Elementary Electrochemistry
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Lecture 36
Dissociation Constant of Weak Acids

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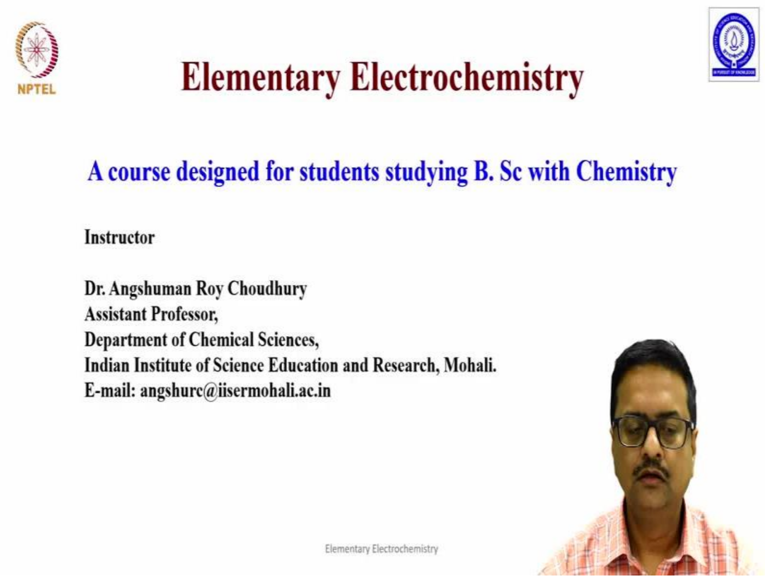

Elementary Electrochemistry

A course designed for students studying B. Sc with Chemistry

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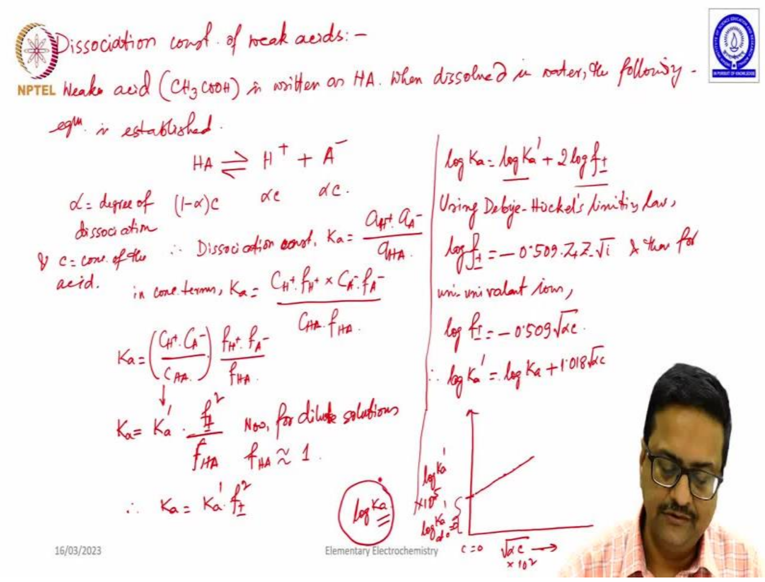

Dissociation const. of weak acids:-

Weak acid (CH_3COOH) is written as HA. When dissolved in water, the following - eqn. is established.

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

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

α = degree of dissociation

& c = conc. of the acid.

$\therefore$ Dissociation const. $K_a = \frac{a_{H^+} \cdot a_{A^-}}{a_{HA}}$

in conc. terms, $K_a = \frac{C_{H^+} \cdot f_{H^+} \times C_{A^-} \cdot f_{A^-}}{C_{HA} \cdot f_{HA}}$

$K_a = \left(\frac{C_{H^+} \cdot C_{A^-}}{C_{HA}}\right) \frac{f_{H^+} \cdot f_{A^-}}{f_{HA}}$

$K_a = K_a' \cdot \frac{f_\pm^2}{f_{HA}}$ Now, for dilute solutions $f_{HA} \approx 1$.

$\therefore K_a = K_a' f_\pm^2$

$\boxed{\log K_a =}$

$\log K_a = \underline{\log K_a'} + \underline{2 \log f_\pm}$

Using Debye-Hückel's limiting law,

$\log f_\pm = -0.509 \cdot Z_+ Z_- \sqrt{i}$ & thus for uni-univalent ions,

$\log f_\pm = -0.509\sqrt{\alpha c}$.

$\therefore \log K_a' = \log K_a + 1.018\sqrt{\alpha c}$

Welcome back to the course entitled Elementary Electrochemistry. In this lecture, we are going to discuss about the determination of dissociation constant of weak acid using the conductance measurements dissociation constant of weak acids. We will discuss both weak monobasic acid and then weak di-basic acid like oxalic acid as well. So, suppose the weak acid for us let us assume it to be acetic acid is written as HA, A is the anion part of weak acid and H is the H plus ion of that acid.

So, weak acid is written as HA when dissolved in water the following equilibrium is established. HA dissociates into H plus plus A minus if you assume that alpha is the degree of dissociation and C is the concentration of the acid then at equilibrium the individual concentrations of these species will be 1 minus alpha C whereas, concentration of H plus is I will alpha into c concentration ofA minus is also alpha into C. So, one can easily write the value of dissociation constant Ka activity of H plus into activity ofA minus divided by activity of HA.

So, in concentration terms one can write Ka equal to CH plus into F H plus that is the activity coefficient multiplied by CA minus into fA minus divided by CHA into f HA. So, one can further rearrange this expression for Ka as CH plus into CA minus divided by CHA into f H plus into fA minus divided by f HA. And further one can write Ka equal to Ka prime in terms of concentration this term is written as Ka prime multiplied by f plus plus minus square by f HA.

Now, for dilute solutions f HA can be assumed to be equal to 1 therefore, Ka can be written as Ka prime into f plus minus square. So, now taking log on both side log Ka equal to log Ka prime plus 2 log f plus minus. So, now one can use divide the limiting log and replace the value replace this log f plus minus by something called the is it is the ionic product. So, using Debye Huckel's limiting law one can write log f plus minus equal to 0.509 into Z plus Z minus square root of i. And then for uni uni valent ions one can write that as log f plus minus is equal to minus 0.509 square root of alpha c.

So, therefore one can write log Ka prime which is this one equal to log Ka plus 2 into log f plus minus that turns out to be 1.018 into square root of alpha C. So, now if you try to plot the value of log Ka prime multiplied by 10 to the power 5 in y axis and square root of alpha C in x axis multiplied by 10 square one will get a nearly straight line for a decent range of concentration. So, when you extrapolate it to C equal to 0, you will get the value of log Ka prime at C equal to 0 which essentially means, that it is the value of log of Ka.

So, from that one can calculate the value of the activity product of dissociation or rather the dissociation constant of weak acid using this method. So, this plot becomes important one has to do this experiment and using various concentration one has to calculate longer Ka prime using conductometry method and from that one can determine the value of Ka.

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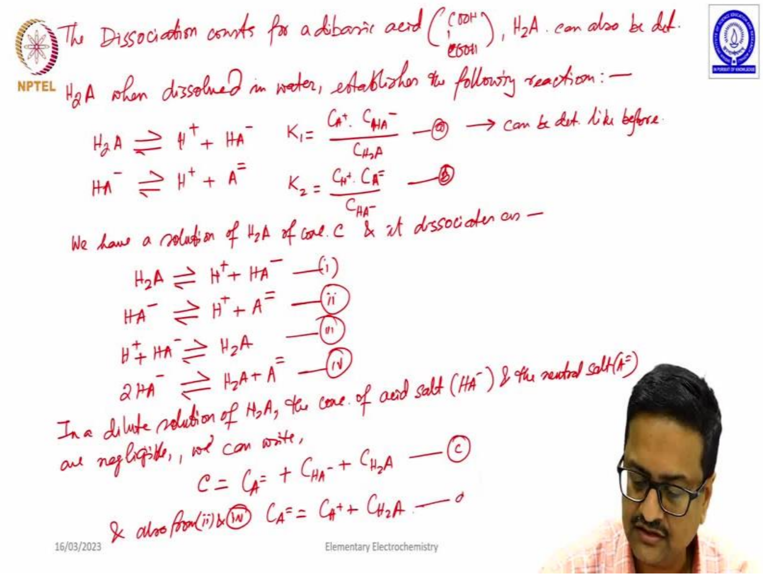

The Dissociation consts for a dibasic acid ($\begin{matrix} COOH \\ | \\ COOH \end{matrix}$), H_2A. can also be det.

H_2A when dissolved in water, establishes the following reaction:—

$H_2A \rightleftharpoons H^+ + HA^-$ $\quad K_1 = \frac{C_{H^+} \cdot C_{HA^-}}{C_{H_2A}}$ — ⓐ → can be det. like before.

$HA^- \rightleftharpoons H^+ + A^=$ $\quad K_2 = \frac{C_{H^+} \cdot C_{A^=}}{C_{HA^-}}$ — ⓑ

We have a solution of H_2A of conc. C & it dissociates as —

$H_2A \rightleftharpoons H^+ + HA^-$ — (i)

$HA^- \rightleftharpoons H^+ + A^=$ — (ii)

$H^+ + HA^- \rightleftharpoons H_2A$ — (iii)

$2HA^- \rightleftharpoons H_2A + A^=$ — (iv)

In a dilute solution of H_2A, the conc. of acid salt (HA^-) & the neutral salt ($A^=$) are negligible,, we can write,

$C = C_{A^=} + C_{HA^-} + C_{H_2A}$ — ⓒ

& also from (ii) & (iv) $C_{A^=} = C_{H^+} + C_{H_2A}$ — d

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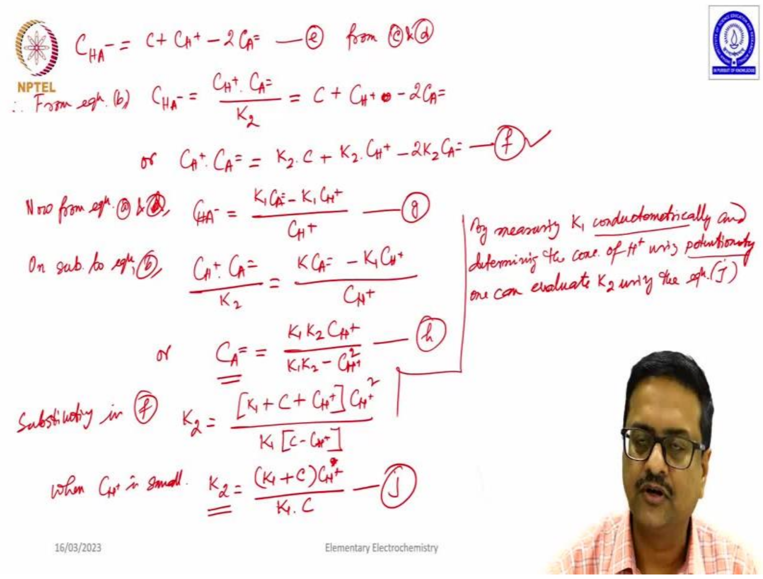

$C_{HA^-} = C + C_{H^+} - 2C_{A^=}$ — ⓔ from ⓒ & ⓓ

∴ From eqn. (b) $C_{HA^-} = \frac{C_{H^+} \cdot C_{A^=}}{K_2} = C + C_{H^+} - 2C_{A^=}$

or $C_{H^+} \cdot C_{A^=} = K_2 \cdot C + K_2 \cdot C_{H^+} - 2K_2 C_{A^=}$ — ⓕ ✓

Now from eqn. ⓐ & ⓑ, $C_{HA^-} = \frac{K_1 C_{A^=} - K_1 C_{H^+}}{C_{H^+}}$ — ⓖ

On sub. to eqn. ⓑ, $\frac{C_{H^+} \cdot C_{A^=}}{K_2} = \frac{K C_{A^=} - K_1 C_{H^+}}{C_{H^+}}$

or $\underline{\underline{C_{A^=}}} = \frac{K_1 K_2 C_{H^+}}{K_1 K_2 - C_{H^+}^2}$ — ⓗ

Substituting in ⓕ $K_2 = \frac{[K_1 + C + C_{H^+}] C_{H^+}^2}{K_1 [C - C_{H^+}]}$

when C_{H^+} is small. $\underline{\underline{K_2}} = \frac{(K_1 + C) C_{H^+}^2}{K_1 . C}$ — Ⓙ

By measuring K_1 conductometrically and determining the conc. of H^+ using potentiometry one can evaluate K_2 using the eqn. (J)

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The dissociation constant or constant for a diabetic acid for example, oxalic acid which is written as H2 A can also be determined. This dibasic acid when dissolved in water establishes the following reactions or reaction equilibriums, what are those? First it dissociates from H2 A to H plus plus HA minus that is mono dissociated acid ion and then this HA minus for the dissociates as H plus plus A double minus. So, for the first reaction K1 is written as CH plus into CHA minus divided by CH2 A, and the dissociation constant K2 is CH plus CA 2 minus divided by CHA minus. So, this is equation a and this is equation b.

So, this Ka can be determined like before right using different methods described for monobasic acid, but then for K 2 we need to use a different slightly different method. So, we assume that we have a solution of H2A of concentration C and it dissociates as follows. H2A dissociates as H plus plus HA minus, equation 1. HA minus further dissociates as H plus plus A double minus, equation 2. Then again H plus combines with HA minus giving you H2A equation 3 and 2 HA minus also disassociates as H2A plus A double minus which is equation 4.

So, when these 4 equations are established in a dilute solution of H2A that is oxalic acid for example the concentration of acid salt that is HA minus and the neutral salt that is A double minus are negligible then we can write that C the concentration of oxalic acid is equal to concentration of A double minus plus concentration of HA minus plus concentration of un-dissociated H2A, which we write equation as C.

And also, from equation 2 and 4 we can write that CA double minus is equal to CH plus plus CH 2 A, which we write as equation d and CHA minus equal to C plus CH plus plus sorry minus 2 CA double minus write it as e, is written from c and d, using equation c and d we can write this. So, now from the equation b, we can write CHA minus is equal to CH plus into CA double minus divided by K2 which is then equal to C plus CH plus minus 2 CA double minus or CH plus into CA double minus is equal to K2 into C plus K2 into CH plus minus 2 K2 into CA double minus, we write this equation as equation number f.

Now, from equations a and b sorry a and d, we can write CHA minus equal to K1 CA minus K1 CH plus divided by CH plus as equation g. And then on substitution to equation b one can get CH plus into CA double minus divided by K2 is equal to K1 CA double minus minus K1 CH plus divided by CH plus or simplifying CA2 minus is equal to K1, K2 CH plus divided by K1, K2 minus CH plus square which we write as equation number h. So, now we substitute this in equation number f which is here and then rearranging, one can solve for K2 as K1 plus C plus CH plus into CH plus H square divided by K 1 into C minus CH plus.

Now, when CH plus is small, see, remember that the solution is a very dilute solution and it is a weak dibasic acid so, it dissociates very little. So, at infinite dilution the CH plus is extremely small. So, then one can ignore the each term here and rewrite K2 as equal to K1 plus C into CH sorry plus divided by K1 into C. So, now by measuring the value of K1 conductometrically and determining the concentration of H plus using potentiometry one can evaluate K2 using this equation j.

So, in a combination combined method of conductometry and potentiometry one can determine the dissociation constant of second dissociation constant of dibasic acid. So, I think with this you will be able to solve some of the problems that you may encounter in various textbooks and one more lecture in which I will try to solve some of these problems which I have given you in one of the previous lectures hope you tried to solve those already.

So, we will discuss those problems and then we will conclude the course with the experimental demonstrations of conductometry titration followed by their calculations. So, thank you very much till the next lecture where we will talk about some of the solutions of problems. Thank you.