Elementary Electrochemistry
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Lecture 29
Application of Conductance Measurement: Part 01

Welcome back to our course entitled Elementary Electrochemistry. In the previous class, we have discussed about how to determine the conductance of a solution and from that how to calculate the specific conductance, equivalent conductance etcetera and we have derived some of the expressions related to those physical quantities and we also discussed about the units of those physical quantities.

In today's lecture I am going to discuss some of the arbitrations of conductance measurement or conductivity measurements and subsequently the last week of this course we will do some demonstrations based on conductance measurement.

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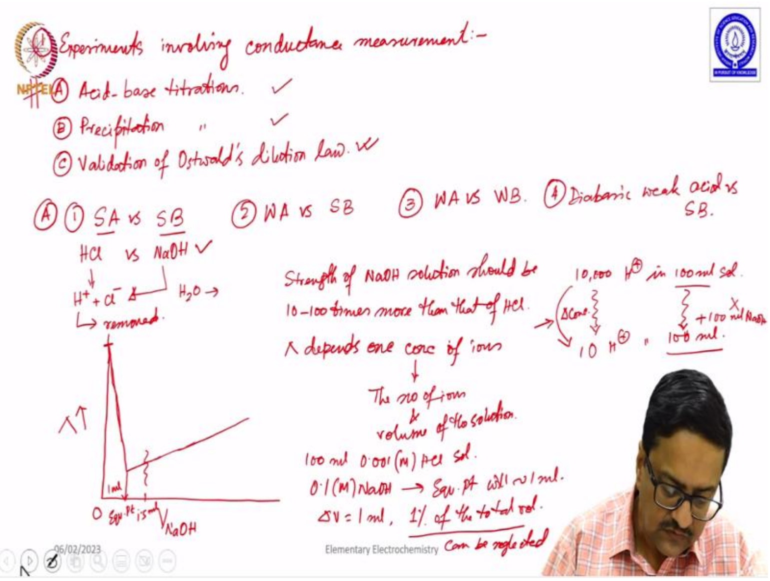

① Experiments involving conductance measurement:-

Ⓐ Acid-base titrations. ✓

Ⓑ Precipitation " ✓

Ⓒ Validation of Ostwald's dilution law. ✓

Ⓐ ① SA vs SB ② WA vs SB ③ WA vs WB. ④ Diabasic weak acid vs SB.

HCl vs NaOH ✓

$H^+ + Cl^-$ → removed. H_2O →

Strength of NaOH solution should be 10-100 times more than that of HCl.

Λ depends on conc of ions → The no of ions & volume of the solution.

10,000 $H^{\oplus}$ in 100 ml sol. → Δconc. → 10 $H^{\oplus}$ " 100 ml. + 100 ml NaOH ✗

100 ml 0·001 (M) HCl sol.

0·1 (M) NaOH → Equ. pt will ~1 ml.

ΔV = 1 ml, 1% of the total vol. can be neglected

So, today we will start our discussion based on experiments involving conductivity measurement or conductance measurement. So, for this experiment what we need is the conductivity cell which we have drawn in the past and the cell should have a suitable electrode normally a platinum electrode of one square centimeter area kept at 1 centimeter apart and the cell constant is then what?

So, the experiments that we want to theoretically understand are this, different types of acid base titrations, B precipitation titrations and C validation of Ostwald's dilution law. So, we have already this Ostwald's dilution law in one of the earlier lectures. So, we will not talk about it in this lecture today. We will concentrate on A and B. This acid base titrations that we are talking about can be of different types.

Number one strong acid versus strong base. Number two, weak acid versus strong base. Number three weak acid versus weak base and number four dibasic weak acid versus strong base. So, let us start discussing about the case of strong acid and strong base with using the example Hcl versus NaOH. So, we know is that Hcl being a strong acid it will remain fully dissociated as H plus, plus Cl minus.

So, when we have NaOH to this water is formed and H plus ions are removed continuously. So, what do we know about H plus ions? The conductivity of H plus ions is extremely high. So, as soon as we start removing the H plus ions from a solution the conductivity of that solution should tend to decrease. How should that decrease happen? If we try to lock the value of conductance of a given solution with the volume of NaOH added H plus ions having very high ionic conductivity.

The solution initially will have when no volume of NaOH is added will have a very high value of conductivity at the beginning, but then with addition of NaOH this conductivity will decrease very sharply and linearly and then when the H plus ions are consumed that is the neutralization has taken place on addition of NaOH solution this conductivity will slowly rise.

So, the point at which this transformation happens is your equivalent spot. Now, to be able to do this experiment successively and without incorporating much of error we need to remember a few things. The point number one and the most important point is the strength of NaOH solution should be 10 to 100 times more than that of Hcl solutions. Why is that? We all know that conductance lambda depends on concentration of ions and concentrations depends on the number of ions and volume of the solution.

So, if I suppose have at the beginning say for example 10,000 H plus ions in 100 ml solution due to this neutralization to a value of 10 H plus ions and 100 ml solutions I am fine because the volume does not change. So, I can easily calculate the change in concentration, but then while doing so I am adding NaOH solution. So, this 100 ml will not remain 100 ml. If the NaOH solution is of equivalent strength of Hcl.

So, for this neutralization we will need another 100 ml of NaOH that means the volume will partly universally increase and increase in volume will have effect on change in concentration. Therefore, we should try to make this change in volume as negligible as possible. So, suppose if we take 100 ml 0.01 molar Hcl solution then we should use a 0.1 molar NaOH solution so that the equivalent points will come around 1 ml.

So, the change in volume of the solution is 1 ml which is just about 1% of the total volume. Also this change can be neglected. So, one has to keep this in mind that use a very strong solution of (()) (09:40) is measured accurately and I have shown you up to this part for your understanding, but once you do the experimentally up to about this point. If you endpoint is up to 1 ml one can do this experiment up to 1.5 ml at the most because then further addition of NaOH for the dilutes.

And the volume increases as a result the conductance value becomes incorrect and you may see that this is no longer a straight line and so on. So, with strong acid and strong base one can expect a graph like this, hope you are able to understand.

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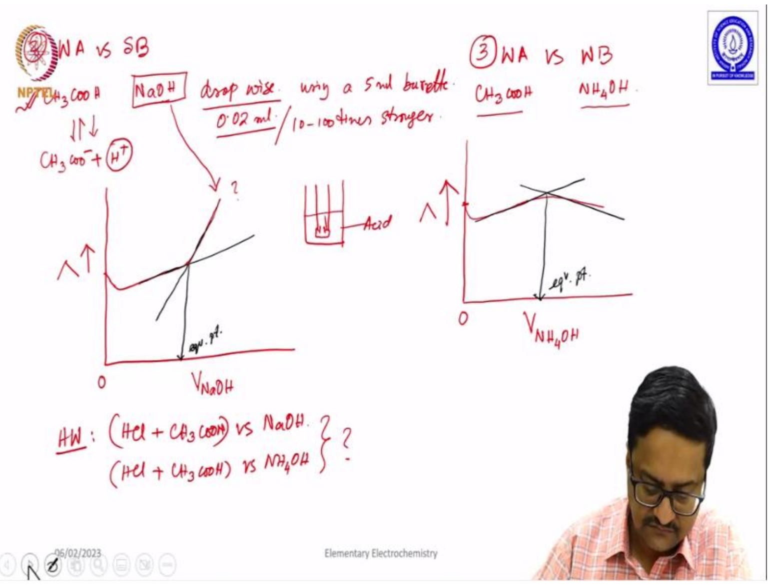

The next thing is weak acid versus strong base. Here, my weak acid is acetic acid and strong base is NaOH. What happens in case of a weak acid? It stays partially dissociated like this as well as the solution without any NaOH addition will not have very high conductivity. So, when we have not added any sodium hydroxide solution the conductance should be moderate not like very high as was the case with Hcl.

So, now what is happening is when I am adding NaOH drop wise that is using a 5 ml burette and adding drop means 0.02 ml of a solution which is again 10 to 100 times stronger than acetic acid. This will continuously start removing H plus. So, as soon as you add the first drop the conductance will decrease, you get another drop the conductance tends to still decrease.

But after addition of every drop when we try to equilibrate this disassociation becomes more fragile and more H plus ions are generated. Hence, the conductance will start increasing. So, after this initial drop the conductance of the solution will slowly increase and near the equivalent point it will deviate from linearity and beyond equivalent point it will continuously increase.

So, this point where the deviation starts one has to drop a tangent on this line and at tangent on that line wherever the two tangents meet will be your equivalent spot. So, using acetic acid in the conductivity cell this experiment we do we will see that we will do it in a weaker we take the solution of acid in weaker and in such a conductivity cell where you have the electrodes like this.

And the solution goes in between the electrode and in the (13:56) the conductors of the solution. So, this will be the nature of weak acid versus strong base plot and I hope you understand the reason for this nature. So, now if I try to draw the second line the weak acid versus weak base. Suppose, acetic acid versus ammonium hydroxide you know that it is very difficult to do this kind of titrations using an indicator because thought indicator is suitable for this weak acid versus weak base estimations.

So, it is best done using the conductivity measurement. So, now I want you to think about what should be the nature of this conductance versus volume of NH 4 OH block. So, initially what is happening we have acetic acid as dissociated like acetate and H plus irons. So, we will have a moderate conductivity somewhere here with 0 volume of chromium hydroxide and then initially the conductance will form.

And then it will slowly increase and beyond equivalents point what was happening here will not happen there because I was adding NOH which immediately which is already dissociated and it increases the conductance of the solution significantly so there was an increase in conductivity whereas NH3OH is not a strong electrolyte it is again a weak electrolyte so the conductivity will go like this.

So, what is happening here is now we need to draw a tangent here, we need to draw another tangent there wherever the two tangents meet that will be your equivalence point of this particular titration of weak acid versus weak base is that clear. This portion is same as that and the right hand side portion where after the equivalent spot is slowly decreases because ammonium hydroxide is a weak electrolyte.

And we are adding more and more ammonium hydroxide against the volume of the solution is increasing and as a result the concentration is decreasing and the conductance is going to decrease. So, this is what will happen with weak acid and weak base combination. So, I want to give you a homework think about what will be the plot of a mixture of Hcl and acetic acid titrated with NaOH solution.

So, this you should think and try to drop yourself and you can write to me we can discuss about this over email. Similarly I should give you this thing also that if it is Hcl plus acetic acid done with ammonium hydroxide what will be the nature of these two titrations.

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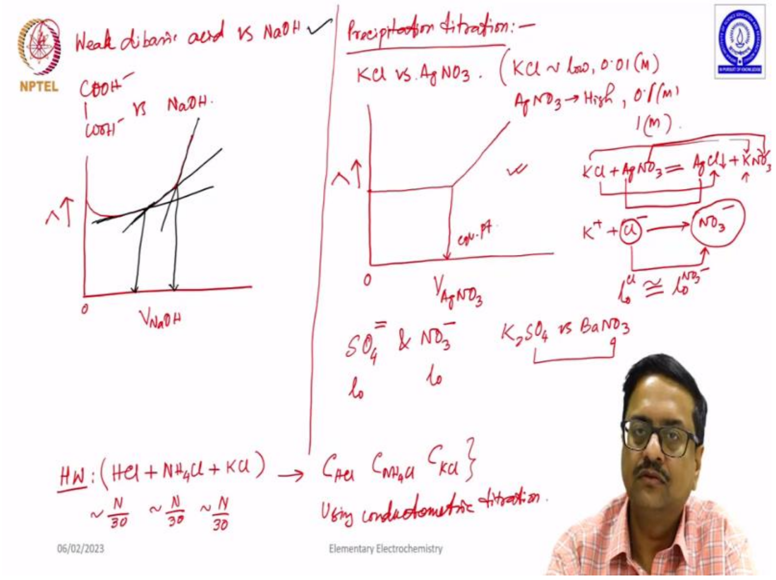

What do you think will happen in case of weak dibasic acid versus NaOH say for example Oxalic acid versus NaOH. If you remember the experiment of this using potentiometry we could see the disassociation of acetic times two times and you could determine the (())(19:00) acids. In this case what will happen is not going to be very sharp. So, you see both the acids are weak so the neutralization when it happens it will not be very, very prominent or sharp.

So, initially it will decrease then it will go on slowly increasing after the first neutralization has taken place. The curve will bend little bit and then when it is over with NaOH it will go up. So, if you get a graph like this, if you get a plot like this I think I should write volume of NaOH here and it is 0 volume of NaOH what one has to do is one has to draw a tangent here, one has to draw a tangent there and one has to draw a third tangent here.

So, this one will indicate the first equivalence points, this one will indicate the second equivalent points, but this changes will not be very, very prominent or very sharp. So, it is not advisable to do this kind of titrations using conductometric method rather one should try to do this using a potentiometric method that we have already discussed. The next type of conductometric titration is the conductometry precipitation titration.

In case of a conductometric precipitation titration one has to choose the pair of compounds very precisely or very weak with lot of consideration depending on the speeds of those ions the plots will pick up different. So, I am giving you one example of Kcl and Ag NO3. So, as you know Kcl is used as a standard solution for determination of cell constant of a conductivity cell.

And it is very easy to handle Kcl as it is not hydroscopic and is free flowing salt. So, one can use Kcl as a standard for this type of experiments. So, I am trying to determine the concentration of either Ag NO3 or unknown Kcl depending on whatever you want to prefer. Only thing was to remember that we are taking Kcl in weaker. So, the concentration of Kcl should be low maybe 0.01 molar and the concentration of silver nitrate should be high that is either 0.1 molar or even just 1 molar.

So, now when we have not added any silver nitrate it will have a recent conductance and then when we slowly start adding silver nitrate what will happen Kcl plus Ag NO3 we will get Ag Ag cl as precipitated and KNO3 will form. So, the iron that is present Kl plus still remains chloride gets precipitated, silver gets precipitated, nitrate is convert that means in your solution which have K plus, plus cl minus after the experiment cl minus ions are replaced by NO3 minus ions keeping the concentration of K plus (()) (23:50).

Now, if you look at the table for the transport number or the ionic conductivity of these two ions chloride and nitrate you will see that the ionic conductance of chloride and nitrate are about the same. So, what will happen when adding silver nitrate drop wise there would be much changing the conductance, but then when all the chloride is precipitated and no more silver chloride gets precipitated.

If you are continuing to add silver nitrate beyond that point the conductance of the solution will continuously increase. So, this sharp endpoint will be giving you the equivalence point the point where the straight line changes its slope with a (())(24:50) concentration of Kcl solution. One can use Kcl solution as standard and determine silver nitrate unknown in that case one has to take silver nitrate in the weaker and add a 10 times or 100 times strong Kcl solution from burette.

So, you remember we should use a 5 ml micro burette and use 2 ml Kcl solution or silver nitrate solution at a time. So, the value for l0cl minus is about the same as l0NO3 minus and hence you will get this kind of lock. If you take two different ions say, for example, SO4 2 minus and what I am trying to say that if it is K2SO4 versus barium nitrate then you are trying to compare sulfate with nitrate.

So, depending on the corresponding values of these two l0 the nature of the graph will change. Here sulfate is getting replaced by nitrate if nitrate has higher l0 value so the conductance will continuously increase. If nitrate has a lower l 0 value than sulfate the conductance will decrease. So, you will have to think and replot this graph for this kind of precipitation titrations.

So, I am giving another homework. If I give you a mixture of Hcl plus NH4Cl plus Kcl in a mixture each of the order N by 30. I want to know the individual concentration of Hcl and NH4Cl and Kcl this is about N by 30. These are all made approximately and then I want to exact concentrations of chloride, I want concentration of Hcl ammonium chloride and potassium chloride in this solution using a conductometric titrations.

So, this is a homework for all of you. So, try to solve this problems, you try to draw the graphs. We will probably discuss this in the next lecture. Thank you.