ideal behavior even at low concentrations this you have seen in the previous lectures. So, their equilibrium constant kinetic properties et cetera should be expressed in terms of their activities. Only when the solution is very dilute that is at in finite dilution their activities can be replaced by concentration and that can be done using activity coefficient will be equal to 1.

So, this statement is an outcome of a table which I am going to quickly write here it is the table for acetic acid where we have a varying concentration and the values that are measured are k prime in terms of concentration, this k prime is ionization constant and this value k using activity. So, k prime these numbers are to be multiplied by 10 to the power these are multiplied by 10 to the power 5 into also 10 to the power 5.

So, I am talking about concentration. So, when I am writing 2.8, that means the concentration is 2.8 to 10 to the power 5 molar then the values are 1.77 and 1.75, you can see that they are fairly close or very similar. When the concentration is increased about 10 times from 2.8, it goes to 21.8 you see that the value of k prime is 1.78.

And these for 1.75 still they are fairly similar. But then when we further increase it by say 5 times about 102.8, this now starts to change then further increased by about 9 times to 948.0 the values changed to 1.83 and 1.75 which remains to be the same. Then at 2,000.0 it is 1.83 and 1.74 whereas, at 5000 it is 1.85 and 1.74.

So, what we see is that with increase in concentration, the value of k prime increases from lower concentration to higher concentration. Whereas, the value of k that is the value of ionization constant in terms of activity remains to be same throughout the range of concentrations. So, you can understand the difference between 2 and 5000 is an order of 25,000 times.

So, the constant it can increase in concentration, the value of k prime has increased significantly whereas that of k did not increase. So, we need to develop a relationship between the concentration and activity and then use appropriate values of concentration to get the correct activity et cetera.

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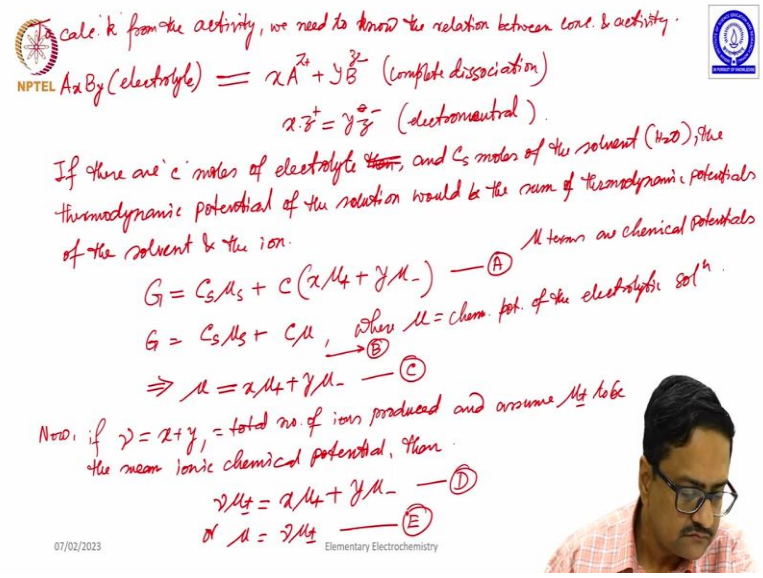

To calc. k from the activity, we need to know the relation between conc. & activity.

A_xB_y (electrolyte) $\rightleftharpoons xA^{z+} + yB^{z-}$ (complete dissociation)

$x \cdot z^{+} = y z^{-}$ (electroneutral).

If there are 'c' moles of electrolyte ~~them~~, and C_s moles of the solvent (H_2O), the thermodynamic potential of the solution would be the sum of thermodynamic potentials of the solvent & the ion.

μ terms are chemical potentials

$$G = C_s\mu_s + c(x\mu_+ + y\mu_-) \text{ — } Ⓐ$$

$$G = C_s\mu_s + C\mu, \text{ where } \mu = \text{chem. pot. of the electrolytic sol}^n. \rightarrow Ⓑ$$

$$\Rightarrow \mu = x\mu_+ + y\mu_- \text{ — } Ⓒ$$

Now, if $\nu = x + y$, = total no. of ions produced and assume $\mu_\pm$ to be the mean ionic chemical potential, then.

$$\nu\mu_\pm = x\mu_+ + y\mu_- \text{ — } Ⓓ$$

$$\text{or } \mu = \nu\mu_\pm \text{ — } Ⓔ$$

07/02/2023

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So, to calculate k from the activity we need to know the relation between concentration and activities. So, let us take a solution of an electrolyte A x B y and when you dissolve this in water it completely dissociates into x A z plus, plus y B z minus such that x into z plus is equal to y into z miners. So, that electrically neutral that is a plus and minus are charges on those particular cations and the anions. If there are c moles of electrolyte and Cs moles of the solvent in this case water, the thermodynamic potential of the solution would be the sum of thermodynamic potentials of the solvent and the ions.

So, one can write G that is Gibbs free energy of the solution is nothing but C s mu s plus C into x mu plus, plus y mu minus I write this equation at equation A where mu terms are chemical potentials. So, mu s is chemical potential of solvent, mu plus is chemical potential of cations, mu minus is chemical potential of anion.

And simultaneously we can also write that G equal to C s mu s plus C mu where mu is equal to chemical potential of the electrolytic solution. This equation we write it as equation B. And this mu is equal to x mu plus, plus y minus which is equation C you need to follow this equation numbering scheme because this derivation will be a little long and one has to keep going back and forth for doing the mathematical replacements of physical quantities.

So, now if mu is equal to x plus y that is the stoichiometry coefficients which is equal to the total number of ions produced and assume mu plus minus to be the mean ionic chemical potential, then one can write that mu into mu plus minus is nothing but x into mu plus, plus y into mu minus we write this equation as equation B or you can also write mu equal to nu into mu plus minus which we write as equation E.

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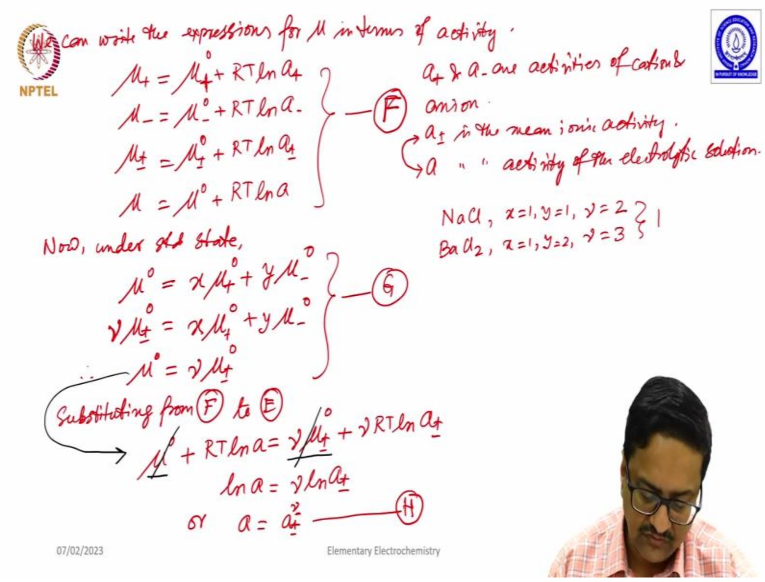

We can write the expressions for μ in terms of activity.

$$\left.\begin{aligned} \mu_+ &= \mu_+^0 + RT\ln a_+ \\ \mu_- &= \mu_-^0 + RT\ln a_- \\ \mu_\pm &= \mu_\pm^0 + RT\ln a_\pm \\ \mu &= \mu^0 + RT\ln a \end{aligned}\right\} — Ⓕ$$

a_+ & a_- are activities of cation & anion.

$a_\pm$ is the mean ionic activity.

a " " activity of the electrolytic solution.

NaCl, $x=1, y=1, \nu=2$ } 1
$BaCl_2$, $x=1, y=2, \nu=3$

Now, under std state,

$$\left.\begin{aligned} \mu^0 &= x\mu_+^0 + y\mu_-^0 \\ \nu\mu_\pm^0 &= x\mu_+^0 + y\mu_-^0 \\ \therefore \mu^0 &= \nu\mu_\pm^0 \end{aligned}\right\} — Ⓖ$$

Substituting from Ⓕ to Ⓔ

$$\cancel{\mu^0} + RT\ln a = \cancel{\nu\mu_\pm^0} + \nu RT\ln a_\pm$$

$$\ln a = \nu\ln a_\pm$$

$$\text{or} \quad a = a_\pm^\nu \quad — Ⓗ$$

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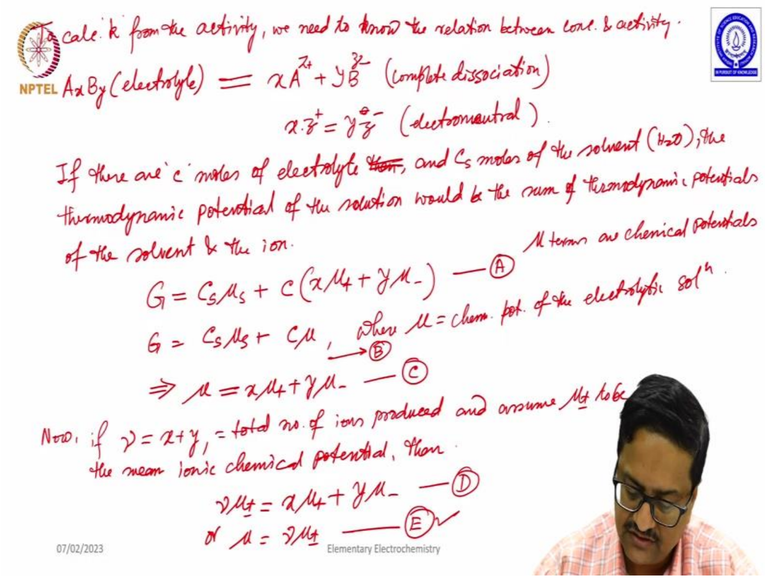

To calc. k from the activity, we need to know the relation between conc. & activity.

$$A_xB_y \text{ (electrolyte)} = xA^{z+} + yB^{z-} \text{ (complete dissociation)}$$

$$x \cdot z^+ = y z^- \text{ (electroneutral)}.$$

If there are 'c' moles of electrolyte ~~then~~, and C_s moles of the solvent (H_2O), the thermodynamic potential of the solution would be the sum of thermodynamic potentials of the solvent & the ion.

μ terms are chemical potentials

$$G = C_s\mu_s + c(x\mu_+ + y\mu_-) \quad — Ⓐ$$

$$G = C_s\mu_s + C\mu, \xrightarrow{} Ⓑ \text{ where } \mu = \text{chem. pot. of the electrolytic sol}^n.$$

$$\Rightarrow \mu = x\mu_+ + y\mu_- \quad — Ⓒ$$

Now, if $\nu = x + y$, = total no. of ions produced and assume $\mu_\pm$ to be the mean ionic chemical potential, then.

$$\nu\mu_\pm = x\mu_+ + y\mu_- \quad — Ⓓ$$

$$\text{or} \quad \mu = \nu\mu_\pm \quad — Ⓔ ✓$$

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So, now for our thermodynamics knowledge from the knowledge of your previous thermodynamics course we can write the expressions for mu in terms of activity. So, we can write for mu plus is equal to mu plus 0 plus RT ln a plus with standard notations mu plus means the chemical potential of the cation at standard state. Similarly, mu minus equal to mu minus 0 plus RT ln a minus. Similarly, mu plus minus equal to mu plus minus 0 plus RT ln a plus minus and also mu equal to mu 0 plus RT ln a all these 4 equations are numbered together as F.

In this case a plus and a minus are activities of cation and anion. a plus minus is the mean ionic activity and a is the activity of the electrolytic solution. So, now under standard state we can also write that mu 0 is equal to x mu plus 0 plus y mu minus 0. Similarly, nu into mu plus minus 0 is equal to x mu plus 0 plus y mu minus 0. Therefore, you can write that mu 0 is equal to nu into mu plus minus 0 these 3 equations are also term together as equation G.

So, now, what we will do is we start substituting from F to E from F to equation E that is if you go back equation E is this an equation F are those. So, now, I am substituting from F to equation E and we can write that mu 0 is equal to sorry mu 0 plus RT ln a is equal to nu mu plus minus 0 plus nu RT ln a plus minus. So, now, if you look at it carefully, mu 0 is same as nu mu plus minus 0. So, from here one can see that these 2 are same.

So, you can cut these 2 and rewrite this expression as ln a equal to nu ln a plus minus or you can simply write a equal to a plus minus to the power nu. So, this equation is numbered as equation H. So, now, we have got a relationship between the activity of the electrolytic solution and mean ionic activity in terms of the stoichiometry coefficients. So, now, I just want to highlight one point here about the stoichiometry coefficient.

Suppose, you are talking about NaCl. So, x equal to 1, y equal to 1, so, nu equal to 2 if you are talking about BaCl 2, x equal to 1, y equal to 2, so, nu is equal to 3. So, like that this relationship is either a relationship of square or cube or to the power 4 and so on based on the stoichiometry of the salt that we are dealing with.

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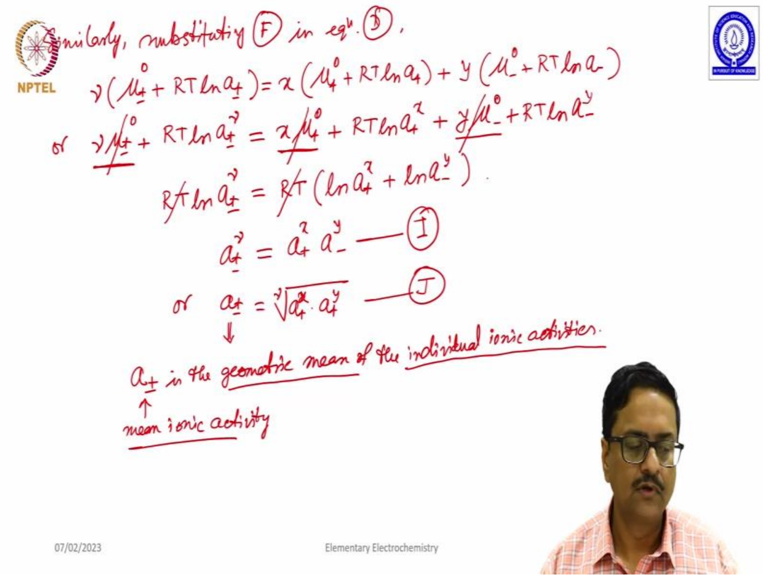

Similarly, substituting Ⓕ in eqn. Ⓔ.

$$\nu(\mu_{\pm}^{0} + RT\ln a_{\pm}) = x(\mu_{+}^{0} + RT\ln a_{+}) + y(\mu_{-}^{0} + RT\ln a_{-})$$

or $$\cancel{\nu\mu_{\pm}^{0}} + RT\ln a_{\pm}^{\nu} = \cancel{x\mu_{+}^{0}} + RT\ln a_{+}^{x} + \cancel{y\mu_{-}^{0}} + RT\ln a_{-}^{y}$$

$$\cancel{RT}\ln a_{\pm}^{\nu} = \cancel{RT}(\ln a_{+}^{x} + \ln a_{-}^{y}).$$

$$a_{\pm}^{\nu} = a_{+}^{x}a_{-}^{y} \quad \text{—} \quad Ⓘ$$

or $$a_{\pm} = \sqrt[\nu]{a_{+}^{x}\cdot a_{+}^{y}} \quad \text{—} \quad Ⓙ$$

↓

$a_{\pm}$ is the geometric mean of the individual ionic activities.

↑

mean ionic activity

07/02/2023

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So, similarly substituting the equation F in equation D, one can write nu into mu plus minus 0 plus RT ln a plus minus equal to x into mu plus 0 plus RT ln a plus, plus y into mu minus 0 plus RT ln a minus or nu mu plus minus 0 plus nu I can take it up when we were trying to multiply nu with RT ln a plus minus we can write it as RT ln a plus minus to the power nu is equal to x mu plus 0 plus RT ln a plus to the power x plus y mu minus 0 plus RT ln a minus to the power y.

So, now, you can see that this nu plus nu into mu plus minus 0 is equal to sum of this and this quantity. So, one can cancel these mu plus minus 0 with mu plus 0 mu minus 0 and get rid of that and then we are left with the equation RT ln a plus minus to the power nu equal to RT ln a plus to the power x plus ln a minus to the power y or we can remove RT now and you can simply write a plus minus to the power nu is equal to a plus to the power x and a minus to the power y we write the situation as the equation I.

Further one can write that a plus minus is equal to nu at root of the product of x plus to the power x into a plus to the power y and we write this equation as J. So, this essentially means physically that a plus minus is the geometric mean of the individual ionic activities this a plus minus is mean ionic activity which is the geometric mean of the individual ion activities.

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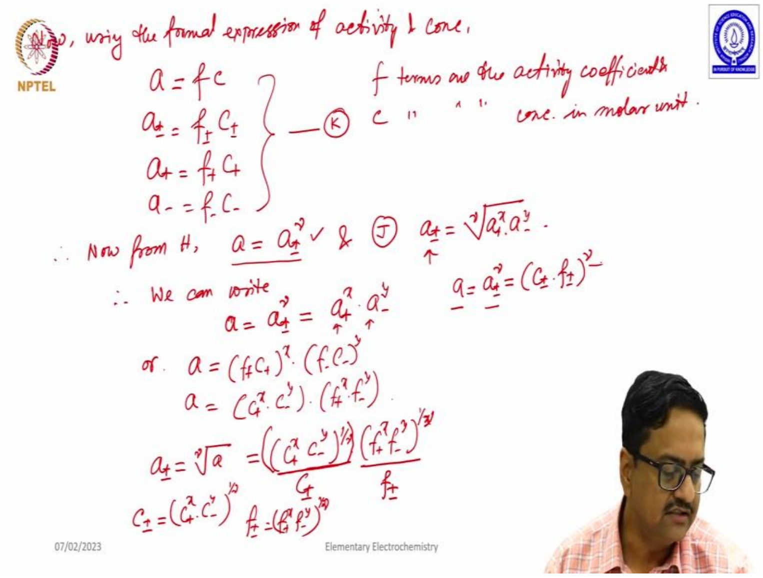

Now, using the formal expression of activity & conc.

$$\left.\begin{aligned} a &= fC \\ a_\pm &= f_\pm C_\pm \\ a_+ &= f_+ C_+ \\ a_- &= f_- C_- \end{aligned}\right\} \text{— (K)}$$

f terms are the activity coefficients

C " " " conc. in molar unit.

∴ Now from H, $\underline{a = a_\pm^\nu}$ ✓ & (J) $\underset{\uparrow}{a_\pm} = \sqrt[\nu]{a_+^x . a_-^y}$.

∴ We can write

$$a = a_\pm^\nu = \underset{\uparrow}{a_+^x} \cdot \underset{\uparrow}{a_-^y}$$

$$\underline{a} = \underline{a_\pm^\nu} = (C_\pm \cdot f_\pm)^\nu$$

or. $a = (f_+ C_+)^x \cdot (f_- C_-)^y$

$$a = (C_+^x . C_-^y) . (f_+^x . f_-^y).$$

$$a_\pm = \sqrt[\nu]{a} = \underbrace{((C_+^x C_-^y)^{1/\nu}}_{C_\pm} \underbrace{(f_+^x f_-^y)^{1/\nu}}_{f_\pm}$$

$$C_\pm = (C_+^x . C_-^y)^{1/\nu} \quad f_\pm = (f_+^x f_-^y)^{1/\nu}$$

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So now, using the formal expressions of activity and concentration one can write activity is equal to f C, a plus minus equal to f plus minus C plus minus, a plus equal to f plus C plus and a minus equal to f minus C minus all these together we term it as the equation k where the f terms are the activity coefficients and C terms are the concentration in molar unit. Now, from H, a equal to a plus minus to the power nu and J gives me a plus minus equal to nu at root of a plus to the power x a minus to the power y.

So, we can write a equal to a plus minus to the power nu which is equal to a plus to the power x into a minus to the power y because a plus minus is nu at root of a plus to the power x into a minus to the power y. So, now we replace these terms with the corresponding activity coefficient and concentration. So, we can further write in place of a we write f into C or we can still continue with a on the left hand side and replace the terms here with f and C.

So, what we write is f plus C plus e to the power x into f minus C minus to the power y which is equal to C plus to the power x C minus to the power y into a plus to the power x f minus to the power y which is equal to a. So, from this equation, we know that a plus minus is equal to nu at root of a which essentially means that it is equal to C plus to the power x C minus to the power y to the power 1 by nu into f plus to the power x f minus to the power y by 1 by nu.

So, we can write that this term is equal to C plus minus and this term is equal to f plus minus. So, using these substitutions I can write that a equal to a plus minus to the power nu which is equal to C plus minus into f plus minus to the power nu is it right. We should write C plus minus equal to C plus C minus to the power x and y and to the power 1 by nu and f plus minus is equal to f plus to the power x f minus to the power y to the power 1 by nu. So, now, we are using this equation a equal to a plus minus to the power nu and a plus minus is nothing but this which is C plus minus and f plus minus.

So, I am writing here it is a plus minus to the power nu and this entire quantity is equal to C plus minus. So, when you write C plus minus with this power up here the power that goes there, so, nu remains in this expression.

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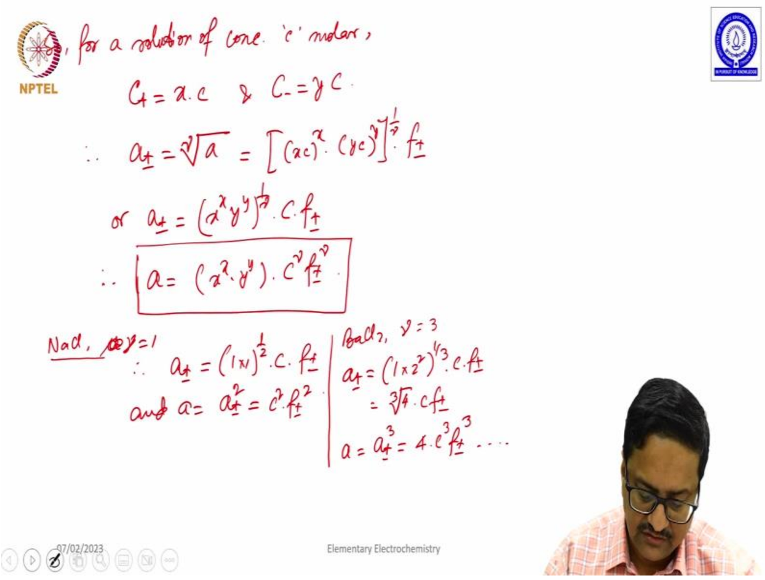

So, for a solution of conc. 'c' molar,

$C_+ = x.c$ & $C_- = y\,c$.

$\therefore\ a_\pm = \sqrt[\nu]{a} = \left[(xc)^x.(yc)^y\right]^{\frac{1}{\nu}}.f_\pm$

or $a_\pm = (x^x y^y)^{\frac{1}{\nu}}.c.f_\pm$

$\therefore\ \boxed{a = (x^x.y^y).c^\nu f_\pm^\nu}$

NaCl, $\nu = 1$

$\therefore\ a_\pm = (1\times 1)^{\frac{1}{2}}.c.f_\pm$

and $a = a_\pm^2 = c^2.f_\pm^2$

BaCl$_2$, $\nu = 3$

$a_\pm = (1\times 2^2)^{1/3}.c.f_\pm$

$= \sqrt[3]{4}.c f_\pm$

$a = a_\pm^3 = 4.c^3 f_\pm^3 \ldots$

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So, for a solution of concentration C molar one can write C plus equal to x into C and C minus equal to y into C. Therefore, which a plus minus we know is nu at root of a which is equal to x C into to the power x, y C to the power y whole to the power 1 by nu into f plus minus or a plus minus equal to x to the power of x y to the power y whole to the power 1 by nu into c into f plus minus. Therefore, a equal to x to the power x y to the power y C to the power nu f plus minus to the power nu.

So, now, if we do it for say sodium chloride nu equal to 1. Therefore, a plus minus is equal to 1 into 1 to the power half into C into a plus minus or and a equal to a plus minus square that is C squared into f plus minus square. Similarly for barium chloride nu equal to 3. So, you can write a plus minus as equal to 1 into 2 squared to the power 1 by 3 into C into a plus minus which essentially means cube root of 4 into C f plus minus and a equal to a plus minus cube which is equal to 4 C cube f plus minus cube like that for different electrolytes.

So, one can easily calculate these quantities while you know the particular electrolyte.

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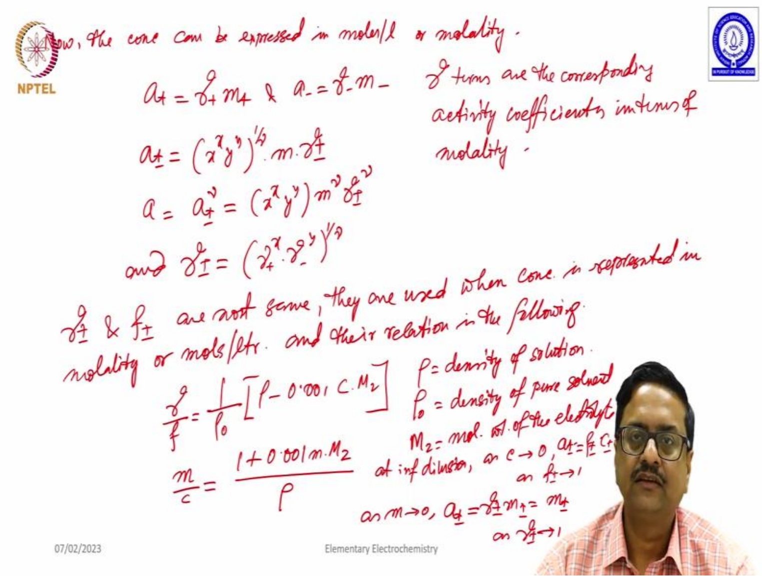

Now, the conc can be expressed in moles/l or molality.

$a_+ = \gamma_+ m_+$ & $a_- = \gamma_- m_-$

γ terms are the corresponding activity coefficients in terms of molality.

$a_\pm = (x^x y^y)^{1/\nu} . m . \gamma_\pm$

$a = a_\pm^\nu = (x^x y^y) m^\nu \gamma_\pm^\nu$

and $\gamma_\pm = (\gamma_+^x . \gamma_-^y)^{1/\nu}$

$\gamma_\pm$ & $f_\pm$ are not same, they are used when conc. is represented in molality or mols/ltr. and their relation is the following.

$$\frac{\gamma}{f} = \frac{1}{\rho_0}\left[\rho - 0.001\, C.M_2\right]$$

$$\frac{m}{c} = \frac{1+0.001 m.M_2}{\rho}$$

ρ = density of solution.

ρ_0 = density of pure solvent

M_2 = mol. wt. of the electrolyt

at inf dilution, as $c \to 0$, $a_\pm = f_\pm C_\pm$

as $f_\pm \to 1$

as $m \to 0$, $a_\pm = \gamma_\pm m_\pm = m_\pm$

as $\gamma_\pm \to 1$

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Now, the concentrations can be expressed in moles per liter or molality. So, then the a plus is gamma plus m plus and a minus is equal to gamma minus a minus where gamma terms are the corresponding activity coefficient in terms of molality. So, similarly, a plus minus is equal to x to the power x y to the power y to the power 1 by nu multiplied by m into gamma plus minus m is the concentration in molality a equal to a plus minus to the power nu which is equal to x to the power x y to the power y into m to the power nu gamma plus minus to the power nu.

And also gamma plus minus is equal to gamma plus to the power x gamma minus to the power y whole the power 1 by nu. So, these terms gamma plus minus and f plus minus are not same, they are used when concentration is represented in molality or moles per liter and their relation is the following gamma by f is equal to 1 by rho 0 into rho minus 0.001 C into M 2 and molality by concentration in moles per liter is nothing but 1 plus 0.001 m into M 2 divided by rho where rho is the density of solution, rho 0 is the density of pure solvent, M 2 is the molecular weight of the electrolyte.

So, at in finite dilution as C tends to 0 a plus or minus is equal to f plus minus into C plus minus is equal to C plus minus as f plus minus also tends to 1. Similarly, as m tends to 0 a plus minus is equal to gamma plus minus into m plus minus which is again equal to m plus minus as gamma plus minus tends to 1 at in finite dilution. So, hope you were able to follow this derivation of relationship between the activity and concentration and concentration is 2 different units like molality and moles per liter.

I would like to suggest that you go through a textbook for this derivation once again, to understand it better. So, we will continue from here in the next week. Thank you.