Elementary Electrochemistry
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Estimation of HCL and Ammonium Chloride in a Triple Mixture using NaOH

Welcome back to the experimental session of Elementary Electrochemistry course. In the previous videos we have shown you a few conductometric, potentiometric titration, and then two conductometric titrations, which were, the conductometric were on weak acid and strong base, strong acid and strong base. And now in this third experiment, we are going to combine two types of titrations. One is acid based titrations which you have already seen and a precipitation titration using silver nitrate to determine the concentration of chloride.

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So, in this particular experiment I have prepared an unknown solution of a triple mixture which you can see is a mixture of hydrochloric acid, ammonium chloride and potassium chloride and the overall strength of this solution in terms of chloride is approximately N by 100. So, we want to use conductometric method to estimate the concentration of individual components that is HCL, ammonium chloride and KCL.

HCL is as you know is a strong acid, ammonium chloride is a salt of strong acid and weak base and potassium chloride is a salt of strong acid and strong base. So, what we can do in this experiment is that, if we take this solution in our beaker inside the conductivity cell, it will give me the conductance of all the ions combined and then. So, when we start with titration of this triple mixture with NaOH.

It will first react with HCL consume H plus and replace it by Na plus ions and conductance will slowly reduce. We will see a steep decrease in concentration till the H plus ions are consumed. Once H plus ions are completed consumed then it will start hydrolyzing ammonium chloride and produce HCL and that HCL will react with the added NaOH. So, what will happen is there will be hydrolysis followed by neutralization of the acid produced.

So, we will see a slight difference in the conductance, we will see that the conductance is not changing as fast as it was changing before, but it will reduce slowly and then when the entire ammonium chloride is consumed we will see that further addition of NaOH increases the conductance of the solution. So, we will first see a steep decrease in concentration, then a shallow decrease in concentration, and then increase in conductance with addition of NaOH.

So, this will give us the estimation of the concentration of HCL, so that you have one line and the second line, and the meeting point will give you the concentration of HCL. And then the second line when it ends, there will be an increase in conductance and from there you will get the end point for ammonium chloride. So, this one experiment with NaOH in the burette will give you estimation of HCL and ammonium chloride.

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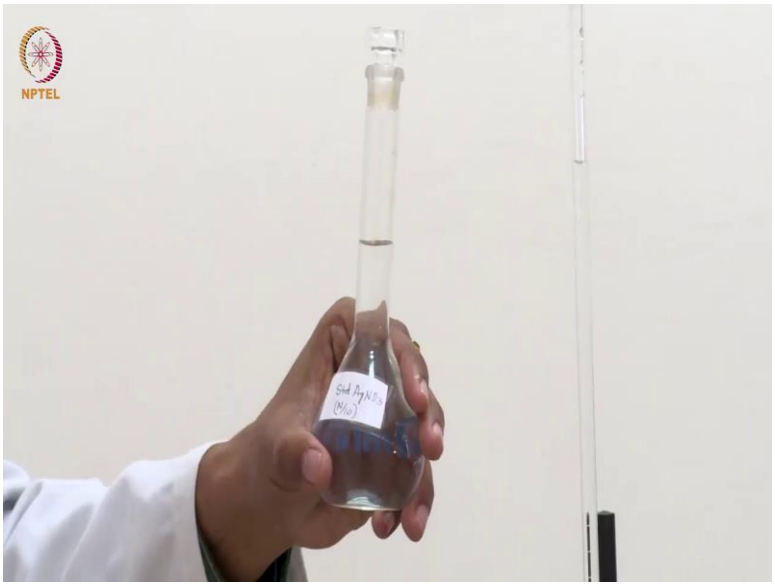

Then we have to discard the solution, take the fresh solution of this triple mixture which is mixture of HCL, ammonium chloride and potassium chloride and we will then titrate that mixture using a standard silver nitrate solution which we have prepared again using the very accurate weighing method, using weighing bottle and the 4 digit balance. So, this is a standard N by 10 silver nitrate solution.

So, this silver nitrate when we add to a mixture of chloride we will see that a precipitation occurs, silver chloride gets precipitated, we have described this precipitation titration in the theory lecture in the previous week. So, you should now be able to understand what is happening during this titration. So, in this titrations chloride ions will be continuously removed and replaced by nitrate ions which has about the same conductivities.

Therefore, during the neutralization or during the titration of chloride with silver nitrate as long as there is chloride left there will not be much change in conductance, it will remain almost the same, but then towards the end of titration beyond the equivalence point is reached. When we add more and more silver titrate we will see an increase in concentration, we will see an increase in conductance and that will indicate the end point of this reaction or end point of this titration.

So, we will have to plot again the volume of silver nitrate versus conductance in a graph paper and then in the following lectures I will show you how one can do the calculation and find out the concentrations of this components in this mixture. So, this experiment has two parts one part it is with NaOH titration and the other part is with silver nitrate and titration, method of titration is the same.

We will keep on adding gradually the amount of the solution from burette and will note down the values of conductance continuously and then plot it.

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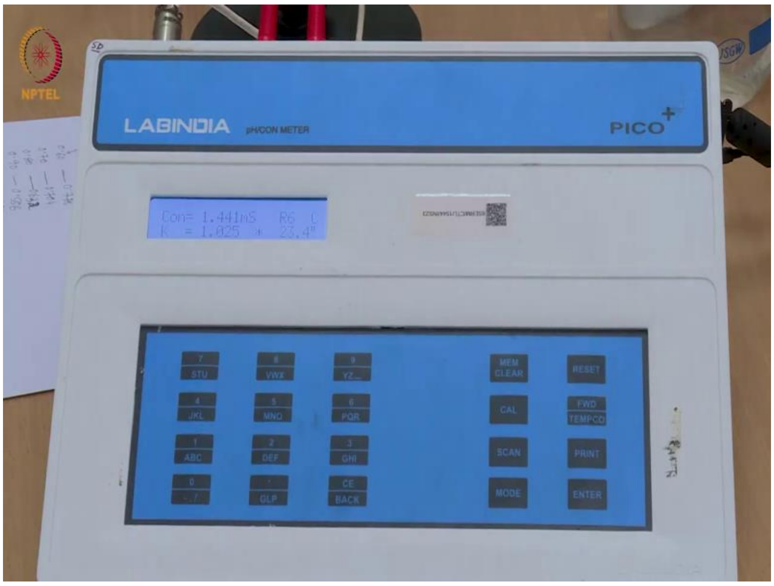
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K = 1.025 * 23.4°
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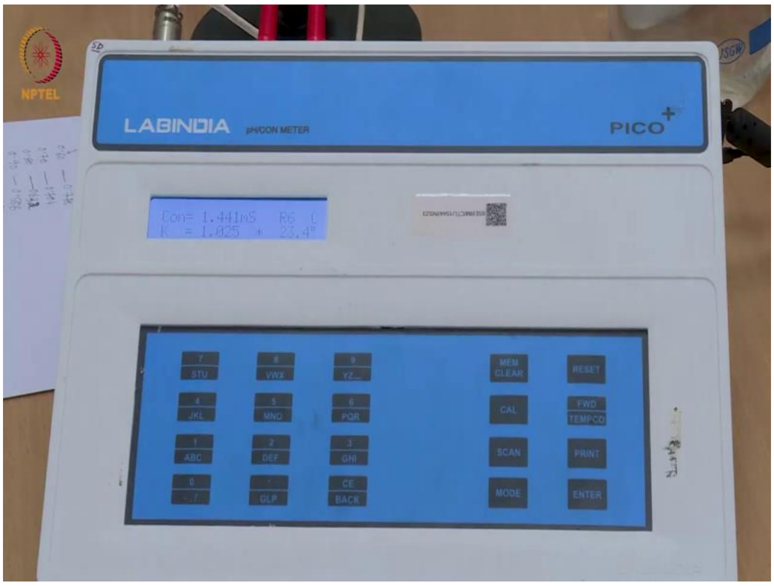
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NPTEL
LABINDIA
pH/CON METER
Con= 783.3uS R6 C
K = 1.025 * 23.8°

So, now what we have in your screen, we have a solution of 0.01 molar KCL and the conductance that is reading here is 1.441 milli-siemens with a cell constant of 1.025. So, we will require the value of cell constant in the calculation.

So, to start the experiment we first need to remove this KCL solution, clean the electrode as before and then add little amount of water so that the electrode is dipped inside water and the conductance is read in micro-siemens, and then we will add 10 ml of this unknown triple mixture and start the titration. So, now I have kept a small amount of water in this beaker and the electrode is dipped.

You can read the measurement here it shows conductivity about 8.06 micro-siemens. So, that kind of conductivity is very good for a good quality water. So, now to that I am just going to add this solution of triple mixture about 10 ml of that using this pipette. So, I am going to pipette out 10 ml of triple mixture from this conical flask, and add it to this water present in the beaker, and then start the titration using N by 10 NaOH standardized 10 by 10 NaOH.

You may be able to see that the conductance of the solution is increasing. because now I am adding 3 salts HCL, ammonium chloride and potassium chloride in a mixture. So, all the ions that are coming here are now conducting and it contributes in the conductivity of this solution. So, we should make it homogenous. So, after making it homogenous we can see that the conductance value of this triple mixture solution is about 783.3 micro-siemens.

So, we should note down these value as my burette reading at zero volume of NaOH. Remember that here the reading is already in micro-siemens. So, write down 782.2 or 782.3 micro-siemens that is my starting point. So, here about one third is HCL, one third is ammonium chloride, and then one third is potassium chloride. I have taken 10 ml of the solution.

So, the endpoint for HCL should come somewhere close to about 0.3 to 0.4 ml and for ammonium chloride it should come around 0.6 to 0.7 ml. So, we have to be very, very careful while adding this solution of NaOH drop wise, we should not add too much at a time we always should maintain our gap of 0.04 ml each step and homogenize it and take the reading.

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NPTEL
LABINDIA
pH/COND METER


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So, now I have added 0.04 ml of NaOH and we see that the conductance has reduced to 740.8. So, we will continue adding small amount 0.04 ml each time and take the reading. So, at 0.08 ml the conductance has now further reduced to about 704.1 micro-siemens. Now another 0.04 ml is added, so I have reached 0.12 and we see that there is a significant change 673. While adding one has to make sure that the drop falls inside the solution and it does not fall outside because every drop here is very important because it is 10 times more concentrated then the solution that we are analyzing.

So, if one drop falls outside the measurement will go wrong. So, now we have added another 0.004 ml and reached 0.16 and you see again there is a significant decrease from 673 to 629.3 micro-siemens.

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So, now I have added one more portion of 0.04 ml and reach this 590.9. If you see the difference between the initial readings, it was 782, then 740 difference is 40, 740 to 704 is again difference of about 40. Then it is 673 the difference is like 30, then 629 so 630 that means about 40. So, about 30 to 40 micro-siemens difference is coming even now with 629, 630 becoming 590. So, that gap of conductance between the readings is maintain like about 40 micro-siemens which means that we are still constantly decreasing the conductance because still we are having HCL in solution.

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pH/COND METER


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Now we have reached 0.24 ml and the conductance is 548.2. So, again about 40 micro-siemens decrease in conductance. So, with 0.28 we are now close to the… What happened, it is not reading. So, the electrode was above the water level, so it was not reading the correct value, we should wait for it to stabilize and homogenize as well. So, then you know that we are close to the neutralization point.

You see now it is stabilizing to about 516.2 micro-siemens. So, what we see is now here when we added 0.04 ml of the solution of NaOH the reduction in conductance is not in the range of 40 micro-siemens, the reduction is in the range of about 30 micro-siemens. Now, we will add one more block of 0.04 and we will see that probably the conductance will either stay unchanged or we will start slowly increasing.

So, we have now reached a stage where it is 0.32 milliliter of NaOH and the conductance has changed to 483.6. So, still it is reducing, but now it is reducing slower earlier it was reducing by 40 micro-siemens, now it has come in the 30 micro-siemens, that means it has deviated from its linearity. So, now I have added another 04 that is we have reached 36 and we see that it has reduced to 457.3.

So, 460 and 83 is like 26 micro-siemens reduction. That means the straight line which was coming is now slowly bending and changing its slope, that indicates that we are very close to the equivalence point for HCL.

Now, I have added another portion of 0.04 ml of NaOH and homogenizing it again as usual. So, we have reached 0.4 ml and we see that the conductance is now reduced to 441.5 which means the difference is just about 16, 17 micro-siemens which indicates that probably we have reached the endpoint.

And from here we will see a range where there will be almost no change in conductance for a while because now we will consume HCL and means it will hydrolyze ammonium chloride and HCL will be consumed by NaOH. Let us see how the reading changes

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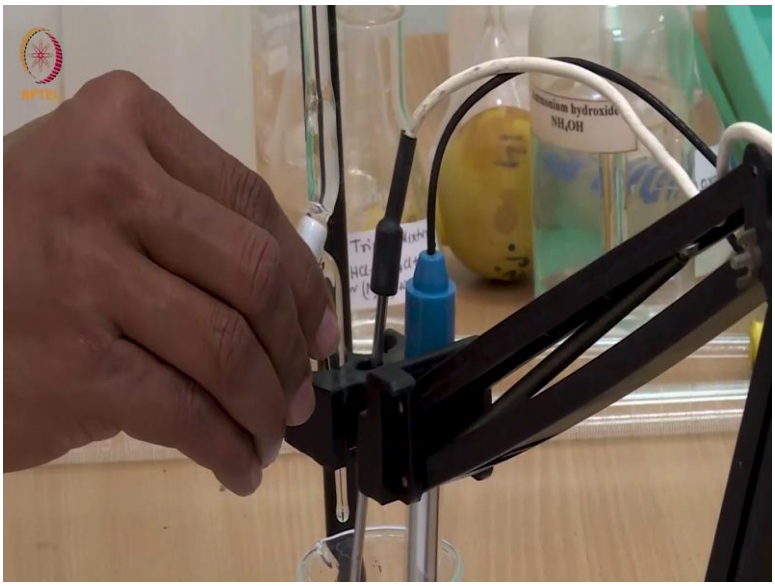

So with 0.44 millimeter, it is staying all the same 443, so it is slightly increasing, but I would say it is staying the same within the experimental error limit 444.6. So, now we should continue this addition till we start seeing that the conductance is increasing. What is happening at this point is that ammonium chloride is getting hydrolyzed and producing ammonium hydroxide and HCL and we are then neutralizing that HCL using NaOH from the burette. So, we see that the reading is not changing 0.445 that is 445.5 micro-siemens. So, for last three readings the conductance has not changed at all, I would say it has not changed at all.

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So, we are reaching a region where we will see a parallel line parallel to the x axis, straight line parallel to x axis. So, this is the region where you will get the concentration of ammonium chloride, if we just use this region for our calculation. Again the value is 444.2 this I would say is a very good experimental data where these points are coming at same value even after adding NaOH.

So, now the reading is 447, this is an indication f slight increase and with more I think it may start to show increasing trend, because if ammonium chloride that was present in this solution is almost consumed or is completely consumed, it will start to increase. So, when the hydrolysis of ammonium chloride ends and the reaction is over there is no H plus ion present in the solution.

Then with addition of more and more amount of NaOH we will see a constant increase in conductance. So, let us continue addition as usual. So, every time when you add 0.4 ml you may end up seeing that the drop has formed at the tip of the burette, but it has not completely formed and fallen in the solution then you need to take the drop in solution by touching the edge of the beaker, so that the drop falls in the titration solution.

So, now I have added another 0.04 ml, so it is now 0.6 ml and it shows 449 maybe 450, maybe 449 450. So, what we are seeing a slight increasing trend. So probably the end point for ammonium chloride is now passing. We will see the exact 10 point when we plot. With 0.64 ml, now we see a further increase 451 maybe 452 it will be, because at this point the conductance value slightly fluctuates because it is not fully certain yet that the entire ammonium chloride has hydrolyzed.

So, it may take a while for the conductivity cell to give you the correct or accurate reading of conductance. So, I will take this as 452. So, there is an increase of 2 micro-siemens for every 0.4 ml here.

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So, with 0.68 ml the reading is 454, maybe it will reach 455, if we wait and let it homogenize and equilibrate because at this point the neutralization has just happened and if the instrument also takes a while to read the conductance very accurately.

See it is slowly increasing, but now it is stabilizing to 455. These points which are very close to the neutralization points we need them very accurately to draw the actual graph, but these points will not be useful for finding out the endpoint as you know that we will have to draw a tangent through all the points which are falling in the straight line. So, while when we do that we will see that these points which are slowly changing from constant to a increasing trend, these points will not fall in the straight line.

So, we will not need these points for accurate endpoint determination, but to show the trend how it changes we will need these points. Now we have reached 0.72 and the value is probably going to be 458 or maybe even 459, if we allow it to stabilize, equilibrate and stabilize. So, we take this reading as 456.4 and we will continue. So, now it is coming out slightly higher 462. So, now we see a change of about 6 plus 4 about 10 micro-siemens more 462.9, 463 is 9 micro-siemens.

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Now, I am adding another portion of 0.4 and after that I will add a slightly larger quantities because I then need the points which are distant from the equivalence point. So, we have now reached a value of 0.8 ml and it shows about 467, 468 maybe, it will homogenize and give the reading close to 468.

So, it is reaching that value of 468 maybe plus minus 0.1 and while plotting those last digit will not become so significant. So, now I will add 0.1 ml portions and note down the conductance value to get the points which are beyond the equivalence points because now we are seeing that the values are constantly increasing. Now, I have added 0.1 ml. So, with 0.1 ml I have reached as 0.9 ml.

And the conductance value has now increased significantly because I have added 0.1 ml, it should reach a higher value, so it is 485.3, 485.1, 485 maybe the correct value, 485.2 I am taking. So, we will add three or four more fractions of 0.1 ml to get 3 or 4 more points which will then give me the liberty to draw the straight line through those last 4, 5 points. So, now with 1 ml of NaOH I have reached a value of conductance 510.6 micro-siemens.

So, we will continue addition in 0.1 ml portions for next another 3 or 4 readings. Since now I am adding a larger quantity I should wait for a while for the conductivity meter to give me the correct value. So, that when we try to plot these lines should form a nice straight line. So, it is now coming like 551.2, 551.2 is my reading after 1.1 ml. Now I have added one more portion of 0.1 ml so reached 1.2 ml.

And we wait for the cell to give us the correct reading which may take about 5 to 10 seconds. So, now it is going to be about 600 micro-siemens 599.3, where should we take a decision whether we should stop or not. If we look at our readings here the readings for last 5 points are with 0.8 it is 468, 0.9 it is 485, 1 ml is 510, 1.1 is 551, and 1.2 599 that is 600. So, in last two readings the increase is like 40 to 50 micro-siemens.

Whereas before that their increase was about 15 to 20 micro-siemens that means we have not reached a point where we have a constant gap between the consecutive readings over the range of additions which we were seeing at the beginning where we are seeing a gap of about 40 micro-siemens for each addition of 0.04 mm. So, here I decide that we cannot stop at this point we have to continue for another maybe 3 or 4 readings when this gap will become nearly uniform.

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The gap in the conductance should become nearly uniform. I have reached 1.3 ml and let us see where the conductance value reaches, it should reach somewhere about 640, if we have reached the uniform increase in conductance point, because with NaOH we should see some kind of uniformity in increase with a certain amount that has been already added. So, here that the expected value we are not getting that means we have not reached a point where with a certain amount of NaOH we see a certain amount of increase in conductance.

So, we will take 2 or 3 more readings and stop the experiment and then plot and see there maybe one or two points which are not exactly accurate. Now, I have reached 1.3 ml and the reading for 1.3 ml is 143. So, now we have reached a point where with 0.1 ml addition we are reaching a stage where it is increasing by about 40. So, I will add one more portion of 0.1 ml and reach 1.4.

And expect to reach the conductance of 680 around that point 680, 688 something like that. So, now we see that we are reaching little more than 688, 695, 697 which is about 0.40 to 0.50 micro-siemens increase from the previous value. So, these are within the experimental error limits 695.9, 696. So, this will be our endpoint for this triple mixture versus NaOH titration.

So, we have seen a change that was happening between 0.28 and 0.4 ml, so the constant decrease, got reduced, and the plots results or the conductance values were flat for a while, and then it started increasing slowly, and we continued up to 1.4 ml which is much beyond the endpoint of this triple mixture titration. So, with this we are finishing the first part of this triple mixture estimation with NaOH.

So, from the graph we will get the concentrations of HCL and ammonium chloride, but will not know the concentration of KCL from this experiment. To do the experiment with KCL, we will have to do this titration using a solution of silver nitrate which I will show after this experiment. So, we will continue the experiment in the next video. Thank you.