**Course on Analytical Chemistry**
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**Module 9**
**Lecture No 45**
**Electrochemical Methods – I (Contd.)**

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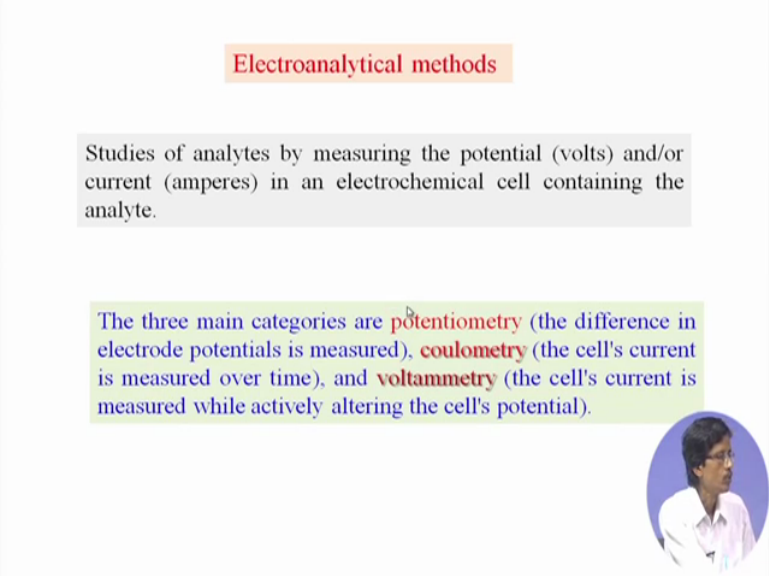


Good evening everybody we were talking about that analytical methods which are utilising some electrode potentials and we basically consider this as the Electroanalytical methods, so when we consider that is some electrode potential or the current or the voltage and be a measurable quantity for you analysis, then we get the corresponding Electroanalytical methods. So this study basically includes when you have the analyte and will be able to measure corresponding potential and or current, so potential in volt and the current in amperes in any electrochemical cell containing the analyte.

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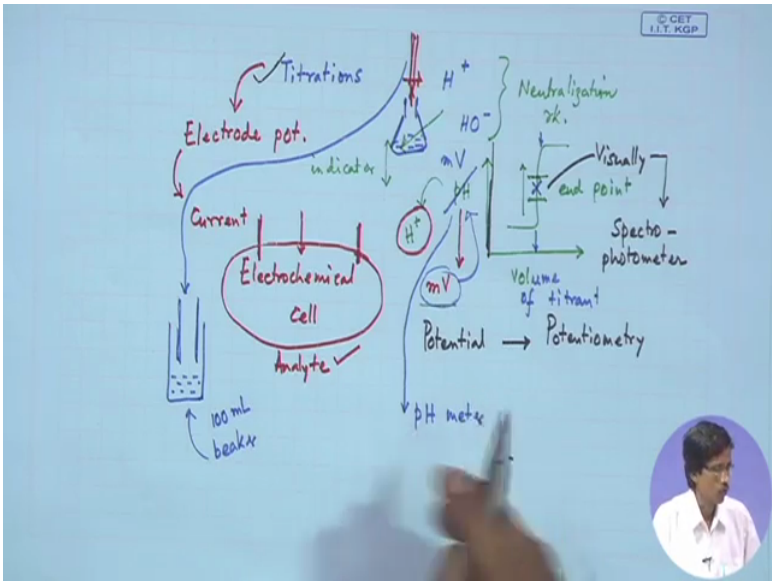


So is a very simple technique what we can consider that the different types of titrations what we are looking from our or earlier classes that titrations what we know that the corresponding neutralisation reaction between H plus and HO minus that means hydrochloric acid and the corresponding base as the sodium hydroxide.

So when we get this particular neutralisation reaction we try to monitor from their is that, we basically add some indicator and that indicator will change its 2 colors one is in the acidic form and the other will be in the basic form and when we know that a passes through some pH value so this is the typical plot where one axis will be utilising for the volume of the titrant that means if we add the corresponding acid or the base and another is the particular parameter.

So when we consider the neutralisation reaction in terms of the neutralisation of the acid or the base or any carbonate or the bicarbonate salt what we see that this particular one is the pH that means the corresponding hydrogen ion concentration and that hydrogen ion concentration we can monitor so there should be some pH and we can locate the corresponding endpoint by using that particular solution few drops of those indicators which can change from one color to the other that means we are passing through this particular color change range for the corresponding indicator.

So this particular parameter basically is dependent on the corresponding concentration of the hydrogen ion and its neutralisation. So when we consider that any other sort of titration and we will utilise corresponding electrode potentials say or the current we can use. So this will

see that how we can co-relate this particular parameter this pH to some electrode potential which is your millivolt.

So the voltage you can measure so this corresponding electrochemical cell if we have and within that electrochemical cell if we take the analyte in it and the same burette basically so this is the typical burette pipette reaction what we know that this is giving you that corresponding (())(4:13) edition of the hydrogen ion. So within the electrochemical cell so the sensing point means the sensing point is your electrodes.

So those electrodes are available and if we can externally measure the corresponding rain which is passing or the voltage between these 2 electrodes that is why we are discussing about the corresponding electrochemical cell as well as the galvanic cell. So what amount of that potential can be developed by inserting these 2 electrodes such that we can monitor the corresponding change in the analyte concentration so will be monitoring because something we are adding and some sort of this neutralisation reaction is happening and we will try to monitor corresponding millivolt say how you measure that is the corresponding potential we can measure so that is once we measure this potential we will get a technique which can be termed as the potentiometry.

So we all know that the potentiometer, what is potentiometer? So this will be immediately the as the corresponding potentiometric titrations and since we have the pH and here without using any instrument or anything or any meter or your analysis. This is your corresponding color change so visually we detect the endpoint and sometimes this particular detection if we have a very low concentration which we cannot detect through our eyes so we can take the help of a corresponding spectrophotometers that we have seen at how we can use the spectrophotometer or the different spectrochemical analysis.

Now if we consider that how we measure the pH values because we should know that this measurement of this pH value we all know that there is one small bench top type of instrument is available to everybody and is nowadays is available to everywhere. So is your pH meter, so this pH meter you have something that means we will find that a electrochemical cell arrangement will be utilised to detect something which is your the corresponding millivolt values and this millivolt values can be co-related to your pH.

So what we have earlier studied is a very interesting one that we just plot this as the pH and the corresponding volume of the analyte, so it is not voltage do not make any mistake over

here that is the volume of the titrant, okay. So if we get that that particular millivolt so if the pH meter is available to measure the pH and if one of the parameter is by measuring the corresponding voltage of the cell, the electrochemical cell.

So instead of plotting this pH values we can plot this millivolt values over there and what will happen if we want to see the change in these millivolt values. So if this is the axis whether will get this sort of plot or the other sort of plot where we can clearly detect the corresponding endpoint, we can pinpoint this particular range in the middle of this thing at means it is not changing much from this volume to this volume.

So if we can find that this sudden change in this millivolt values are also there, so like that of our titrimetric method using indicator and the pipette burette titration the manual titration what we can have can also be utilised for your potentiometric estimation or the potentiometric titration, so this gives rise to our one of the most important electrochemical methods if we can use the potential to measure the corresponding endpoint or detect the endpoint.

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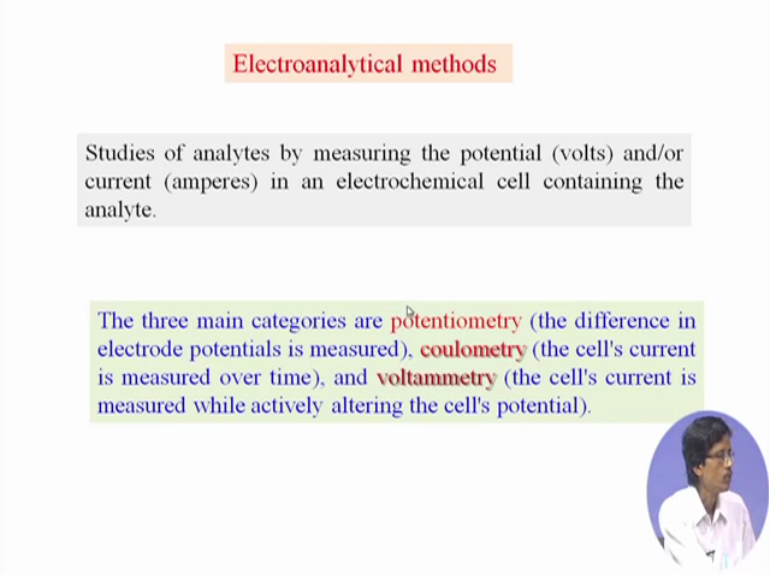


So is the first thing what we will be seeing here that is why the measuring of potential so in volts or in millivolts and at the same time also will find that in some other methods that once we measure the potential we should also be able to measure the corresponding current in any electrochemical cell containing the analyte, so that is the very most important thing to our concern is that you must have a electrochemical cell and that particular spectrochemical cell will have the corresponding analyte.

That means if you have a unknown base in your electrochemical cell, so instead of using the typical conical flask what we use for your titration, the acid-base titration. Now is that that you must have something that means you have the electrochemical cell and we all know that is not very complicated situation of making a electrochemical cell because if you have something because in our previous class we have seen that when you are tipping a iron nail in a copper sulphate solution that gives rise to a corresponding cell of your depositions of copper on the iron electrodes.

So you have something that is half-cell so if you just simply complete that for 2 half-cells and you can do the same interactions within a burette that means your container is nothing because earlier we are going for this titration say using a conical flask. So you have the conical flask over there now this electrochemical cell, the concept of getting a corresponding electrochemical cell it should have a wide mouth thing that means the simple beaker how you can use that thing. Say of 100 millilitre capacity and you have the corresponding analytes in it. You have already taken and the measured volume of this what you are there in this conical flask also for your titration.

So then you just this particular part that means what is electrochemical cell, so this is your electrochemical cell, you have to insert the electrodes, the cathode as well as the anode and you just add the corresponding analyte that means this burette will come over a here so this burette will be there and drop by drop addition of that particular titrant will change the responding reaction medium that means it will go from a one particular basic side to the acidic side and during that process you have a corresponding or continuous engine in the corresponding millivolt values and we will try measure because this has a digital reader means the display unit of this pH meter will record the corresponding values of your millivolts.

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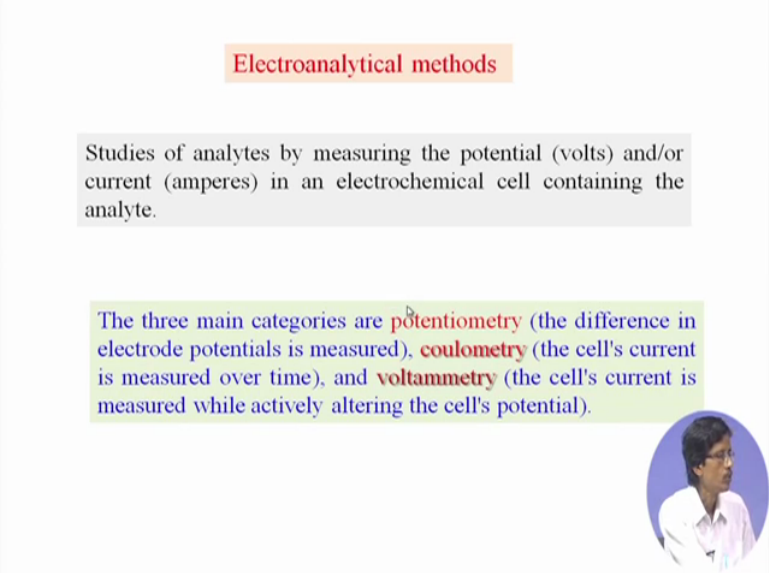


So what we see for this analytical method utilising the electricity so definitely we will get 3 main categories so what are those main category that we should know very nicely, the first one so far we are discussing here now is that your potentiometry, like that of your potentiometric titrations. So what we measure there, we measure the difference in electrode potential between the 2 electrodes.

So is a very useful and the most simplest technique that the measurement of the electrode potential by using 2 electrodes inserted within a cell and that is your electrochemical cell. Now if we measure we try to measure the corresponding rent, the cells current is measured over time that means how much charge basically not typically the current it is the charge what amount of charge in terms of coulombs.

What we can pass so that the coulometry is the passing of the electrical charge to that particular solution and something is happening and we all know that when we use that particular charge to a system, either the charge you take out the electronic charge we take out all the detachment of the electrons from the system is your oxidation or the addition of the electrons the system that means the reduction.

So this particular system should give you a corresponding oxidation as well as the action and the third category is your voltammetry, so is a different type of thing means you have the cells current is measured while actively altering the cells potential means you have voltage, the volt and the ampere.

So the voltage as well as ampere will now measure, so at certain point you have a huge change of the corresponding current which is passing through that particular point and we get some information not only regarding the finding out the unknown analyte concentration part the nature of the corresponding electrode active species means whether you have a oxidising species or a reducing species and the electrodes are responsible for your oxidation and reduction of that particular species.

We can monitor for a voltammetric measurement that we will see and this also give rise to the corresponding both of the voltammetric sensors you can sense that thing that means some analyte concentration which is unknown so unknown analyte concentration can monitor using this particular voltammetric technique.

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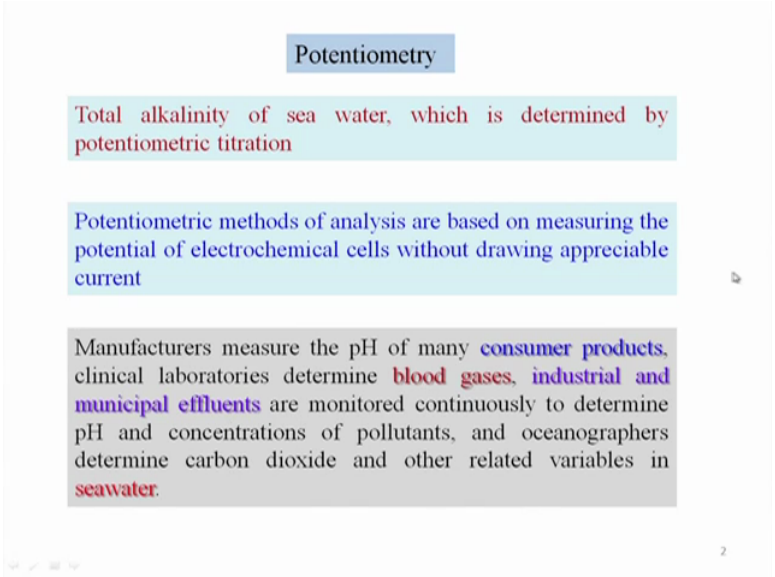


So the first one will be just discussing over now is your potentiometric, so how you get how you do the potentiometric titration so forced thing what we can see is that how you get the corresponding potentiometric titration curves. So is a very useful technique or determining the alkalinity of seawater because we know that the seawater is alkaline. How much alkalinity you have means if you have a very low concentration, not all the time you can go for your corresponding conventional or manual acid-base titration using some indicator but your potentiometric titration are very much useful to determine the corresponding alkalinity of the seawater.

How much alkaline salts are available in your sea water like that of your sodium carbonate or potassium carbonate or sodium bicarbonate or potassium carbonate in those seawater. So this

potentiometric method of analysis is based on measuring of the potential of the electrochemical cells without drawing appreciable current which is very important that the cell is not meant for drawing the current but still you will be using some electrochemical cell such that we can monitor corresponding change in concentration, the change in the corresponding concentration of say 1 species which can be your the corresponding ferrous ion concentration and any other oxidising agent.

So large number of industrial places or some other applications for our live processes or the analytical chemistry which we apply for analysing the blood or the urine or any other fluids what is available from our body that means the corresponding clinical chemistry, so the clinical analytical chemistry is also will be relying on this simple pH meter what we are discussing now.

So anything related to your pH that means your consumer products, your creams the face creams we use the soaps and all whatever we consume as our daily needed, so that can be utilised for your pH determination then clinical laboratory is basically determining not only the pH of the blood but also the dissolved gases because the dissolved gas like that of your carbon dioxide is more so how we can monitor the corresponding concentration of carbon dioxide by using this technique.

Then what we just drain out the industrial and municipal effluents, so the bases or the acids whether these are the effluents because we know depending up on the industrial activity what we can have either you discharge into some drain water or ultimately to the river water or to the seawater that a solution which is your municipal effluent and that principal effluent and have either acidic nature or a basic nature.

So direct monitoring by inserting those electrodes consider that the container is taking your effluent you can go for the potentiometric estimation for determination of your pH and the amount of the corresponding species which is responsible for giving you that pH of your municipal effluent.

So very first thing what we do and what we determine is that the determination of the pH of anything starting from your any other solution the water we drink the blood we have or the municipal effluent we can have and it also gave another advantage to us that continuously we can determine that particular pH and once we determine that particular pH and what we are throwing away what we are discharging in the riverbed or the seabed is the corresponding

concentration of the pollutants which are responsible for giving you the required amount of the acids or the bases means the acidic substances or your basic substances to give you the corresponding pH of that particular solution.

And people who were dealing with the oceanic activity that means oceanographers, they basically determine the corresponding amount of carbon dioxide and other related variables which is dissolved in the seawater. So how much your seawater is contaminated that basically can be determined by this particular type of titration which we consider as your potentiometric titration.

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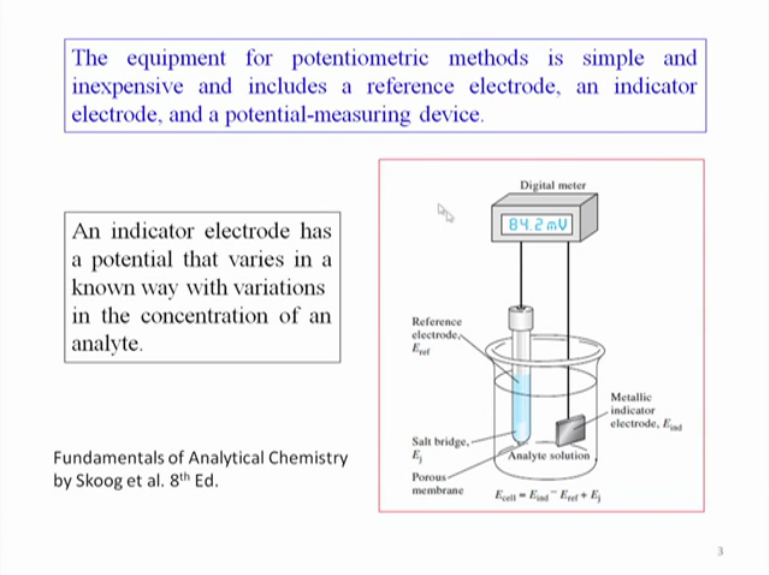


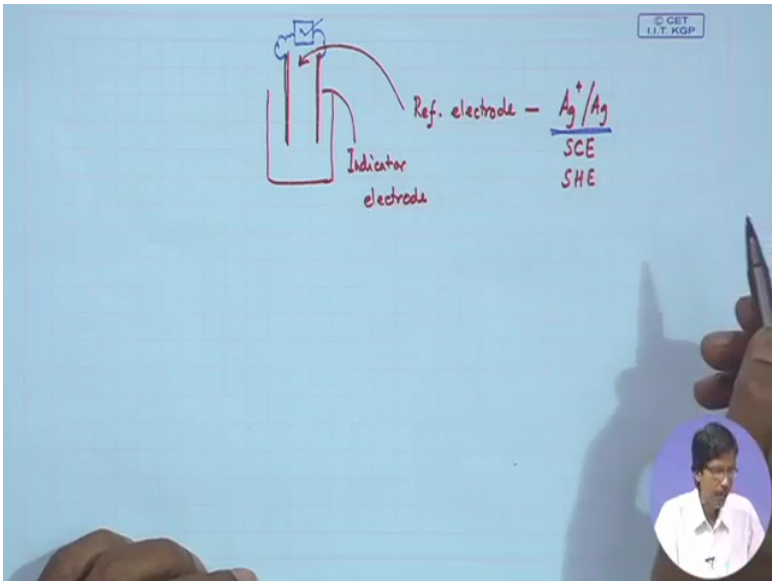


So is a very simple one as I told you are not is also inexpensive and it includes the reference electrodes, and indicator electrodes and a potential measuring device. So as we have seen in

our previous class that we use the corresponding electrochemical cell, so in this particular electrochemical cell you have something for that potentiometric methods, so we have a reference electrodes so this is reference electrodes what we have seen this reference electrodes as we have seen we are discussing for that is also for your silver silver chloride or silver ion silver electrode or simple saturated calomel electrodes or standard hydrogen electron.

So we determine this particular half-cell potential by attaching these 2 standard hydrogen electrode and with respect to the standard hydrogen electrode we found the corresponding potential of this, so this can behave as a corresponding reference electrodes for your measurement and another can be your indicator electrodes, so which is your you can consider this as for in other measurements as the working electrode but this is your indicator electrodes.

So combination of these 2 that means we have 2 electrodes so what are this corresponding available potential, so you have to measure the corresponding potential out of this curve thing and this one, so a potential measuring thing that means a reader is available so that reader will record the corresponding potential between these 2 and that can be reported with respect to the corresponding silver silver ion electrodes or the silver silver chloride electrodes or saturated calomel electrodes. So you have to measure the corresponding potential between these 2 electrons.

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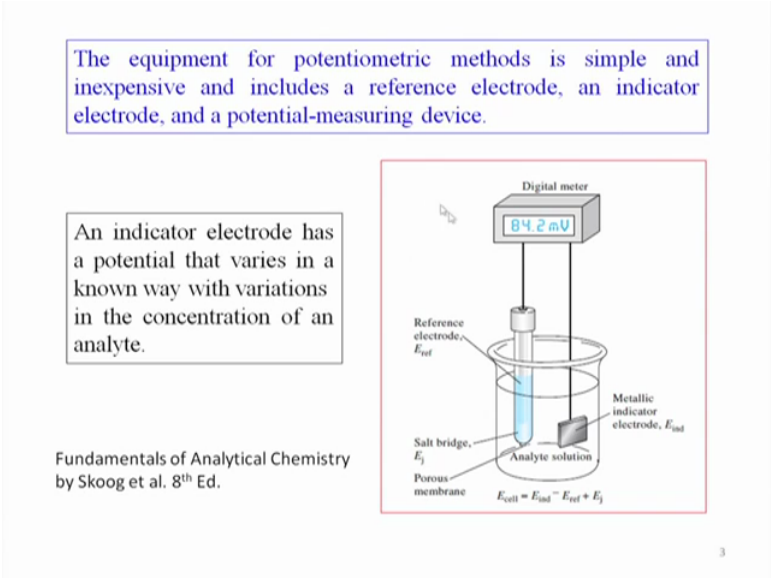

So what we get over there is that a simple system that where you have a digital meter and this particular digital meter what we are talking about that you can consider at what we see digitally that means it has a typical display unit and display unit say what is shown over here is typically your 84.2 millivolt at means in the range of simple millivolt you have it and you have it and you have taken open beaker as I told you just now and you have the analyte.

Only thing is not there that is not the complete arrangement for your potentiometric titration for recording some neutralisation reaction or some precipitation reaction or some redox reaction, so you can monitor all these together utilising this particular technique, so as I just now told you that is the corresponding figure for it but we have taken from any book that is the Skoog book that you have the reference electrode.

So is the E ref, E ref value is there and you simply insert some your metallic indicator electrodes it can be a Platinum wire only or it can be some plate, the metallic plate. So that will give you the corresponding potential as your E indicator but within this particular reference electrode you have some porous membrane at the bottom this this round point that is you have the porous membrane and the salt bridge because this indicator is directly inserted to within the analytes solution.

But this you see is glass case, so casing is the glass and can have some porous membrane is that you can get the corresponding exchange of the solution generation such that the electrodes is exposed to the corresponding concentration of your analyte and is not that you analyte will get go inside and contaminate this thing but it selectivity that means the membrane what you have we all know that the membrane is not that is a typical thing that is just controlled the corresponding passage of the ions and we get somewhere that is ion selective.

So if we talk in terms of the corresponding thing that you measure the corresponding potential in terms of your millivolt value in the pH meter and the corresponding proton sensation, the corresponding proton what is going or what is exposed for this, so the proton concentration is move through this porous membrane, so we can detect the change in the corresponding proton concentration by measuring the potential value where you have the corresponding E cell.

That means it is the complete cell and these are the 2 half-cell values that means we all know that the potential for the corresponding indicator electrodes we call it as the electrodes right,

so the right-sided electrodes minus the corresponding left-sided electrodes that is the usual convention what we use to calculate out the corresponding potential that means a total potential for the cell plus some collecting value we use that you can have a (())(24:25) as we have seen that some inverted u tube we use to get that cell. So this is the corresponding value for your junction it is the junction potential.

So once we add up all these 3 together you get the corresponding cell potential values and when these cell potential values will be changing will that particular display will record that thing and will get that thing also your measurements that as an indicator electrodes has a potential that varies in a known way by variations in the concentration of the analyte. So what is your analyte now that you now get all this information that you have a pH meter or a digital meter you have.

So we are not calling it as a pH meter right now but if it can sense the corresponding concentration of the hydrogen ion what we see here is that even the concentration of that hydrogen ion is changing that will directly (())(25:25) is your analyte because analyte corresponding term for your analyte what will be looking for your analysis is the generalised term what can be applied to your proton? What can be applied to your corresponding something which is your reductant?

That we can determine that reducing agent like your ferrous ion, if we want to determine the concentration of unknown ferrous ion what will you do? You will try to reacted with some oxidising agent like your permanganate or dichromate or the ferric ion concentration and you go for electron transfer reaction but here how the proton is going for your electron transfer reaction so that is the very basic simple thing, is that will have some proton concentration. So the change in proton concentration will be sensed in terms of the charge transfer in terms of the electron transfer.

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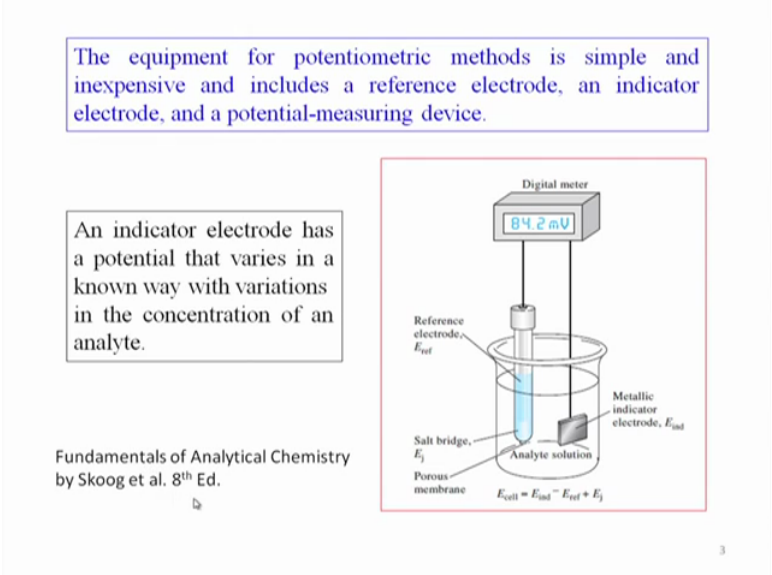


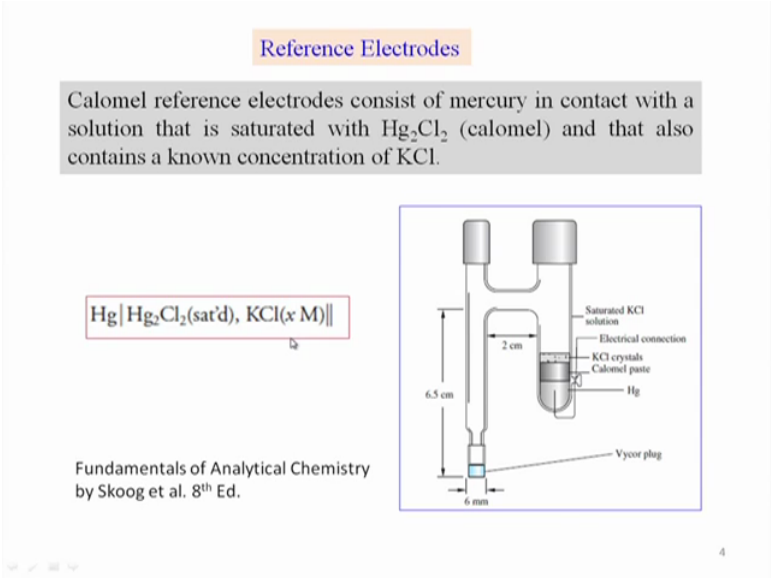


So this is particularly the figure and this thing is very detail is available in your book the fundamentals of your analytical chemistry written by Skoog and West. So the reference electrode the first thing, the first component what we use your reference electrode, so as we discussed earlier once again we just recall back that saturated calomel electrodes the SCE.

The calomel electrodes are consisting of a mercury in contact with a solution that is saturated with mercurous chloride and the corresponding name of this traditional name or you can consider it as the corresponding trade name without knowing the formula as chemist write as Hg2 Cl2 we can say that it is calomel and also contains unknown concentration of KCl. So Hg2 Cl2 in presence of KCl will give rise to the calomel electrodes where you have the mercury in contact with that.

So the arrangement for that is little bit complicated where we see that you now have a H type of tube these are 2 caps basically, so when you get this H type of tube and you have a long end of 6.5 centimetre type of thing and you have the separation of 2 centimetre and you have a 6 millimetre width for that is there vycor plug which is your typical permeable membrane because this permeable membrane which is made up of some vycor is also a trade name of some material, some polymeric material which can only pass which can only pass you selective ions like your proton.

So is ion selective get what we get so ion selective membrane we get we can consider this as ion selective membrane and your reference electrodes there what we have defined over here is the presence of KCL solution then KCL crystal because it will be within the saturated one as we discussed in case of silver chloride silver electrode that you have the saturated solutions of that because that concentration will not change.

So if you have calomel paste this is your calomel paste little bit darker and you have the mercury at the bottom and this particular one you have and you have some wire fixed over it that you just mercury is connected to some platinum wire that means it gives rise to the corresponding electrical connection for that thing. So the designing of this electrodes what we can have and that basically we know now how to write the half-cell, the half-cell is nothing but your this mercury.

Then you have the calomel and which is there in a saturated KCl solution of some concentration, x molar of that KCl solution. So the x molar of that KCl solution this will give rise to the corresponding values for this reference electrodes because the reference electrode is nothing but a half-cell and that half-cell will have some potential value and which is dependent on the corresponding concentration of your potassium chloride. So we measure that we find that and we then try to co-relate that of your indicator electrode.

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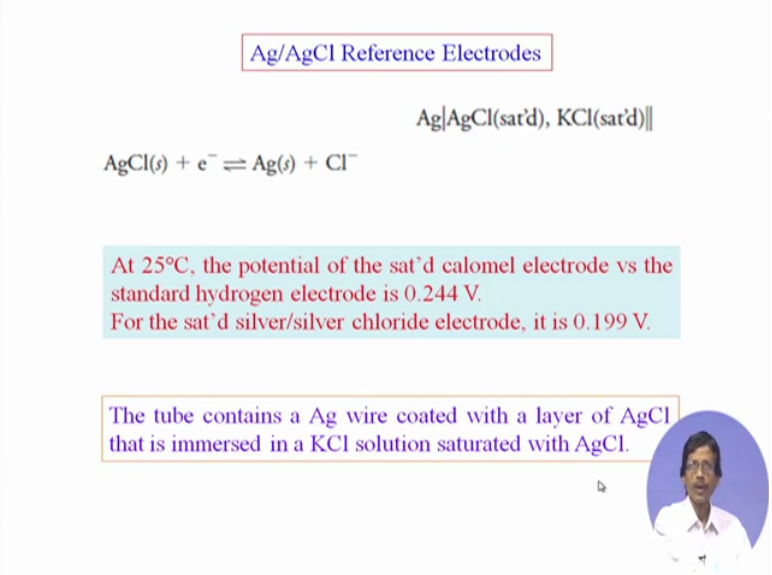


So when you have the indicator electrode, so is like that of your calomel electrodes you can have the silver silver chloride electrodes where you can should be able to write down in form of that corresponding saturation of silver chloride and the corresponding KCl saturated solution and the electrode reaction what we knew earlier in our previous class we discussed it in detail that how you go for the reduction of silver ion to silver in presence of that silver chloride.

So that potential we get that 0.244 volt we get and for the saturated silver silver chloride electrodes we get this 0.199 volt, so the calomel and the silver electrode you have the different values of all these things and we can use this where you have the coated silver wire and layer of silver chloride it has and it is dipped in the KCl solution and the saturated solution of silver chloride. So what we see next that how we can utilise this half-cell and the reference electrode and the indicator electrode for your titrations which we can consider as your potentiometric titration that we will see in our next class, okay. Thank you very much.