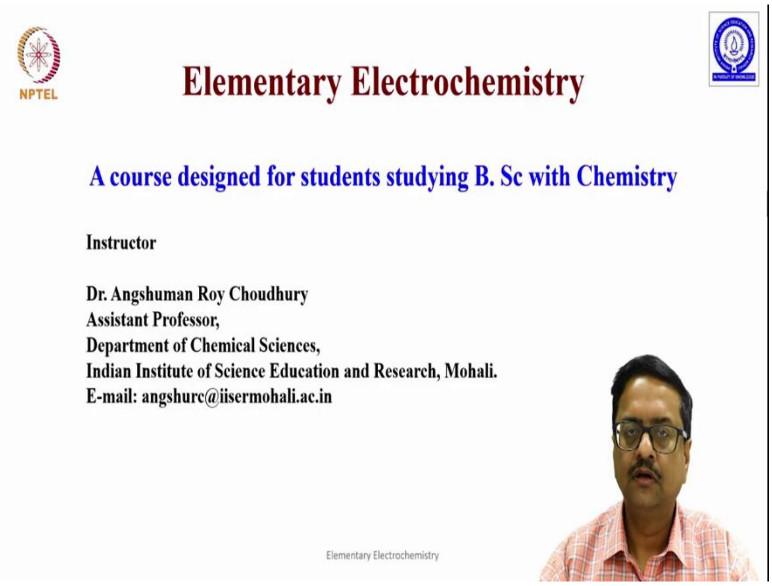
Elementary Electrochemistry
Professor Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali
Lecture 30
Application of Conductance Measurement - Part 02

(Refer Slide Time: 00:17)



Elementary Electrochemistry

A course designed for students studying B. Sc with Chemistry

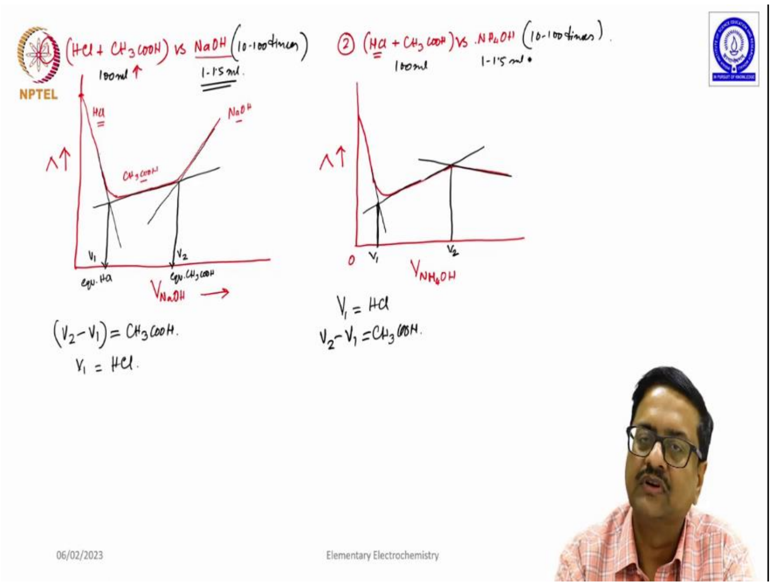
Instructor

Dr. Angshuman Roy Choudhury
Assistant Professor,
Department of Chemical Sciences,
Indian Institute of Science Education and Research, Mohali.
E-mail: angshurc@iisermohali.ac.in

Elementary Electrochemistry

Welcome back to the course entitled Elementary Electrochemistry. In the previous class, we started discussing about some of the applications of conductor metric titrations, or the measurement of conductance.

(Refer Slide Time: 00:34)



$(HCl + CH_3COOH)$ vs $NaOH$ (10-100 times)
100 ml ↑ 1-1.5 ml.

② $(HCl + CH_3COOH)$ vs NH_4OH (10-100 times).
100 ml 1-1.5 ml

$(V_2 - V_1) = CH_3COOH$.
$V_1 = HCl$.

$V_1 = HCl$
$V_2 - V_1 = CH_3COOH$.

06/02/2023

Elementary Electrochemistry

And if you remember that I had given you a couple of few problems are, I had asked you to try to draw the titration plots for some proposed experiments. So the first one that you were supposed to do is a mixture of HCl plus acetic acid versus NaOH. So how it should look like without going into much of the details, I am going to draw the plot and then discuss why it should be like that.

See, when we have a mixture of strong acid and weak acid the strong acid is completely dissociated. And because of that, weak acid dissociation is further suppressed because of our common ion effect. So, the weak acid remains nearly in an dissociated state. So, the conductance that you get is mostly because of the conductance given by HCl.

So, when we are titrating, it with NaOH, it is now just a strong acid strong base titration with addition of more and more NaOH, the conductance should decrease sharply till the H plus ions coming from HCl is left when this HCL concentration is reducing the dissociation of acetic acid increases.

So that near the equivalence point, this straight line starts to deviate from linearity. And beyond the equivalence point for HCl, the graph or the conductance tends to increase because now acetic acid is decomposing and producing more H plus ions before the neutralisation by another amount of NaOH.

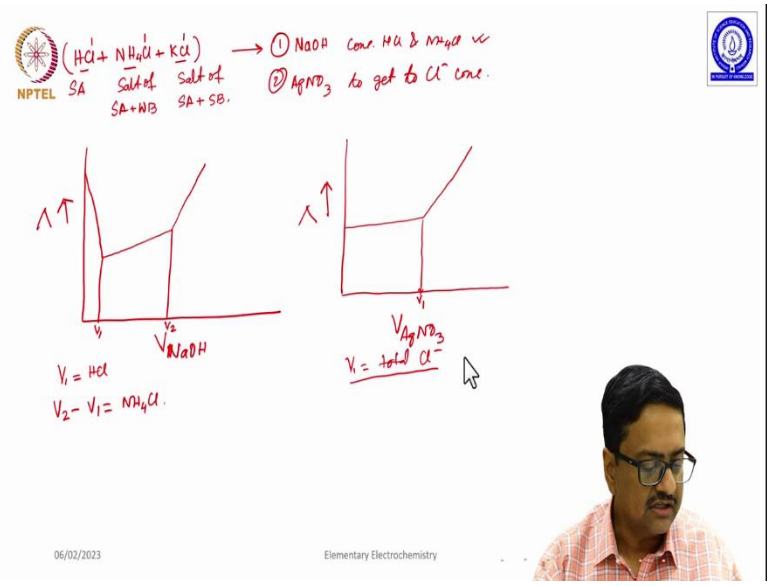
So, you add NaOH, H plus is removed, you let it equilibrate, some mod, H plus is generated the conductance increases. So, this continues till acetic acid is there in solution, and when acetic acid is again getting totally consumed, NaOH takes over. So you get a plot like this So, I have marked three zones, which are mainly tilt by HCl, acetic acid and NaOH. So, in this condition, one has to draw or extend this straight line like this, draw a tangent on that line and draw a tangent from this line to this point, gives you the equivalence point for HCl.

This point gives you the equivalence point for acetic acid. If this is v1 and this is V2, V2 minus V1 is the bullet reading for acetic acid. And v1 is for HCl. Hope you can understand this. So next one, what I gave is number 2 is a strong acid HCl plus a weak acid acetic acid versus a weak base, ammonium hydroxide.

So, as usual the conductance initially will be governed by HCl and with addition of ammonium hydroxide, the conductance will continuously decrease till about the equivalence point me up to the equivalence point when the acetic acid starts to decompose it will carve around it will go up and then when acetic acid is also consumed NH4OH is there will be a change of slope. So, two different slope changes will be evident, you draw a tangent here, you draw a tangent in there you draw a tangent here and you draw a tangent there. So, this will indicate to v1 this will be v2, v1 is for HCl V2 minus V1 is for acetic acid.

So, by doing one titration using ammonium hydroxide one can do this only thing what you need to remember is this should be 10 to 100 times moles concentrated similarly, ammonium hydroxide will be 10 to 100 times moles concentrated so, that the dilution effect is you have may have a 100 ml of this solution and you will need about 1 to 1 point 5 ml of NaOH in this case again 400 ML here you will need about 1 to 1 point 5 ml of that solution of ammonia hydroxide solution.

(Refer Slide Time: 07:00)



$(HCl + NH_4Cl + KCl) \longrightarrow$ ① NaOH Conc. HCl & NH_4Cl ✓

SA Salt of SA+WB Salt of SA+SB.

② $AgNO_3$ to get to Cl^- conc.

$V_1 = HCl$

$V_2 - V_1 = NH_4Cl$.

$V_1 =$ total Cl^-

So, the third problem that I gave you is a mixture of three compounds HCl here plus NH4Cl plus case here I wanted to know the concentrations of these three components individually. So, you can see that this is a strong acid this is a salt of strong acid plus weak base and this is a salt of strong acid plus strong base.

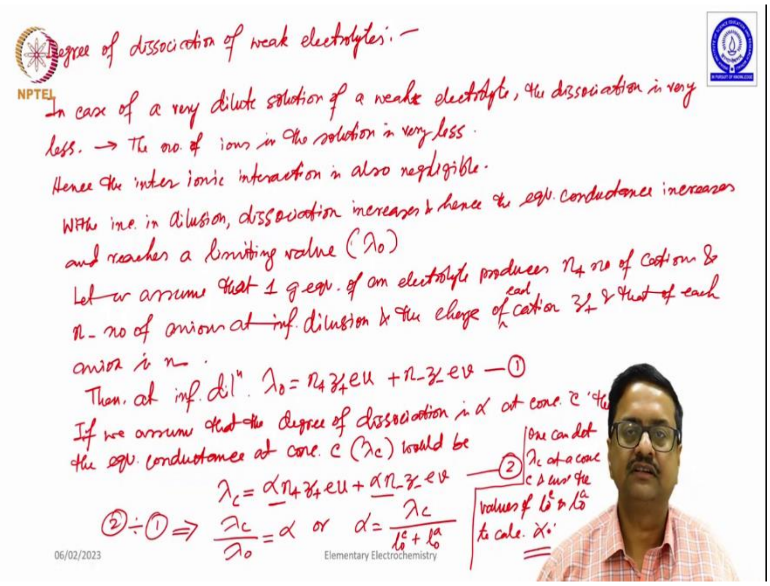
One thing is common here is the anion chloride. So, one can do one titration using strong base in NaOH to get the concentration of HCl and NH4CL and one can do a second titration with AgNO3 to get to total chloride concentration and from that one can subtract the concentrations of these HCl and ammonium chloride and get the concentration off case here.

So, for the first titration the conductance versus volume of NaOH as usual initially it will decrease after all HCl is consumed NH4CL being assault of strong acid weak base we dissociate to produce the corresponding HCl and weak base ammonium hydroxide. So, you are using NaOH age. So, that will consume the HCl generated and then the plot will go like this and at some point after that is consumed it will be like that.

So this v1 and this v2 will be the two endpoints, v1 will indicate the endpoint for HCl and V2 minus V1 will be the endpoint for ammonium chloride v2 minus v1 will be the end point for I ammonium chloride. And then the second titration as you can understand, which we have also discussed in the previous lecture, the conductance of the solution will be measured when doing the titration with, while doing the titration with silver nitrate solution, so, in this case the chloride ion is replaced by nitrate, which has about the same ionic conductivity, so, it will not change and then it will increase.

So, this will give you the volume of total chloride this v1 will give you the concentration of total chloride and then from that one can determine the concentration of KCL independent in addition to these different and conductor metric titrations one can also determine.

(Refer Slide Time: 11:05)



Degree of dissociation of weak electrolytes:-

In case of a very dilute solution of a weak electrolyte, the dissociation is very less. → The no. of ions in the solution is very less.

Hence the inter ionic interaction is also negligible.

With the inc. in dilution, dissociation increases & hence the eqv. conductance increases and reaches a limiting value (λ_0)

Let us assume that 1 g eqv. of an electrolyte produces n_+ no of cations & n_- no of anions ~~at inf.~~ dilution & the charge of each cation z_+ & that of each anion is z_-.

Then, at inf. diln. $\lambda_0 = n_+ z_+ e u + n_- z_- e v$ — ①

If we assume that the degree of dissociation is α at conc. 'c' the eqv. conductance at conc. c (λ_c) would be

$$\lambda_c = \underline{\alpha} n_+ z_+ e u + \underline{\alpha} n_- z_- e v \quad — ②$$

$$② \div ① \Rightarrow \frac{\lambda_c}{\lambda_0} = \alpha \quad \text{or} \quad \alpha = \frac{\lambda_c}{l_0^c + l_0^a}$$

One can det. λ_c at a conc. c & use the values of l_0^c & l_0^a to calc. α.

06/02/2023

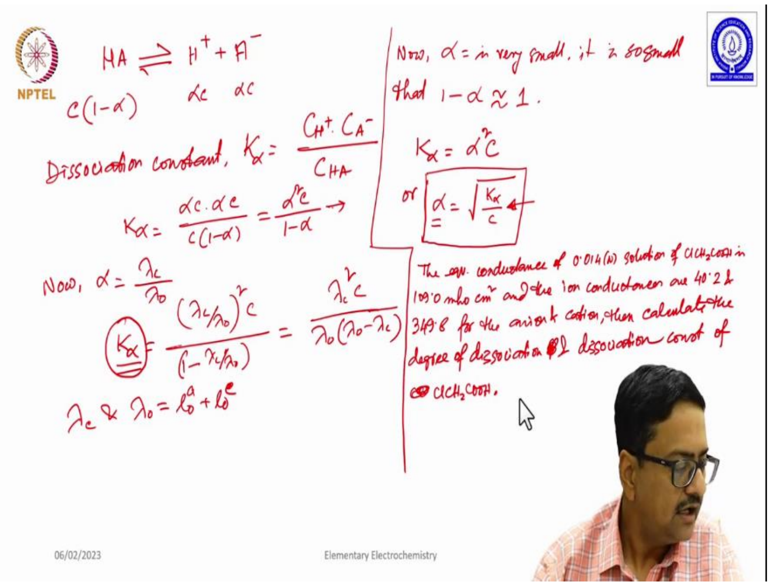
Elementary Electrochemistry

The degree of dissociation of weak electrolytes. So, for this we need to understand the theory behind it. So, in case of a very dilute solution of a weak electrolyte the dissociation is very less which essentially means the number of ions in the solution is very less and hence the inter ionic interaction is also negligible we increase dilution with increase in dilution the association increases and hence the equivalent contract tense increases and reaches a limiting value which we know we write as lambda 0.

So, now, let us assume that one gram equivalent of an electrolyte produces in plus number of cations and a minus number of anions at (())(14:27). And the charge of each cation is z plus and that of each anion is in minus so, then at infinite dilution lambda0 is nothing but n plus z plus eu, u is the speed of the cation plus n minus z minus ev where the v is the velocity of the anion, we write this equation as number 1 if we actually know that the degree of dissociation is alpha at concentration see then the equivalent contractors at concentration c which I am writing as lambda c would be the following law lambda c will be equal to alpha n plus z plus eu plus alpha n minus z minus ev.

So, we write this as so, now, this alpha n plus and alpha n minus or the number of ions or number of cations in the concentration c. So, now, if you divide 2 equation 2 by equation number 1 so, what I am doing is lambda c by lambda 0, we see that if I take alpha out it is equal to alpha or one can simply write alpha equal to conductance at or equivalent conductance at concentration c divided by lambda 0 which is nothing but l0 c plus l0 a. So, one can be determined lambda c at a concentration c and use the values of l0 C and l0 a to calculate degree of association alpha using this expression.

(Refer Slide Time: 18:26)



$HA \rightleftharpoons H^+ + A^-$

$c(1-\alpha) \quad \alpha c \quad \alpha c$

Dissociation constant, $K_\alpha = \frac{C_{H^+} \cdot C_{A^-}}{C_{HA}}$

$K_\alpha = \frac{\alpha c \cdot \alpha c}{c(1-\alpha)} = \frac{\alpha^2 c}{1-\alpha} \rightarrow$

Now, $\alpha = \frac{\lambda_c}{\lambda_0}$

$\boxed{K_\alpha} = \frac{(\lambda_c/\lambda_0)^2 c}{(1-\lambda_c/\lambda_0)} = \frac{\lambda_c^2 c}{\lambda_0(\lambda_0-\lambda_c)}$

λ_c & $\lambda_0 = l_0^a + l_0^c$

Now, α = is very small. it is so small that $1-\alpha \approx 1$.

$K_\alpha = \alpha^2 c$

or $\boxed{\alpha = \sqrt{\frac{K_\alpha}{c}}} \leftarrow$

The eqv. conductance of 0.014(N) solution of $ClCH_2COOH$ in 109.0 mho cm^2 and the ion conductances are 40.2 & 349.8 for the anion & cation, then calculate the degree of dissociation & dissociation const of $ClCH_2COOH$.

06/02/2023

Elementary Electrochemistry

So, what we know is that if I have a weak acid HA which is dissociating as H plus plus A minus at a concentration c this is the concentration of H plus this is the concentration of A minus and this is the concentration of C, HA are dissociated HA. So, one can write the dissociation constant K alpha equal to concentration of H plus into concentration of A minus divided by the concentration of HA, which is nothing but K alpha is equal to alpha c into alpha c divided by alpha c into 1 minus alpha which is equal to alpha square c by 1 minus alpha. Now, in the previous slide we have learned that alpha is equal to lambda c by lambda 0 so, when you replace alpha by lambda c by lambda 0 you get K alpha equal to lambda c by lambda 0 squared c divided by 1 minus lambda c by lambda 0 or in by simplification lambda c squared c divided by lambda 0 into lambda 0 minus lambda c.

So, once again by determining the values of lambda c and calculating the value of lambda 0 from the corresponding l0 A plus lo c one can calculate the dissociation constant of a weak acid efficient now, in general alpha is very small it is So, small that 1 minus alpha can nearly be equated to 1. So, the scale alpha can be written as simply alpha squared c or alpha is nothing but square root of K alpha by the c so, one can calculate the value of alpha also used by determining the value of K alpha from here and placing it in this equation as usual.

So, this is how one can easily determine the dissociation constant and degree of dissociation of a weak electrolyte. So, here I have to give you one problem the equivalent conductance of 0 point 014 normal solution of chloro acetic acid is 100 point 0 mho centimetres square and the ion conductances are 40 point 2 and 349 point 8 for the anion and cation then calculate the degree of dissociation and dissociation constant of total acetic acid. So, it is possible to do this calculation using the method that I have just discussed today. So, with this we will conclude this lecture and I will continue from here in the next class. Thank you.