Elementary Electrochemistry
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Theory of Potentiometric Titrations

Welcome back to the course entitled Elementary Electrochemistry, in the previous class we started learning about potentiometric titrations and we have discussed about the potentiometric precipitation titration.

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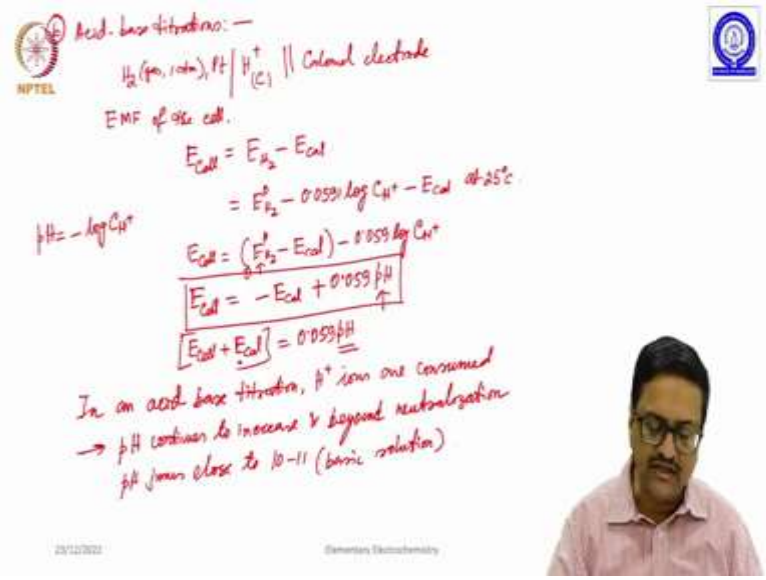

④ Acid-base titrations: —

H_2 (g, 1 atm), Pt | $H^+_{(C)}$ || Calomel electrode

EMF of the cell.

$E_{cell} = E_{H_2} - E_{cal}$

$= E^0_{H_2} - 0.0591 \log C_{H^+} - E_{cal}$ at 25°C

$pH = -\log C_{H^+}$

$E_{cell} = (E^0_{H_2} - E_{cal}) - 0.059 \log C_{H^+}$

$\boxed{E_{cell} = -E_{cal} + 0.059\, pH}$

$[E_{cell} + E_{cal}] = 0.059\, pH$

In an acid base titration, H^+ ions are consumed

→ pH continues to increase & beyond neutralization

pH comes close to 10-11 (basic solution)

Elementary Electrochemistry

So, now in this class we will discuss the potential metric acid base titrations. So, in case of acid base titration we generally need to have a hydrogen gas, one atmosphere coupled with a platinum electrode and H plus of a known or unknown concentration C coupled with calomel electrode so in this case the EMF of the cell will be E cell which is equal to E hydrogen minus E calomel or E hydrogen can be written E 0 hydrogen minus 0.0591 log of concentration of H plus minus E calomel at 25 degrees centigrade.

So, E cell can then easily be written as E0 H 2 minus E calomel minus 0.059 log of concentration of H plus and now, what you know is that this E 0 is 0. So, this is the minus E calomel then I put a plus sign and you know that pH equal to minus log concentration of H plus. So, we can write it as equal to 0.059 into pH

So, using this equation we have a variable pH. So, one can measure the corresponding pH which essentially means E cell plus E calomel equal 0.059 pH. So, one can measure the pH of a cell and continue a titration between acid and base and try to find out what happens to the value of pH when the neutralization takes place and the H plus ions are all consumed and you end up getting a solution of the base.

So, in an acid base titration H plus ions are consumed as a result pH continues to increase and beyond neutralization pH jumps close to 10 to 11 indicating basic solutions. So, this experiment can be done by just measuring the pH of a solution using an electrode which is meant to measure pH which will be calculated with which will be coupled to a calomel electrode and this will give you the value of pH change with the addition of base.

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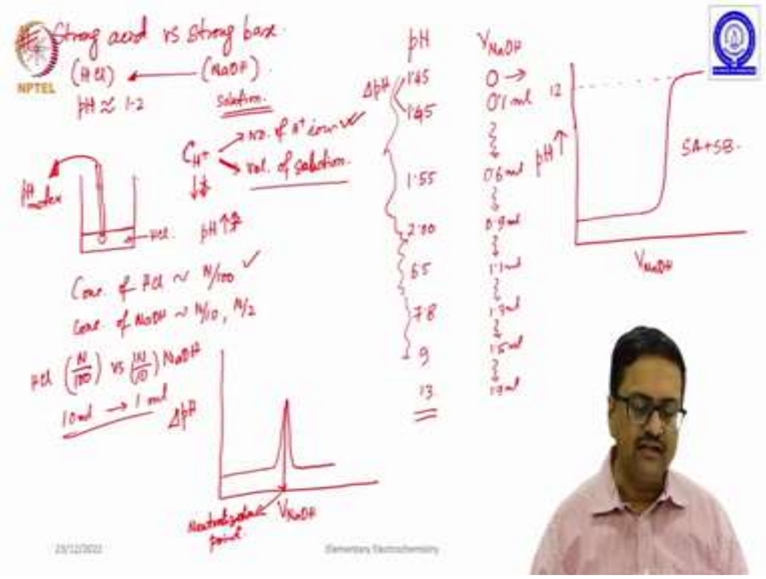

Strong acid vs Strong base.

(HCl) ← (NaOH)

pH ≈ 1-2

Solution.

C_{H^+} → No. of H^+ ions ✓ ; → Vol. of solution.

pH ↑

Conc. of HCl ~ N/100 ✓

Conc. of NaOH ~ N/10, N/2

HCl $\left(\frac{N}{100}\right)$ vs $\left(\frac{N}{10}\right)$ NaOH

10 ml → 1 ml

pH	V_{NaOH}
1.45	0 →
1.45	0.1 ml
1.55	0.6 ml
2.00	0.9 ml
6.5	1.1 ml
7.8	1.3 ml
9	1.5 ml
13	1.7 ml

So, this acid base titrations can we have different types, strong acid versus strong base. So, here I will take an example of HCl versus NaOH. So, in case of a strong acid like HCl, when you take a solution of HCl it is completely dissociated and you will find that the pH of a completely dissociated HCl solution is something around 1 to 2.

So, when we start the titration I will demonstrate this experiment physically in the next class, you take a beaker and you take a solution of HCl in this and deep end electrode which will measure the pH of the solution. So, it goes to a pH meter. So, now, the thing is when you are trying to do this experiment, you need to keep in mind that NaOH which is used to neutralize H plus it is also a solution and when you are adding NaOH solution to a solution of HCl, the overall volume of the reaction mixture is continuously increasing.

And as you know the concentration of H plus depends on two factors, number of H plus ions and the volume of solutions. So, while doing these titration if, while doing this titration by reacting it with NaOH we are continuously reducing the number of H plus ions, reduction of number of H plus ions will result in reduction of H plus ion concentration as a result, pH is going to increase, but while adding NaOH solution to HCl solution, we are also diluting the solution which further will reduce the concentration of the solution resulting in further increase in pH.

So, there will be a problem of double decrease in concentration and double increase in pH and it is not appropriate that is why when this kind of titrations are done, if the concentration of HCl is in the range of suppose N by 100 then the concentration of NaOH is taken at least in the range of N by 10 if not N by 2.

What does it mean it means that we are taking very strong anyway solution so, that it will require a very small amount of NaOH solution to neutralize that HCl solution. As a result, the overall increase in volume of the solution will be minimum. So, because of volume increase the change in concentration will be negligibly small. So, the effect of volume increase on pH can be ignored.

So, I will show when I do the reaction we will use N by 100 about N by 100 HCl vs about N by 10 NaOH so, you can easily understand that for 10 ml of this HCl solution we will leave about 1 mL of that NaOH solution for complete neutralization. So, now when somebody is measuring the pH of a solution with the added volume NaOH.

So, when you have not added NaOH solution 0 volume of NAOH, suppose the pH is 1.45. Now, with slow increase in volume of NaOH say 0.1 ml for strong acid what you will see that this HCl is fully dissociated as a result the pH will not change significantly it may not even show any change initially.

So, for about up to 0.5 to 0.6 ml you may only see the pH is increasing from 1.45 to 1.55 also not more than that, then slowly when you are increasing to a neutralization point suppose about 0.9 ml you may end up seeing that it has gone to about 2.00 and then on further increase to about say

1.1 ml you may see the pH has increased to 6.5 suppose, then it goes you go to 1.3 ml it goes to 7.8 and then at about 1.5 ml it goes to 9 and about 1.7 ml it goes to 13.

So, what you will see is that initially there was no increase much then the pH started jumping and it has gone to a very high value and reached 13. So, when you try to plot these readings in a graph paper, if we just plot pH in the y axis and volume of NaOH in the x axis, you will see that the numbers are falling on a straight line in the beginning and then towards the neutralization it increases over a period of 3 or 4 or 5 reading it increases and goes and then again get stabilized and it gets stabilized say around about 12.

So, this will be denatured of a potentiometric titration curve for strong acid versus strong base. So, now, like the previous experiment, where we were talking about delta E versus delta V, here you can plot delta pH versus volume of NaOH. So, what you will see is again interesting, if you plot delta pH versus V NaOH, you will see that initially there is no increase it may be flat it may be very close to 0 or 0.01 or 0.02 something like that, and then near the equivalence point, it will show a peak it will come down and then again there will be no difference.

So, wherever it reaches a peak, that volume of NaOH is your neutralization point. So, using this method, then, one can easily determine the concentration of unknown solution of HCl using a strong base NaOH without using any indicator.

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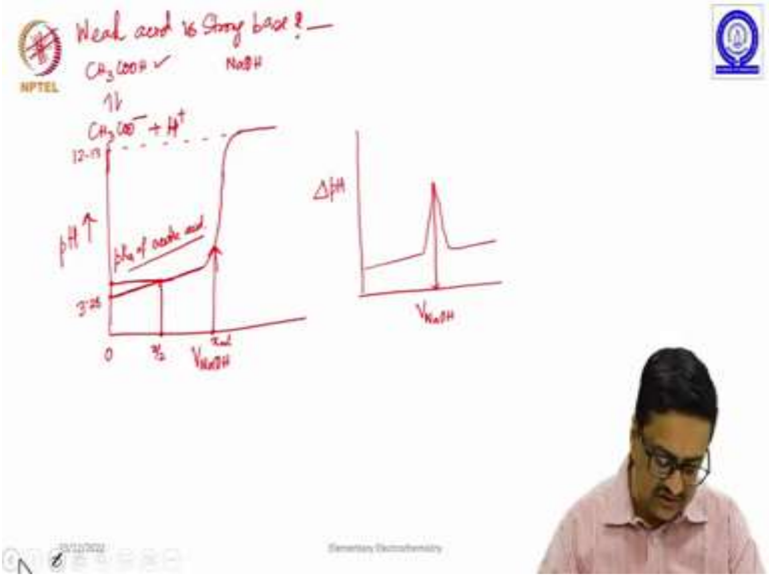

What will happen if you use a weak acid with a strong base? So, suppose weak acid is acetic acid and strong basis NaOH. So, as you know this weak acid is dissociated as CH3 COO minus plus H plus and this dissociation is very feeble in any aqueous medium and most of applying acetic acid stays as unassociated acid.

So, if you do the same experiment using acetic acid in place of HCl, you are going to see something different, you need to take the reading in the same way as I discussed a little while ago and you will then plot this pH versus volume of NaOH.

Now, in this case what will happen, in this case, when you have H plus ions very little the concentration of H plus ion is less. So, in at the beginning at 0 volume of NaOH pH will be little more than the strong acid it will be around 3.7 3.8 or something 3.7 to 3.8 and when you continue to add these, add NaOH drop wise you will see that it is no longer as flat as it was for strong acid the pH is continuously increasing but then near the equivalence point it increases sharp and then the rest of it follows like your strong acid strong base it goes to our 12 to 30.

So, now, when we have this plot and we have the entire data, we will then plot delta p H versus volume of NaOH and you will see that here the plot is slightly in the increasing order then, the peak appears over a bigger wider range and then it increases like this.

So, again this tip will indicate your neutralization point, suppose, the tip indicates that this is the neutralization point at this point where you have the maximum jump. So, this is your neutralization point, so, this volume so, now, we have not yet discussed the method of Henderson equation.

So, using Henderson equation, one can determine or calculate one can determine the pKa of this weak acid and as per Henderson situation, the pH of a solution at half neutralization point suppose this is XML so, that x by 2 ml whatever the pH it corresponds to the pKa of acetic acid.

So, one can determine the pKa of a weak acid using a potentiometric titration you find out the endpoint find out what is the half neutralization point and then from the graph paper you can find out what is the pH at that have neutralization point. So, that will give you the pKa of the weak acid. So, we have discussed about strong acid strong base, weak acid strong base.

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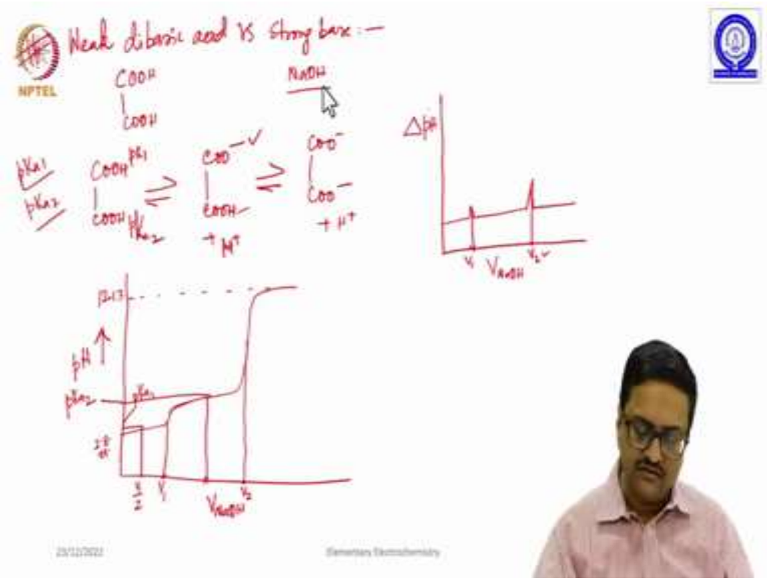

Weak dibasic acid VS Strong base :—

And we will now talk about the third possibility of weak dibasic acid versus strong base. So, weak dibasic acid is oxalic acid versus NaOH. So, now, COOH this is oxalic acid become dissociates in two steps COO minus COOH and then in the second step COO minus COO minus so here it is plus H plus and again here plus another H plus.

So, it has two steps as a result it has pKa1 and pKa 2. So, now if we try to do this experiment as usual I as I have described in the previous case with weak acid, strong base what will happen when I try to plot pH versus volume of NaOH again it will start around 2.8 to 2.9 kind of pH and slowly it will, slowly you will see there is a increase in the pH when it reaches the neutralization of the first part, the first acid it will increase a little and then it will again slowly increase till the second H plus is getting neutralized.

And at that point when the second H plus is neutralized, you will get to see that it forms a solution of NaOH which is pH of 12 to 13. So, now, if we plot this experiment in terms of delta pH versus volume of NaOH you will see that initially it was increasing, you have a small peak like that, again it increases very little and then it all peak and it goes.

So, this first point is V1 first neutralization this second point is your second neutralization. So, that is the point where the first acid is neutralized and this is the point when the second acid is neutralized. So, suppose this is the value for V 1. So, this point which is V 1 by 2 the corresponding pH is your pKa 1 and then this volume V 2.

So, middle point between V 1 and V 2 is somewhere here. So, that it is basically V 2 minus V 1 by 2 the corresponding pH that we get is the pKa 2. So, using this experiment one can determine the pKa 1 and pKa 2 of oxalic acid if you do the experiment very carefully, and also one can as hard of course get the equivalence point or neutralization point.

So, one can estimate the concentration of oxalic acid solution using NaOH or in the reverse way one can do a standardization of NaOH using a standard solution of oxalic acid. So, with this I will stop in this class and in the next class in the next week, we will discuss, we will demonstrate these experiments which I have discussed in today's and the previous class. Thank you.