Analytical Chemistry
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Module 10
Lecture No 46
Electrochemical Methods 2

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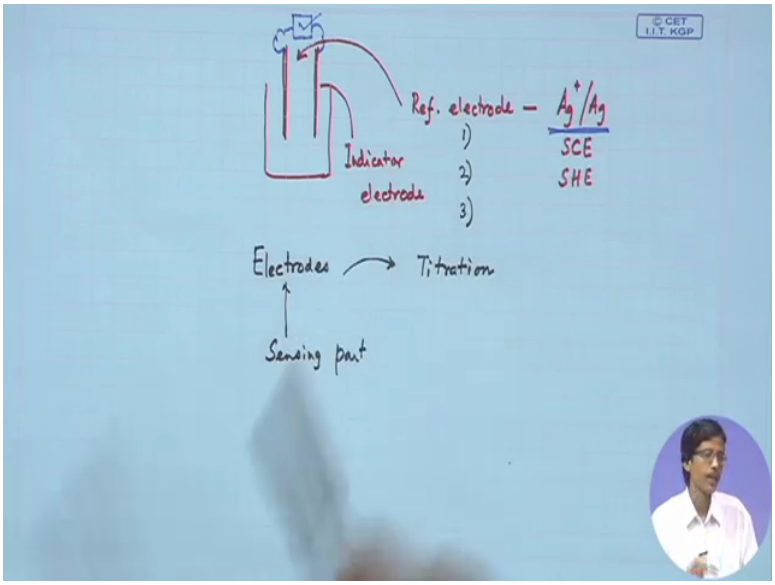

Welcome back so we will be considering the different electrodes, so the most important component what we have seen in our previous class that how you arrange the reference electrodes as well as the indicator electrodes and there are different reference electrodes in our hand and the typical or the very basic design of these electrodes how we can use for your titrations. So that is our problem or our goal to know that how we can use these electrodes because the electrodes are the sensing part when we see the colour we know that we have to see the colour at least for your neutralization reaction or the analysis

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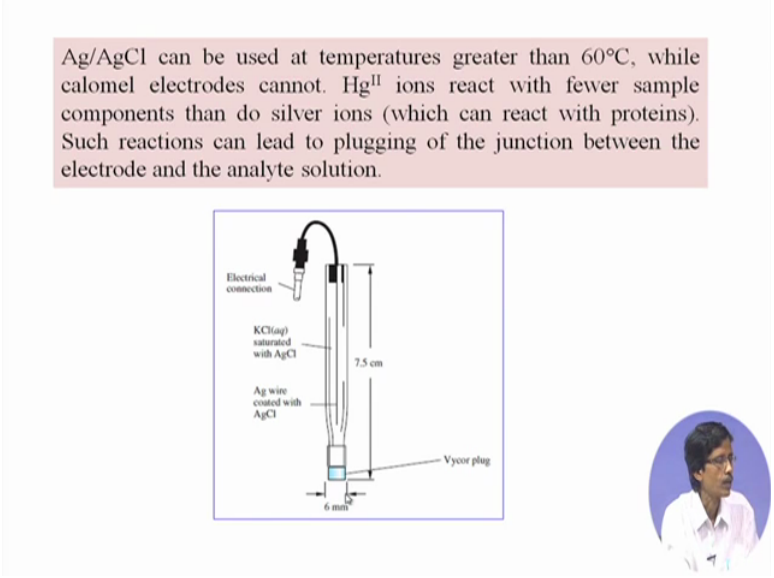

So this is the sensing part that electrodes you have which can record the corresponding potential and you get the corresponding titration, so one after another we are seeing how we can design the reference electrodes and how we can design the corresponding indicator electrodes that we are seeing. So if you have a silver-silver chloride electrode which has a typical advantage and at temperatures greater than 60 degree we can monitor while the calomel electrodes we cannot.

So that is why the designing of these different electrodes with time is also changing and the corresponding designing for its size shape and everything but what was our original electrode that we should always know that how the original electrode has been designed so you have the electrical connections so these electrodes basically we buy like that of your pH metres, pH metre is not that even only you have to buy the corresponding electrodes and if it is a combination electrode you can have everything together you just insert only one part because within this thing that means electrodes itself is not only a electrode but is a combination of several electrodes that means your reference electrodes and the indicator electrodes

What we consider is that working electrodes, so a combination of your reference electrodes and indicator electrodes when they put together we can consider for measuring the corresponding protons the concentration of the protons in the solution is your corresponding pH electrodes or the glass electrodes we call because we use the glass membrane. So glass electrodes we basically use for these so the indicator electrodes and is the rapidly

reproducible changes in the concentration of the analytes so what is the typical definition for that

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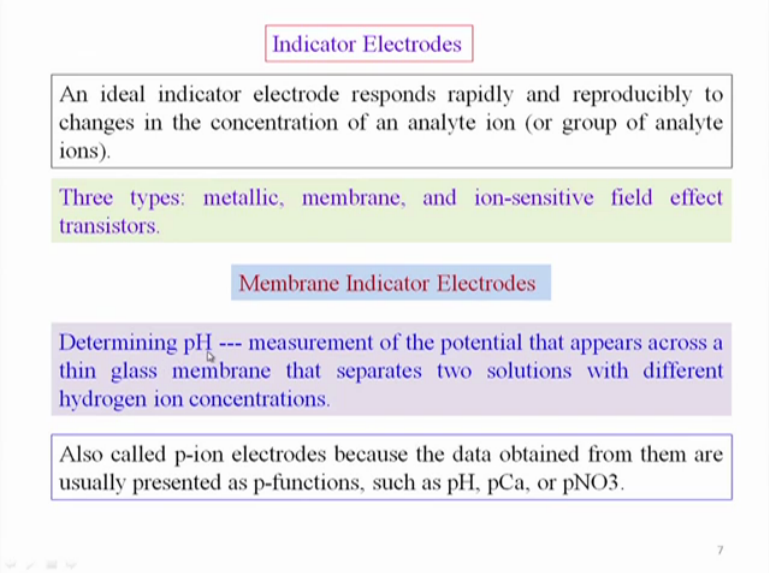

That you can have so you can have so you can have all these types of things that means the metallic, the membrane and ion selective field effect transistors. So we can take the help of the electronics people that the sensitivity for those and you have the corresponding thing we know that in very small amount of electricity or the current if we try to monitor or the measure we will not take the help of an Electrical Engineer, we will take the help of Electronics Engineer

So these field effect transistors can also be used as a typical electrodes, where we can go for that and when we can sense that thing and not only handling a solution but also you can handle the gasses, which is passing over that transistors and transistors can sense that particular one in terms of its change in electrodes potential. then we can have the membrane indicator electrodes like that of your glass electrodes which is utilized for your proton concentration determination, so if we have this membrane and it is attached to that indicator electrode for determining your pH so which we can get like putting everything together that the potential that appears across the thin glass membrane so you see that within the membrane what we also know that for a biological sample or any other sample that attachment of this thing that means around the membrane or the surface of the membrane you can have some potential that we can know.

So we consider that potential as your membrane potential so membrane potential is there depending upon the concentrations which is been separated by that particular membrane that membrane is there and one side of the membrane have you have one solution and the other side you have the different one. So here also if you have a membrane that means the glass membrane we are considering and that glass membrane is nothing but a membrane which is made up of glass and on the both side of that membrane you have two different concentrations of the hydrogen ion and that can be sensed by your electrode potential

So what we get that these things when we determine hydrogen ion we consider that is the corresponding pH which is responsible for determination of your electrodes so use the pH metre, then all these for other different ions it can be your cation or it can be your anion. We consider as p-ion electrode so the ion electrodes are the general term for all these species when we can determine the concentration of hydrogen ion or we can determine the corresponding concentration of calcium ion or the nitrate ions

So you see these are all very much useful for this the determination so the p-ion electrode because the data obtained from them are usually presented as p functions, p functions are nothing but the negative logarithm of your corresponding concentration as we present for your hydrogen ion concentration, so if it is presented for calcium concentration, if it is presented for nitrate concentration you have the corresponding p functions for calcium ions as well as the nitrate ion

But you have to think of or you have to devise or you have to design a corresponding membrane electrode or the membrane indicator electrode which should be selective for your calcium ion or the nitrate ion so like that of your hydrogen ion. Here we take the examples of these two things that means one is the typical cation and another is the typical anion.

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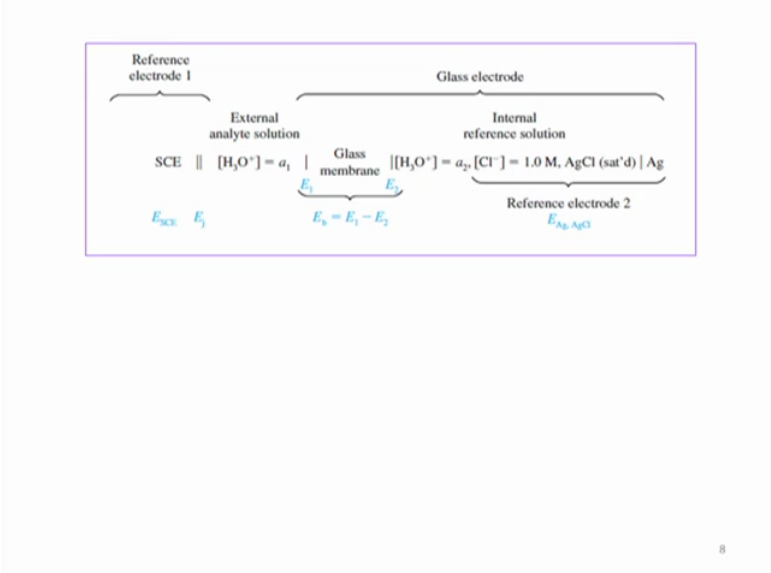

So how to place all these together, so if we have a typical glass electrode as I told you just now that you have a corresponding design of this glass electrode so these particular curly bracket from this point to that point, we consider this as a glass electrode, so what is that is nothing is a very simple one that we put something as a glass membrane, so membrane if we consider that this membrane is there which is attached to your hydrogen ion concentration and you have a internal reference electrode. So this internal reference electrode is nothing but a reference electrode number 2 so within your glass electrode you have a reference electrode which is number 2 and outside you have the another half of the cell you have a standard calomel electrode.

So standard calomel electrode is giving you a potential of your the value as well as this is double line double parallel line we know that these are the corresponding junction so you have the Ej value for that so the junction potential you have. So what basically we are coupling, we are coupling these two that means you have a reference electrode over here and another reference electrode that means the reference electrode 1 and 2 which will give rise to a potential of Eb which is E1 – E2 like that of your left – right potential values and you have the external analyte solution.

So this is your external analyte solution which having activity a1, so we will be monitoring some potential by inserting those electrodes where your activity of these H3O + which is your proton concentration, the hydronium ion concentration, so that proton concentration or the hydronium ion concentration a1 can be monitored or its activity can be monitored by utilising the corresponding change in the potential value

So when we use the glass electrode the activity or the concentration inside the membrane is constant so what you have this membrane so glass membrane this particular one this a2 value, this chloride concentration is your silver-silver chloride but this a2 is within the glass electrode. So a2 concentration is not changing, it is the a1 concentration which is their as your external analyte solution that means what we have taken in your beaker. So that will be monitoring so the concentration outside the membrane so this is your whole cell that means the glass electrodes so the glass membrane you have which is facing your solution which is as your external analyte concentration

So the activity of the hydrogen ion in the analyte concentration you measure and the concentration of the concentration difference that means the concentration difference between a1 and a2 one giving rise to one potential E1 and another giving rise to the potential of E2, so that give rise to along this membrane a potential so the concentration difference produces the potential difference and we measure it at your pH metre. So that way we reach the corresponding measurement for your pH values, how these pH values we can monitor so what you see that you have the external analyte solution and this external analyte solution you can take in a beaker and you insert the reference electrode 1 as well as the glass electrode

But it can so happen that the development of all these things that the typical glass electrode you can have and a composition electrode is also available where this reference electrode 1 can also be inserted within this unit and you get a one single electrode for your measurement, so that basically gives us some very good idea about the glass electrodes for other cation as well as the hydrogen ions.

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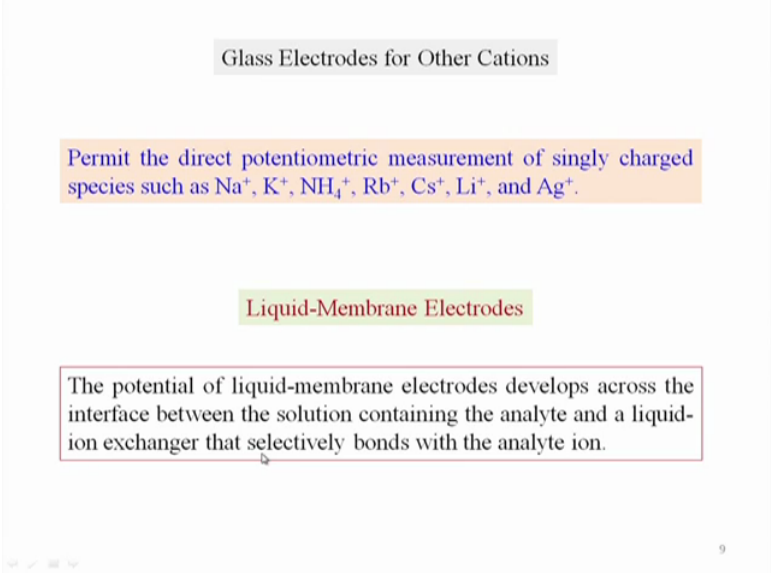

So as I told you that you can determine the corresponding concentration of you calcium as well as the corresponding concentration for your nitrate, but similar type of arrangement which is valid for hydrogen ion can also be available for direct potentiometric measurement of simply charged species such as that of your sodium ion potassium ion, ammonium ion, rubidium ion, cesium ion, lithium ion and silver ion

So the very basic concept or very basic idea what you see that you will be utilized for these ions determination, so we gathered our knowledge to develop a particular type of analysis using the help of your electrodes potential that means the electrochemical method for your analysis of hydrogen ion, but that can be extended so that is a typical analytical chemist job that how you develop a new potential measuring device that is a new glass electrode type where like that of your proton concentration you have sodium ion concentration because we know that your blood sample or any other fluid always we can measure the corresponding sodium ion concentration as well as the potassium ion concentration.

So these are the most vital biochemical fluid, the biological fluid available in our body or any other source also, then any industry handling ammonium ion or all these ions, the battery industry the electrical enzyme industries all they handle these ions because these chemicals all people are handling all these ions. So if you suspect a solution having some concentration of these even in a very low concentration only thing that you have to choose the corresponding electrode which is sensitive to those ions so the development of those things are there then these glass membrane is your solid membrane, the typical structure and the properties of this glass membrane is a material scientist job how to develop those glass membranes, so if you find time you can also leave separately how to get those membranes

So if we extend our that information or idea or the knowledge to apply it to get a liquid membrane type because we are handling all the type the solutions and mostly we are interested all the time to handle that solution for measuring your unknown solutions, so if we have a liquid membrane like that of your solid membrane the glass electrode we are talking about the glass membrane is your solid membrane

So in lieu of that solid glass membrane if you have a liquid membrane electrode developed across an interface that means we consider as an interface like that of your glass membrane one side you have one proton concentration and other side you have another proton concentration similarly here also you develop a interface but interface is around this particular liquid membrane that means we know that a liquid when it is there on a glass surface it forms a film so if the thickness of that particular film is some reasonable one so it can also function as a membrane because we know that you can have invisible liquid like water as well as dichloromethane. So you can have these two so you can have two layers and these layers can function as a corresponding membrane for some of these ions so these liquid ions exchanger that selectively bonds with the analyte

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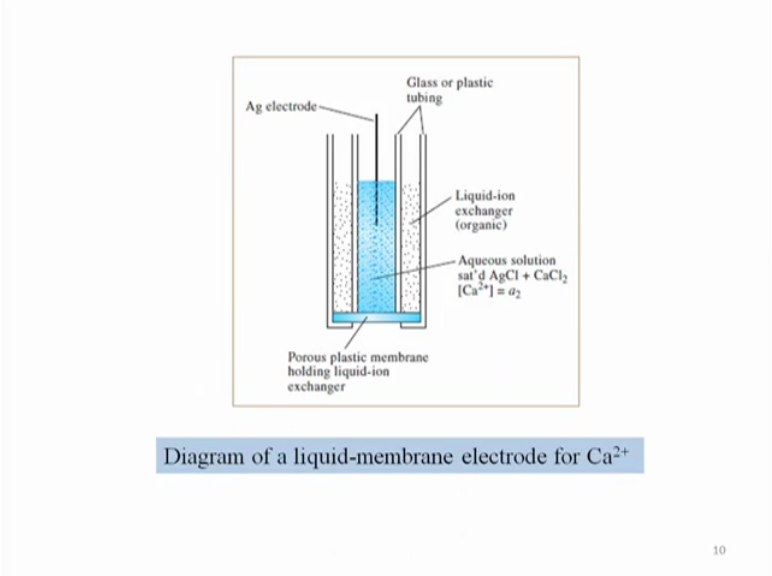

So you have the solution containing analyte and a liquid ion exchanger so which can exchange ions between the exchanger as well as the membrane so it bonds with the corresponding analyte ions and this analyte ions are loosely held over there. So what you see that you have a glass or plastic tubing is there so is a glass either or plastic, so porous plastic membrane holding liquid ion exchanger, so this is the porous membrane which is made of your corresponding plastic material and that plastic material having some liquid and this liquid is your liquid ion exchanger, then we put some aqua solution of silver chloride and the calcium chloride such that you can have some calcium concentration of a2 then this tubing around this tubing what you have the liquid ion exchanger which is the organic liquid.

So you put that organic liquid over here and you insert that corresponding electrode over there and then you get a corresponding liquid membrane electrode, so this is the very basic design of a liquid membrane electrode for calcium 2 + and what you can do. You measure the corresponding pCa concentration using this particular liquid membrane, so the development of this part basically the idea behind this measurement is well know now but the development of the these electrodes how you measure this particular potential using this different types of electrodes. Initially, when people developed those electrodes are very big enough and these are much more complicated but day by day people are developing these things such that we will be reaching somewhere where you can have a micro electrode so these development of these micro electrodes is also very useful

And if you are able to get some microelectrodes of needle set or size, what you can do that you have a solution anything like electrode that means is not a electrode combination, is a combination of all these, so as a combined electrode system and if you get that microelectrode as a needle that combine electrode insert in any solution concerning calcium 2 + anywhere have the corresponding connectivity and the metre what you use for measurement.

Electrode potential you measure that means you have a potentiometer, so this potentiometer will give you the corresponding potential you measure something which is the available to give you the corresponding determination of your calcium ion concentration. So you can have some idea for this from the book also, so how you get now the corresponding potentiometric titrations, so will reaching at that particular point through the development of all these electrodes, their designing and their positioning and all these things

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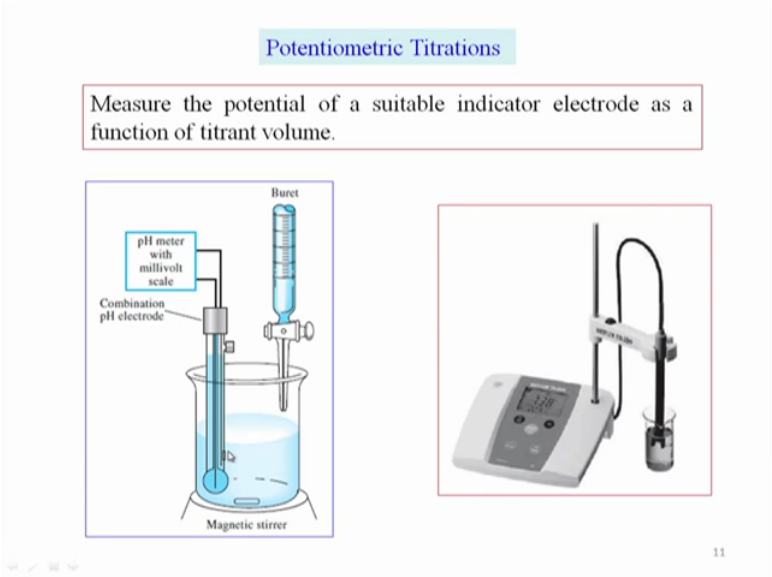

So like your simple titration so what you can have that now you have the titration so you will utilizing the same buret we know that and the buret, with the drop by drop it is adding the solution. The analyte solution it is adding to your container for your titration so what we get that corresponding potentiometric titration can be defined in that way that what we use, we use for the measurement of the potential where you all know now that you have the indicator electrode and that indicator electrode will now sense because you can have the reference electrode and with respect to that reference

The indictor electrode will measure the electrode potential as a function of now titrant volumes, so as I told you in our previous class that against volume you plot something which is lower potential. So with respect to that potential you measure and the volume of these things so this is the corresponding simplest, very simplest desktop arrangement for your pH metre and what you see this is the combined electrode and that combined electrode is inserted in the solution which is in the beaker and you get some values for that and it has two basically two knobs what you see that directly you can measure the magnitude of this what you see from 7.38 from this display that either directly you measure the corresponding values in terms of the pH or you can switch to the different one reading is for your millivolt measurement because what we measure is your electrode potential and that electrode potential is directly converted for your corresponding values of your pH.

So either it is a pH metre or electrode potential measuring device for measuring your electrode potential, so when you directly measure the pH value we know that we get the corresponding neutralization point and how we get the corresponding plot that we measure and we know where we can detect by using the indicator where is your end point. So now if we plot the corresponding electrode potential in fold which is in the Y axis and X axis is your volume of that thing what is being added you get that thing. So this is the simple thing that on the right hand side what we get that you have the pH metre, and that pH metre will give that if you insert the electrode you will be able to measure that sample any unknown and analyte. It can be your blood, it can be your municipal waste, it can be your industrial waste, it can be your sewer water, it can be sea water.

You directly put this electrode inside and you measure the potential and the corresponding voltage so and it can be converted to your pH, so directly you relate pH. But how you do the titration as we all know that the titration what we require is your conical flask. We add the buret and we have the indicator as your corresponding die of methyl red and methyl orange. Now instead of that indicator what you have in your hand is your some indicating device what we consider as your indicator electrode

So without using that die we will be now using an electrode because we want to do this by going for a potentiometric titrations which is the heart of your electrochemical methods of analysis so you get that so is now you get what it looks like so all sorts of different arrangements I showed you and this is the typical diagram for your combination pH electrode, so that combination pH electrode what you can have and that combination pH

electrode have these two output basically so sometimes this can be one single connector so the connector is there, so you attach that particular connector to your pH metre with millivolts scale.

So you have one millivolts scale you measure it in millivolts and you have the corresponding pH in other and you go so the buret is there, the buret is clamped on the other side the way we have clamped this, so this will be clamped on the left and the buret will be clamped on the right and you open up the buret and you have the solution because your analyte is here now and the mixing of of the analyte is also required

So you put everything on your magnetic stirrer and that magnetic stirrer will start the solution with an incremental addition of a volume of the solution, so suppose you determine basically we can do any simple experiment of determination of your washing soda that means sodium carbonate, the unknown concentration of sodium carbonate in a given solution which is taken in your beaker, you add your corresponding acid which is your hydrochloric acid and that hydrochloric acid will give rise to that corresponding concentration so you have the known amount or known concentration of hydrochloric acid

And that hydrochloric acid you add so after addition of 1ml you record the corresponding pH value, after addition of 2 ml you record the pH value and then the different values of pH what you get as that data can be plotted of the different volumes of the corresponding titrants what is being added to the analyte taken in the beaker can be plotted, so this will give you the corresponding volume against the pH values but if you switch on to the millivolt axis at the same time you will be able to measure the electro potential because not only the pH values, will be directly measuring for the E values that means the potential values for some other titrations which can be utilized for your oxidation deduction reaction that means this potentiometric titration is also useful for handling redox titrations and the redox titrations curves will also be similarly you can plot, so what you have so this is the simple one for a potential what we can measure the corresponding precipitation reaction what we can see that the separation for your chloride concentration say what we get for your volume of the silver nitrate.

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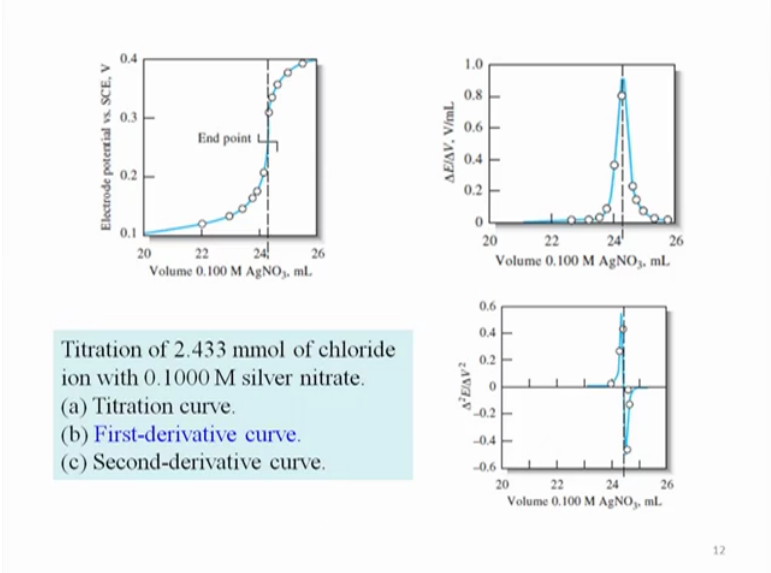

So the nature of this plot is all same whether you go for volume of some acid that means the hydrochloric acid against the electrode potential or the pH, so you can have these things so you can have these as the corresponding plot what we know from your neutralization titration what we would be knowing for several classes that you have the volume and pH and is changing like this.

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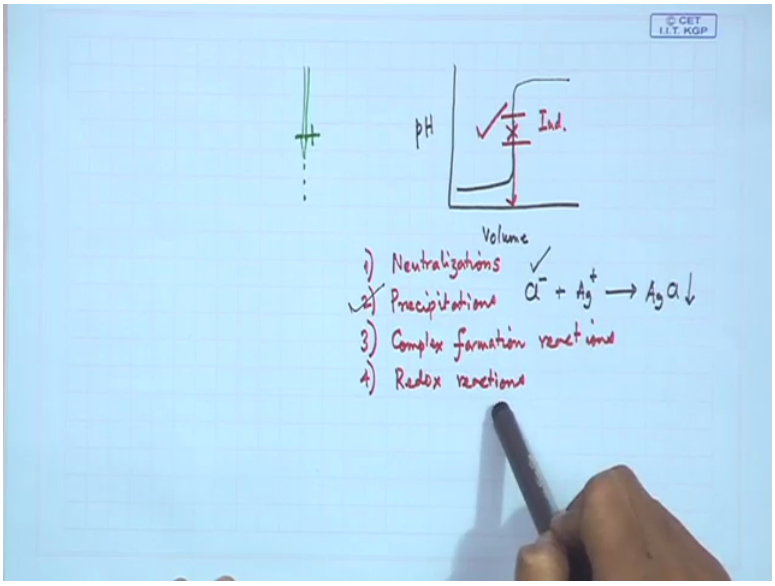

So this change basically and we all know now that how we get the end points so you just extrapolate this point, you get the end point and this is a corresponding range for your indicator which is indicating the change that means it can locate this particular point you get this. So it can be your silver nitrate and all these things and we can detect and we try to detect

this point as a corresponding one, so if it is a corresponding precipitation titration so the plot is also same so the resembling are the resemblance of the plot is for neutralizations, the same plot that means the neutralization reactions, then we can have the precipitation reactions as we see here the plot with the precipitation of silver nitrate. We can have also the complex formation reaction that EDTA is used for your titration of calcium ion or the magnesium ion and also the corresponding redox titrations, the redox reactions.

So all we can handle and in all these cases your plot will be similar, so this staircase type of plot we get so this is the end and you have the volume and you measure the quantity what you will be measuring for this. So if we have the corresponding precipitation titration that means the second titration what we are talking about this is the thing that means the precipitation titration that means the titration of CL – by a silver nitrate solution that means the silver ion giving rise to the corresponding precipitation of silver chloride so as that you determine the unknown concentration of chloride ion which is also a very vital component of your any sample like any industrial sample or any biochemical or biological sample even in our blood fluid.

So blood sample can also be handled for your chloride determination by this particular technique so first one is this plot which is your typical titration club for using a solution where you go for a titration that means the in the beaker what you take is your 2.433 mini mole is, a typical example of your chloride solution, the chloride ion solution and titrating with a higher concentration for that chloride by a lower concentration of silver nitrate such that when we have a 1 is to 1 reaction a volume of silver nitrate will be more such that your error due to that particular delivering of that volume of silver nitrate would be less

So the first derivative plot so this is the point where you want to detect the end point, but you see if you have some mistake that means if you get here or if you get there is not being pointed that where you have some point of that change so straight way we can go for the first derivative plot so when you same data same data say we can use for your first derivative plot and that first derivative plot will pin point the end point over here so which is some 22.2 or something like that. This is also first derivative plot and the most interesting one is that is the second derivative one, the del square E by del V square if you plot that means the change in the corresponding potential values with the change in the volume you plot it because it is changing from some values to 0.1 to 0.4 the potential change

But when you plot the derivative it is 0 to some value and when it is the derivative one so on both the two directions you have these things and you get one it is crossing your base line, so not that you have to find this one you have find this particular base line and this is your end point. So all these titrations you can monitor and you can determine for this determinations and you get the end point such that the only thing that the electro potential you can handle and that electro potential can give rise to the end point for all these determinations of the different types of titrations starting from your neutralizations, the precipitations, the complex formation as well as the Redox reactions ok, Thank you very much.