Electrochemical Technology in Pollution Control

Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 09
Electrochemical Methods

Welcome back, we were discussing about the conductance as an Electrochemical Technique for Pollution Control. I had given you basic ideas about an electrode specific conductivity, molar conductivity etcetera and then I had described to you about two bridges.

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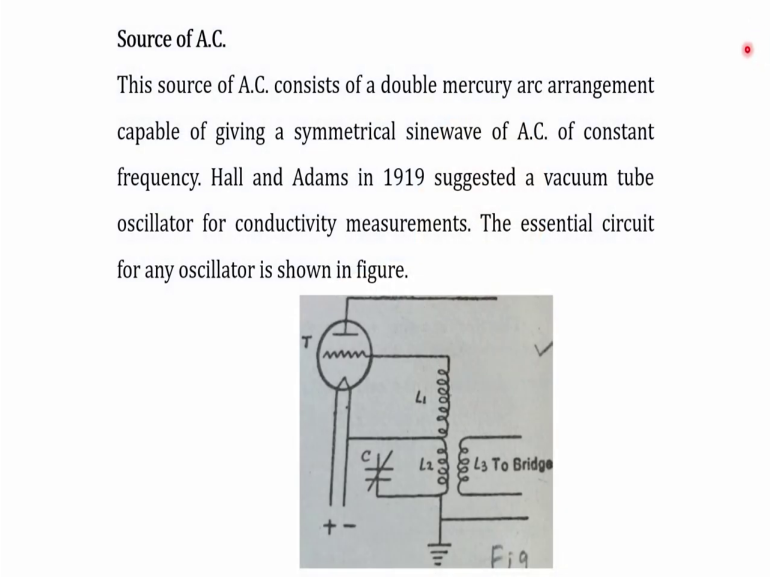

Source of A.C.

This source of A.C. consists of a double mercury arc arrangement capable of giving a symmetrical sinewave of A.C. of constant frequency. Hall and Adams in 1919 suggested a vacuum tube oscillator for conductivity measurements. The essential circuit for any oscillator is shown in figure.

And the source of AC also I had discussed like this and I had told you that such a thing is the available in the market, you do not have to really worry about the how to make this, ok.

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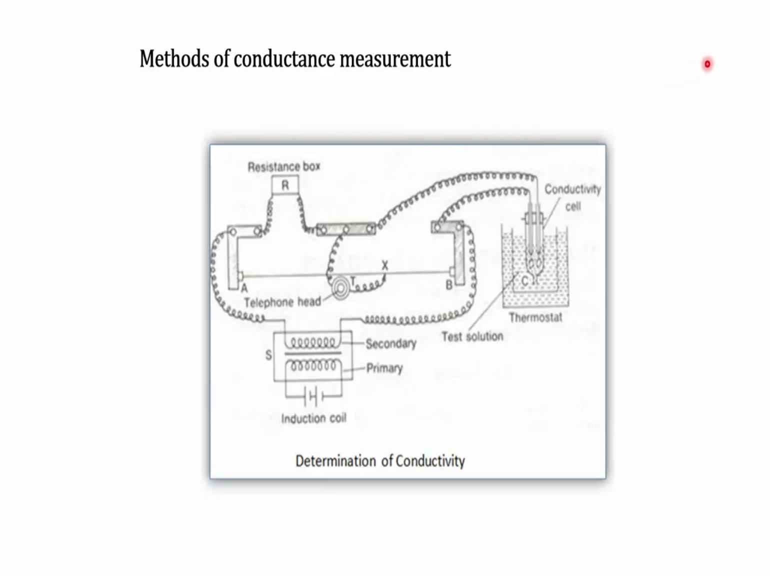

Methods of conductance measurement

Determination of Conductivity

So, how do we measure the conductance? So, it is a fairly simple system and here I have a conductivity cell, and here are there are two electrodes where my pointer is there, 2 small electrodes are there. They are connected to wires externally and then it is connected to the induction coil. And, telephonic head if you want to listen to the sound of the sometimes sound measurements are also you can hear them through the headphones and then I have a resistance box and telephonic head. So, this is how determination is made. Nowadays there are lot of analog equipments as well as digital data that can show you conductance directly, ok.

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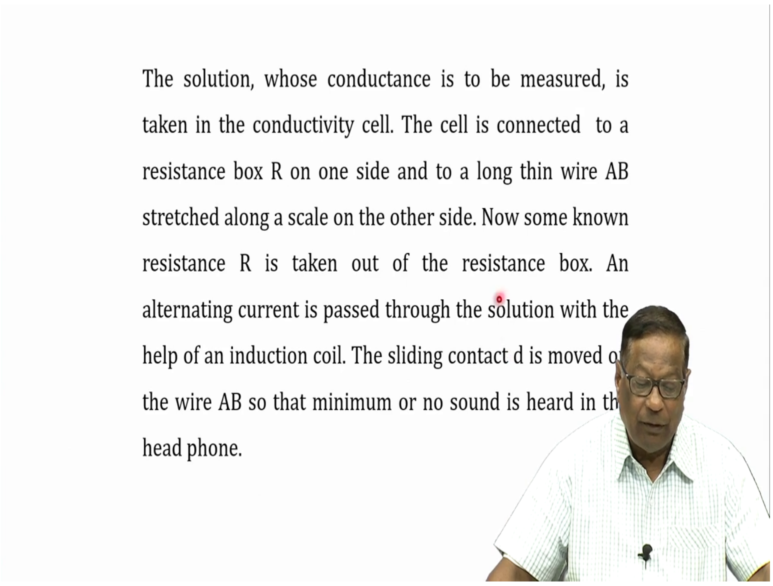

The solution, whose conductance is to be measured, is taken in the conductivity cell. The cell is connected to a resistance box R on one side and to a long thin wire AB stretched along a scale on the other side. Now some known resistance R is taken out of the resistance box. An alternating current is passed through the solution with the help of an induction coil. The sliding contact d is moved o the wire AB so that minimum or no sound is heard in th head phone.

So, the solution whose conductance is to be measured is taken in the conductivity cell that is here in this solution. This is a outside is a thermostat to maintain the constant temperature. So, the cell is connected to resistance box on one side you can go back and see the reference resistance box etcetera they are all there and to a long thin wire AB stretched along the scale just like with (Refer Time: 02:43) bridge.

Some unknown resistance R is taken out of the resistance box. An alternating current is passed through the solution that with the help of the induction coil. And, the sliding contact d is moved on the wire AB so, that minimum or no sound is heard in the headphone that is when the bridge is balanced.

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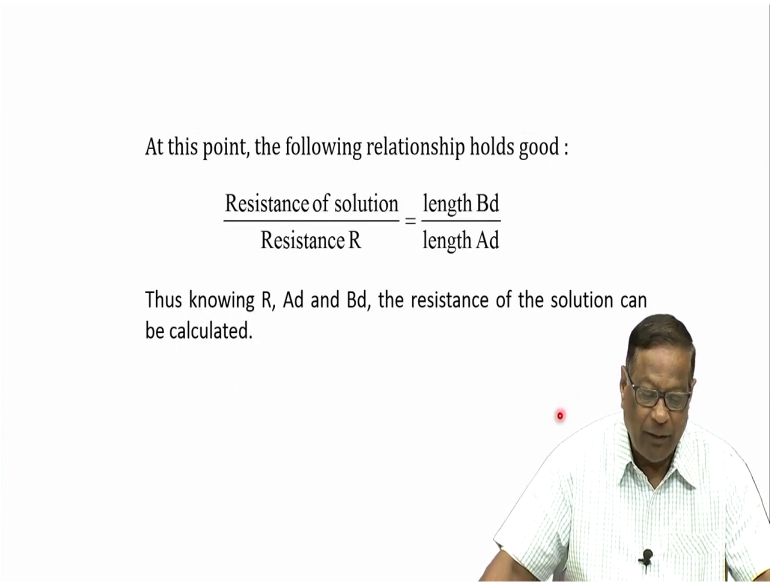

At this point, the following relationship holds good :

$$\frac{\text{Resistance of solution}}{\text{Resistance R}} = \frac{\text{length Bd}}{\text{length Ad}}$$

Thus knowing R, Ad and Bd, the resistance of the solution can be calculated.

So, at this point resistance of the solution and resistance R are exactly equal to length Bd and Ad, ok. So, knowing; we know R, we know Ad, we know Bd because this can be measured it is there just part of the 1 meter wire one half length this is one side this is other side. If we know one side where the sound is minimum, the other side is automatically fixed. So, we know three parameters in this equation. So, resistance of the solution we can calculate.

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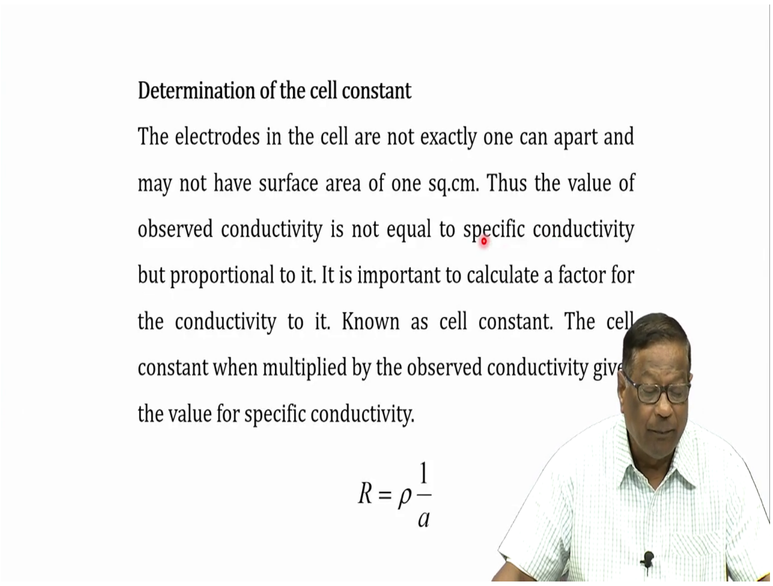

Determination of the cell constant

The electrodes in the cell are not exactly one can apart and may not have surface area of one sq.cm. Thus the value of observed conductivity is not equal to specific conductivity but proportional to it. It is important to calculate a factor for the conductivity to it. Known as cell constant. The cell constant when multiplied by the observed conductivity giv the value for specific conductivity.

$$R = \rho \frac{1}{a}$$

So, determination to do that you also have to quite often, you have to determine the cell constant because, the area of the cell cannot be measured very exactly. The problem is you know up to what accuracy you can measure millimeter or micrometer etcetera. So, it is better to determine the cell constant experimentally.

So, what do we do for that, for that the electrodes in the cell basically are not exactly 1 centimeter apart and it may not have surface area of exactly 1 square centimeter. So, the value of the observed conductivity is not equal to specific conductivity, but it may be nearer 1 centimeter, but not exactly. So, it will be proportional, specific conductivity will be proportional anyway to the area. So, it is important to calculate a factor for conductivity to convert it into specific conductivity for a given cell and for a given set of electrodes. So, that constant is the factor is known as cell constant.

So, the cell constant when multiplied by the observed conductivity gives the value of specific conductivity, it is just a small factor given by this expression; R is equal to rho into l by a, this is specific conductivity definition anyway.

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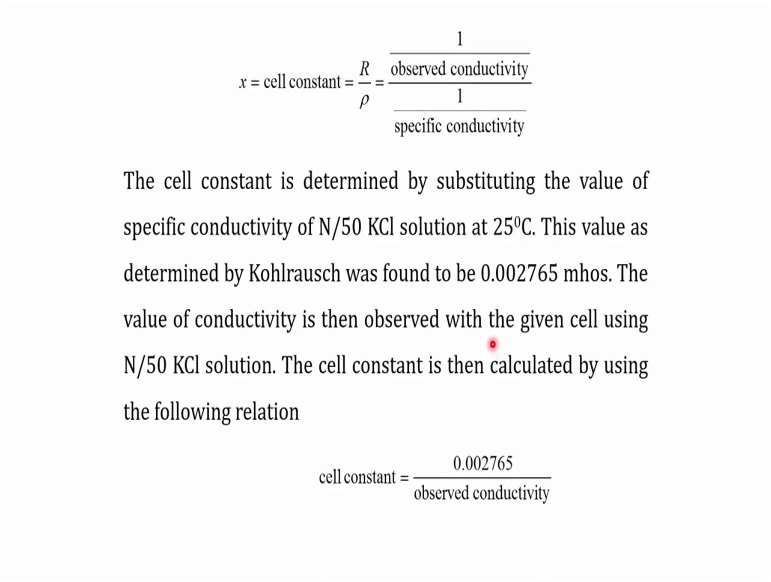

$$x = \text{cell constant} = \frac{R}{\rho} = \frac{\dfrac{1}{\text{observed conductivity}}}{\dfrac{1}{\text{specific conductivity}}}$$

The cell constant is determined by substituting the value of specific conductivity of N/50 KCl solution at 25^{0}C. This value as determined by Kohlrausch was found to be 0.002765 mhos. The value of conductivity is then observed with the given cell using N/50 KCl solution. The cell constant is then calculated by using the following relation

$$\text{cell constant} = \frac{0.002765}{\text{observed conductivity}}$$

So, x is equal to cell constant that is resistance divided by conductivity or I can say 1 over observed conductivity divided by 1 over specific conductivity; this is, these are resistance terms, these are conductivity terms. So, the cell constant is determined by substituting the value of specific conductivity of N by 50 potassium chloride solution at 25 degrees. So, this is the standard convention adopted all over the world, nothing much to think about it. All you have to do is you prepare a cell conductivity cell this is for the manufacturer. So, when you buy a conductivity cell, manufacturer will tell you what is the cell conductivity conduct cell constant.

So, all you have to do is to determine the cell constant, he will say it is approximately this much and you determine for your sets are like that. He will tell then you have to prepare N by 50 potassium chloride solution at 25 degrees and that must be adjusted to a resistance of 0.002765 mhos that is conductance and accordingly resistance you can calculate.

So, the value of the conductivity is then observed with the given cell using N by 50 potassium chloride solution. The cell constant is then calculated by using the following relation that is 0.002765 divided by observed conductivity actually what conductivity you observe, this is the this will give you the cell constant, ok.

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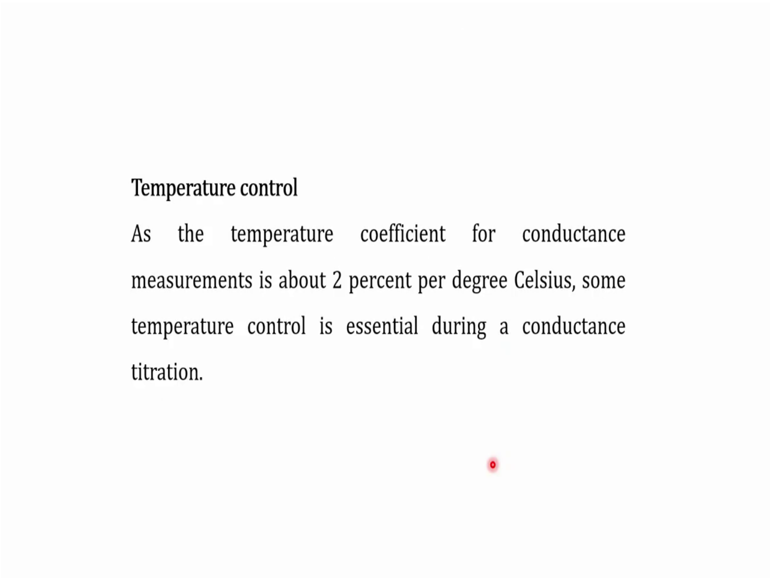

Temperature control

As the temperature coefficient for conductance measurements is about 2 percent per degree Celsius, some temperature control is essential during a conductance titration.

So, we need as I told you earlier, we need a specific control; temperature control is very important because temperature cannot be varied during the experimentation. So, you have to immerse the cell in a water by a water bath and then make take the measurements; so, or you measure the temperature and apply correct conducting correction that also can be done if you know the correction factor.

So, normally temperature coefficient for conductance measurements vary by about 2 percent per degree Celsius some temperature, therefore, some temperature control is a must during a conductance titration. So, what all we can do with the conductance, experiments.

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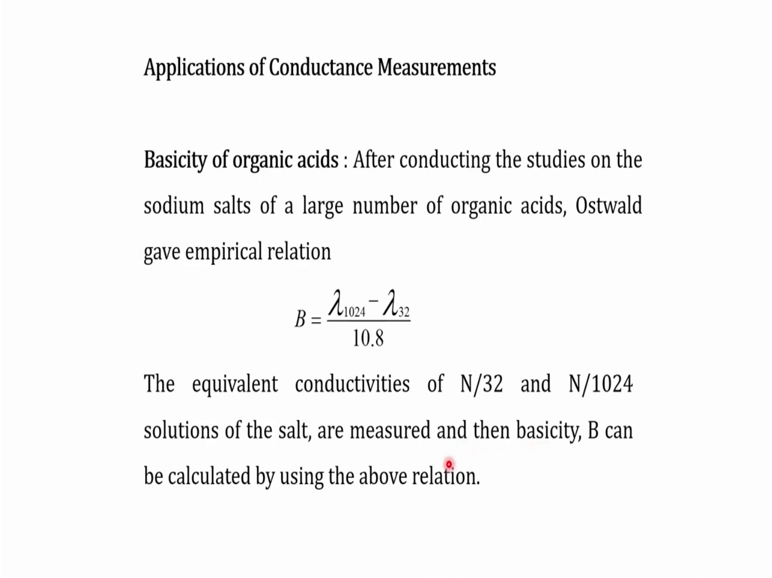

Applications of Conductance Measurements

Basicity of organic acids : After conducting the studies on the sodium salts of a large number of organic acids, Ostwald gave empirical relation

$$B = \frac{\lambda_{1024} - \lambda_{32}}{10.8}$$

The equivalent conductivities of N/32 and N/1024 solutions of the salt, are measured and then basicity, B can be calculated by using the above relation.

We can determine the basicity of the organic acids that is after conducting the studies on the sodium salts of a large number of organic acids. Ostwald gave an empirical relation that is given by B is equal to lambda 1024 minus lambda 32 divided by 10.8. The equivalent conductivities of N by 32 and N by 1024 solutions of the salt are measured and then basicity, B can be calculated using the above relation.

All you have to do is prepare N by 32 and N by 1024 concentrations of the acids and then measure the difference divided by 10.8 can give you the basicity of the organic acids, that is a fairly important parameter physical parameter for most of the organic acids. Like acetic acid, benzoic acid, succinic acid, malic acid a thousands of acids are there. So, the basicity of the organic acids is generally required for calculations.

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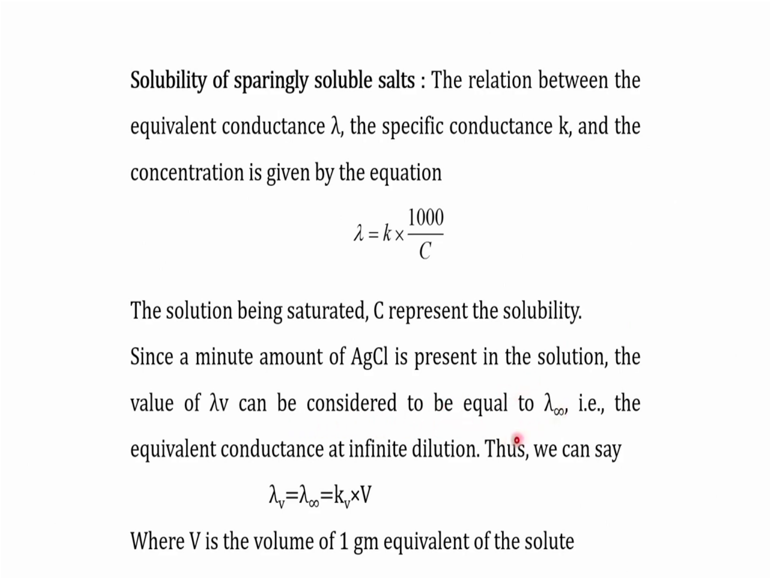

Solubility of sparingly soluble salts : The relation between the equivalent conductance λ, the specific conductance k, and the concentration is given by the equation

$$\lambda = k \times \frac{1000}{C}$$

The solution being saturated, C represent the solubility.

Since a minute amount of AgCl is present in the solution, the value of λv can be considered to be equal to λ_∞, i.e., the equivalent conductance at infinite dilution. Thus, we can say

$$\lambda_v = \lambda_\infty = k_v \times V$$

Where V is the volume of 1 gm equivalent of the solute

So, then I can determine the another fair experiment usefulness of the conductivity measurements is the solubility of sparingly soluble salts; so, here what do I do. You should remember what we had discussed earlier that is I had suggested that you should a sparingly soluble salt is one that is it. If you take a solution and add your salt part of it will dissolve, remaining part will remain and precipitated.

So, the solubility of the salt whatever is the soluble salt ionizes to give you cations and anions. So, the solubility of a sparingly soluble salt if you know the cation and anion can become measured directly. So, because they are all saturated ionic concentrations in a solution if the salt is sparingly soluble, ok. So, it may be 1 milligram in 1 liter, maybe 10 milligram in 1 liter etcetera, whatever is the solubility totally ionized.

So, the conductance measurement will can tell us about the solubility of the sparingly soluble salts because we can measure the cations and anions concentration. So, the relationship between equivalent conductance, specific conductance and the concentration is given by this expression anyway, is not it. So, like that is lambda is equal to k into 1000 by C.

So, the solution is already saturated, C represents the solubility. Since a minute of a minute amount of silver chloride is present in the solution. Assume that we take silver chloride ok, where small amount dissolves in silver; amount of silver chloride dissolves in water and the value of lambda v can be considered to be equal to lambda infinity that is equivalent conductance at infinity.

The equivalent conductance we can say that lambda v should be equivalent to lambda infinity that is nothing, but equal to k v into V, where V is the volume of 1 gram equivalent of the solute. We will have some tutorial classes where we can solve some problems. So, that you will be more familiar with these terms and how to utilize this kind of information in day-to-day life for solving. We will choose problems for about 2 problems from each side, from each experiment or technique and then solve some problems at a later stage.

So, right now if you understand the concepts I will be very happy. So, the idea of sparingly soluble salt I already explained to you know. So, if I say so much is resolved what would be the specific conductivity conductivity at infinite dilution of silver chloride or potassium chloride; potassium not potassium chloride that is highly soluble, cadmium sulfide things like that can be determined very easily.

So, if you come across 10 raise 2 minus 5 equivalent solubility equivalent conductance of silver chloride then you need not be afraid that it is somethings so very highly scientific etcetera, very simple conductance measurements can give you that kind of information. Sometimes you may feel that it is you may come across information that cadmium sulfide solubility product is 10 raise to minus 47.

So, 10 raise to minus 47 is a very difficult number to imagine and more difficult for the common people to imagine how such a number can be arrived at, but it is all in the very simple conductance measurements. So, it is not very uncommon to come across such difficult numbers very very easily, that is the beauty of conductance measurements.

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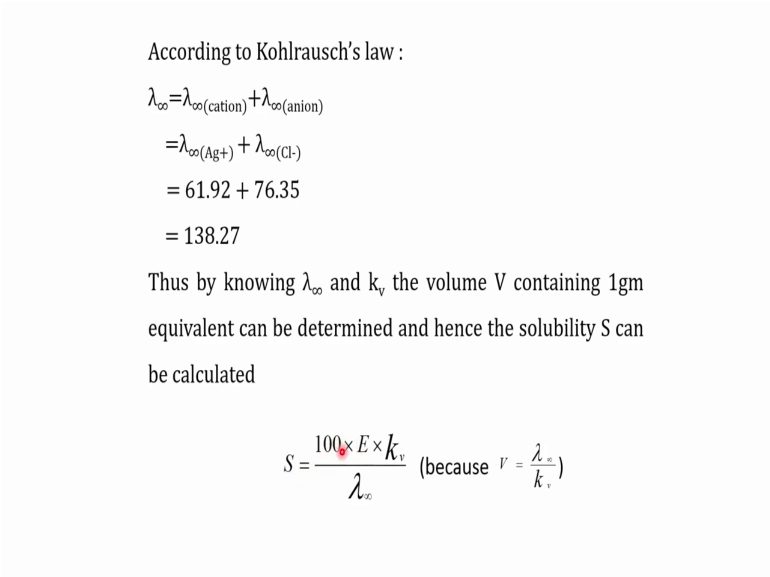

According to Kohlrausch's law :

$$\lambda_{\infty}=\lambda_{\infty(\text{cation})}+\lambda_{\infty(\text{anion})}$$

$$=\lambda_{\infty(\text{Ag}+)}+\lambda_{\infty(\text{Cl}-)}$$

$$= 61.92 + 76.35$$

$$= 138.27$$

Thus by knowing λ_{∞} and k_v the volume V containing 1gm equivalent can be determined and hence the solubility S can be calculated

$$S=\frac{100\times E\times k_v}{\lambda_{\infty}} \quad \text{(because } V=\frac{\lambda_{\infty}}{k_v}\text{)}$$

We have according to Kohlrausch's law lambda infinity is nothing, but lambda cation and plus lambda anion contribution. So, if I take AgCl, I can write lambda infinity that is specific conductance at infinity of silver ion Ag plus plus lambda infinity Cl minus, ok. So, this number is known from the previous table which I had already shown you their specific conductance numbers table, it is there just now I have shown you. From that table I draw their number 61.92 for silver and for chloride it is 76.35; so, the total is 138.27, ok.

So, by knowing lambda infinity and k v the volume of V containing 1 gram equivalent can be determined and hence the solubility S can be calculated. How do we calculate solubility S? It is very simple all I have to do is multiply it by so, if I want to say it by percentage multiply it by 100. So, 100 into E into k v divided by lambda infinity and you should know what is E and what is k v.

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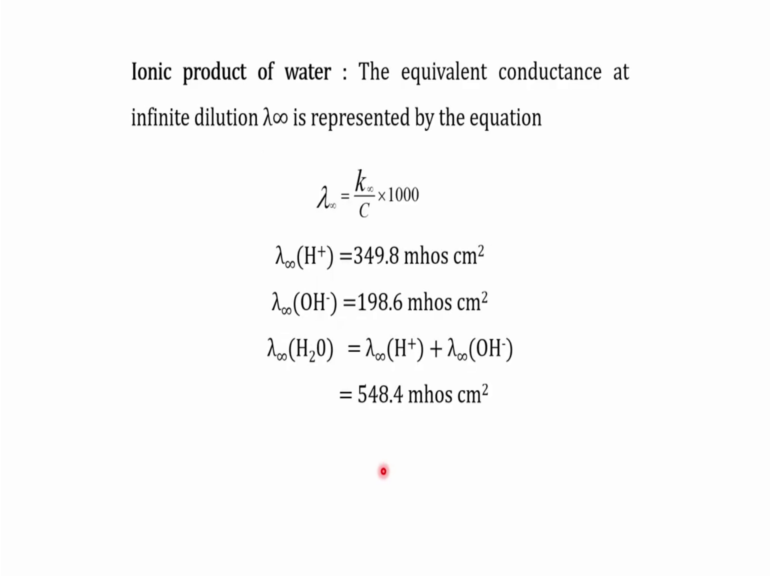

Ionic product of water : The equivalent conductance at infinite dilution λ∞ is represented by the equation

$$\lambda_\infty = \frac{k_\infty}{C} \times 1000$$

$$\lambda_\infty(H^+) = 349.8 \text{ mhos cm}^2$$

$$\lambda_\infty(OH^-) = 198.6 \text{ mhos cm}^2$$

$$\lambda_\infty(H_2O) = \lambda_\infty(H^+) + \lambda_\infty(OH^-)$$

$$= 548.4 \text{ mhos cm}^2$$

So, I can also determine the ionic product of water I had just now explained to you that ionic product of water is approximately 10 raised to minus 14. So, water also can be totally ionized and in the rest can be remaining in an ionized form. So, the product of ionized water that is H plus and OH minus ions is known as ionic product. So, the equivalent conductance at infinite dilution of lambda infinity is represented by k infinity divided by concentration into 1000.

Again from the table I have this information that is lambda infinity of H plus is 349.8 mhos per centimeter square and lambda infinity of the hydroxyl ions is 198.6 mhos per centimeter square. And, lambda infinity of water is nothing, but lambda infinity of H plus and OH minus ions, we assume that there are no dissolved salts in this. So, the total is 548.4 mhos per centimeter square.

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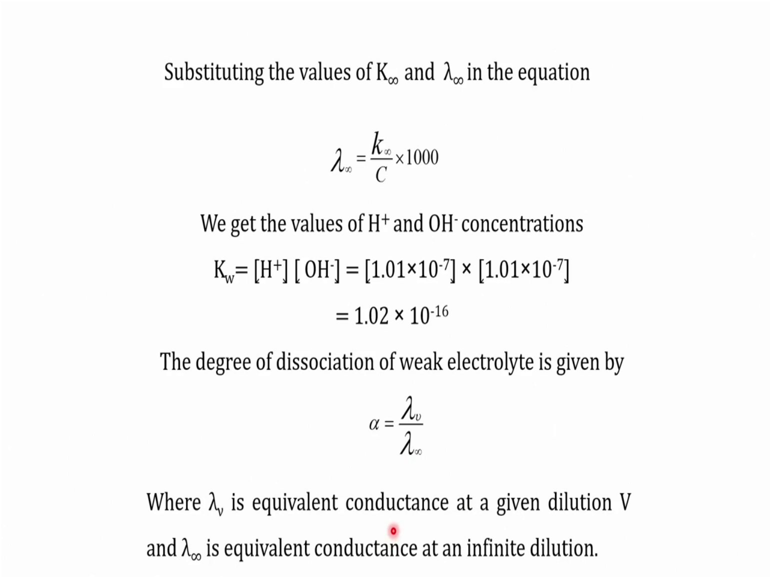

Substituting the values of K_∞ and λ_∞ in the equation

$$\lambda_\infty = \frac{k_\infty}{C} \times 1000$$

We get the values of H^+ and OH^- concentrations

$$K_w = [H^+]\,[OH^-] = [1.01\times10^{-7}] \times [1.01\times10^{-7}]$$

$$= 1.02 \times 10^{-16}$$

The degree of dissociation of weak electrolyte is given by

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

Where λ_v is equivalent conductance at a given dilution V

and λ_∞ is equivalent conductance at an infinite dilution.

So, we can substitute K infinity and lambda infinity values in this equation that is lambda infinity is equal to k infinity by divided by C into 1000. We get the values of H plus and OH minus ions, Kw is equal to this is 10 raised to minus, it should be 10 raised to minus 14, here

1.01 into 10 raised to minus 7; 1.01 into 10 raised to minus 7 and the degree of dissociation of a weak electrolyte is also given by lambda v by lambda infinity. Where lambda v is the equivalent conductance at a given dilution, lambda infinity is the equivalent conductance of at an infinite dilution.

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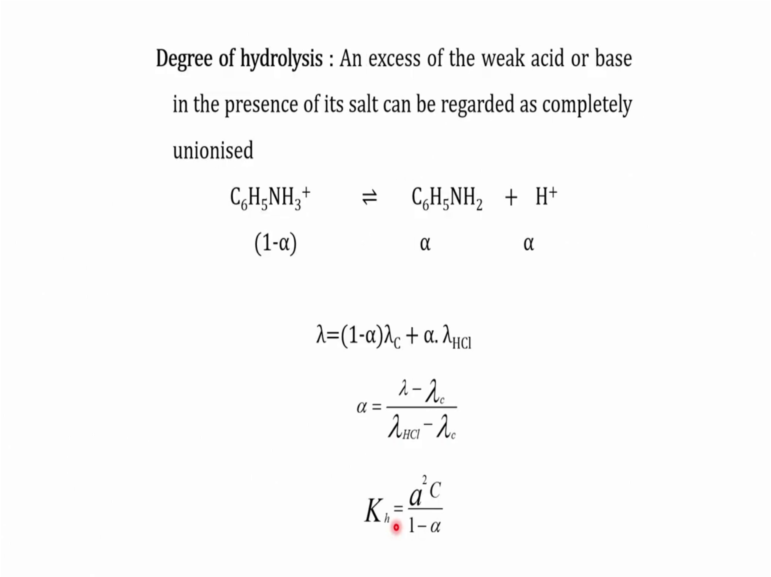

Degree of hydrolysis : An excess of the weak acid or base in the presence of its salt can be regarded as completely unionised

$$\underset{(1-\alpha)}{C_6H_5NH_3^+} \rightleftharpoons \underset{\alpha}{C_6H_5NH_2} + \underset{\alpha}{H^+}$$

$$\lambda = (1-\alpha)\lambda_C + \alpha.\lambda_{HCl}$$

$$\alpha = \frac{\lambda - \lambda_c}{\lambda_{HCl} - \lambda_c}$$

$$K_h = \frac{\alpha^2 C}{1-\alpha}$$

So, degree of hydrolysis again that is about the equivalent, that is about previous one that is about the K w that is ionic product of water. And then we can determine another experiment, another parameter that is very useful and which can be determined by conductometry is the degree of hydrolysis.

So, the degree of hydrolysis these given by an excess of now you can read this equation that is C 6 H 5 NH 2 I have taken aniline C 6 H 5 NH 2 is aniline and in acidic solution it will be NH 3 plus, ok. So, excess of weak acid or base in presence of its salt can be regarded as completely ionized and I can write this expression C 6 H 5 NH 3 plus is in equilibrium with aniline plus acid; H plus is nothing, but acid it is a bronsted acid.

So, if this is ionization is alpha H plus also should be alpha, then this should be 1 minus alpha automatic. Alpha molecules of C 6 H 5 NH 3 will give you alpha ions of C 6 alpha ion, this is the alpha the ion, this is the molecule, but anyway the expression is same, alpha ions protonated benzo aniline can decompose to give you aniline and H plus. So, one molecule of this we will give you one molecule of this and one mole of H plus.

So, if alpha moles are dissociating then this is a concentration of this would be alpha, this would be alpha, H plus would be alpha and C 6 H 5 NH 3 would be 1 minus alpha because alpha moles are taken away from here. So, I can write total conductivity of the system is 1 minus alpha in lambda C that is coming from this and this is coming from H plus; alpha lambda H plus. And, we write HCl only to denote that it is in a solution may be HCl solution and this will not contribute C 6 H 5 NH 2 being a molecule, it is not ionized. So, it will not contribute to the conductance so, we neglect this.

So, the total conductance lambda is given by this term as well as this term, that is all; this term alpha into H plus. So, alpha is nothing, but I can solve this equation lambda minus lambda c divided by lambda HCl minus lambda c and K h is given by a square C divided by 1 minus alpha, this is a final expression for the degree of hydrolysis. So, apart from that what else we can do with conductance.

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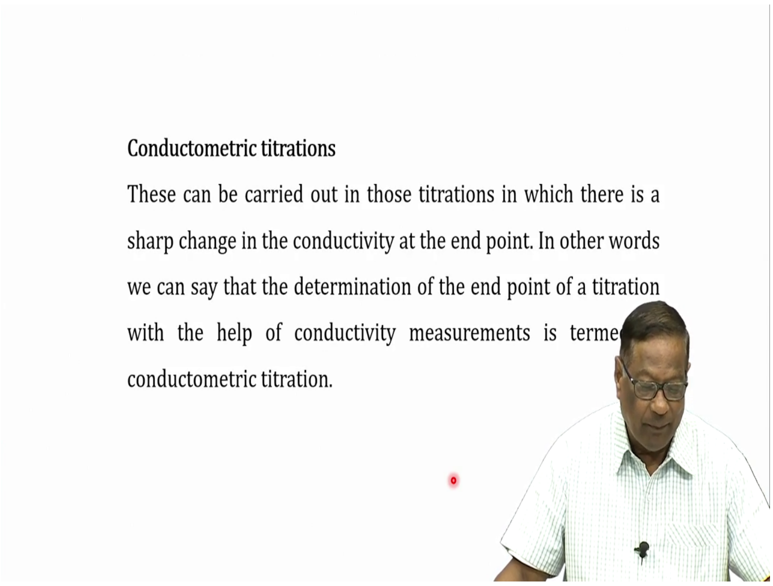

Conductometric titrations

These can be carried out in those titrations in which there is a sharp change in the conductivity at the end point. In other words we can say that the determination of the end point of a titration with the help of conductivity measurements is terme conductometric titration.

So, we can carry out conductometric titrations in which there is a sharp change in the conductivity at the endpoint. In other words we can say that the determination of the endpoint of a titration can be done with the conductivity measurement. So, that is conductometric titration. So, all you do is take a sub solution in a conical flask put another solution from the burette add a little bit put it in a conductivity cell, record the conductance as you increase the volume somewhere there will be end of the reaction and that can be plotted that is how titrations are made.

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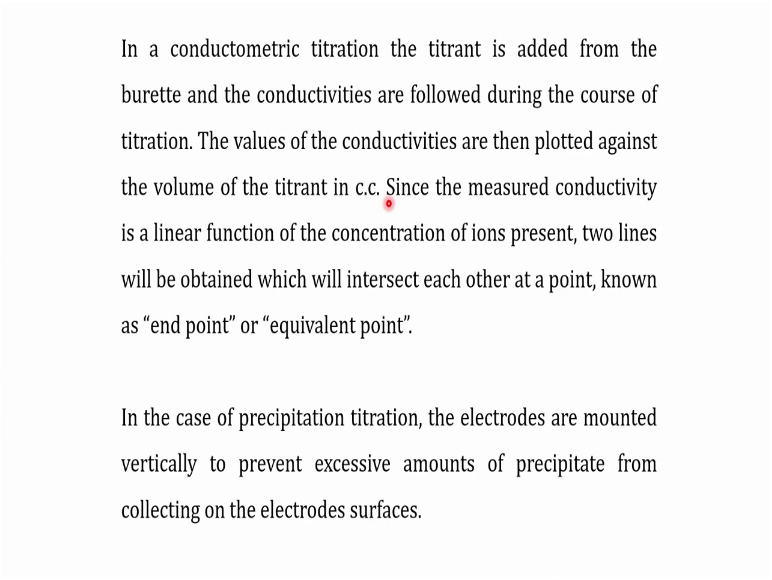

In a conductometric titration the titrant is added from the burette and the conductivities are followed during the course of titration. The values of the conductivities are then plotted against the volume of the titrant in c.c. Since the measured conductivity is a linear function of the concentration of ions present, two lines will be obtained which will intersect each other at a point, known as “end point” or “equivalent point”.

In the case of precipitation titration, the electrodes are mounted vertically to prevent excessive amounts of precipitate from collecting on the electrodes surfaces.

So, in a conductometric titration the titrant is added from the burette and the conductivities are followed by during the course of titration. The values of the conductivities are then plotted against the volume of the titrant, ok. So, the measured conductivity is a linear function of the ions present and two lines will be obtained which will intersect each other at a point, known as the end point or equivalent point. Why do we get two lines? One is before the titration another is after the titration. So, the two lines should intersect that should be the equivalents point.

So, in case of precipitation the electrodes are mounted vertically in a conductivity cell to prevent excessive amounts of precipitate from collecting on the electrode surfaces. Normally, in conductivity measurement if there is no precipitation then the measurements can be done very comfortably by keep on adding, but if it is a precipitation reaction the precipitate may sit on the electrode surface and then you may not be able to get the correct conductance or resistance.

So, what we do is to prevent excessive amount of precipitate from collecting on the this electrode surface we mount them vertically. So, that the precipitate will settle at the bottom on its own account of gravity, that is all.

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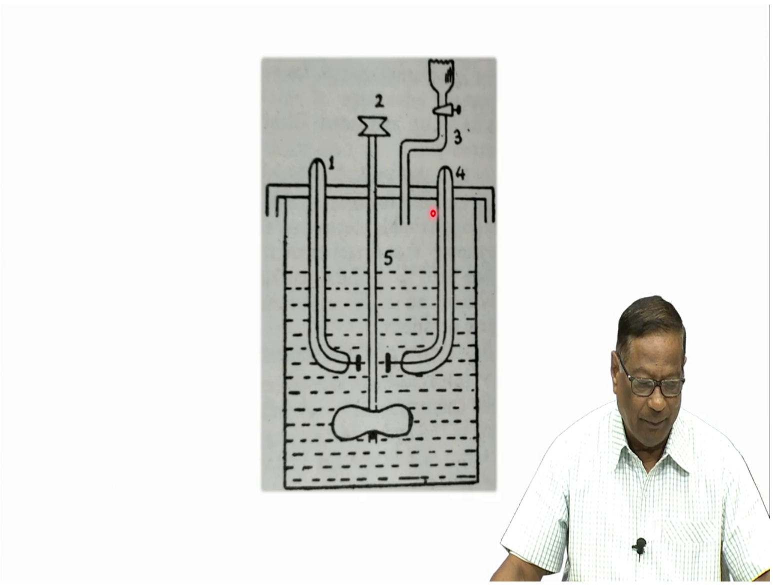

So, like this the electrodes are; the electrodes are mounted like this, here you see my pointer that is one electrode, another electrode is here, I have a stirrer and then 2 these are the wires fused in a glass. So, that wires are not directly exposed to the aqueous solution, only this part of the wire is exposed in their solution, here is my burette a very simple arrangement nothing very complicated about it.

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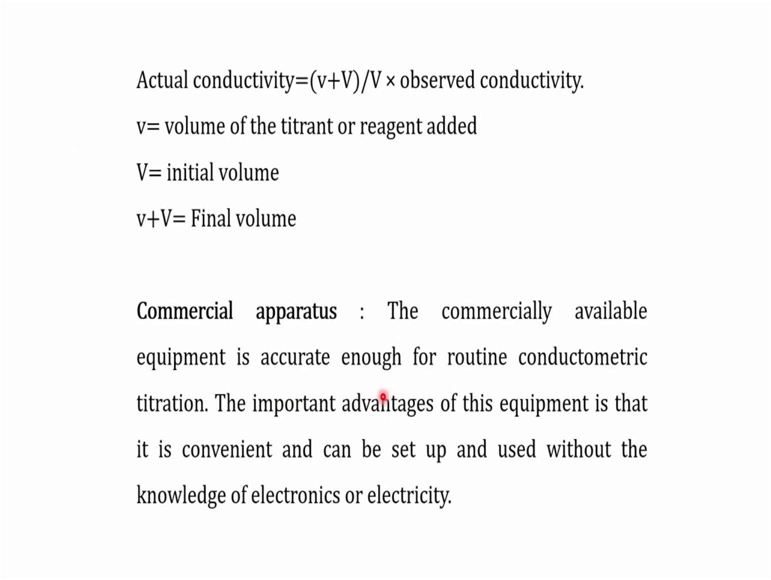

Actual conductivity $=(v+V)/V \times$ observed conductivity.

$v=$ volume of the titrant or reagent added

$V=$ initial volume

$v+V=$ Final volume

Commercial apparatus : The commercially available equipment is accurate enough for routine conductometric titration. The important advantages of this equipment is that it is convenient and can be set up and used without the knowledge of electronics or electricity.

So, actual conductivity will be of a will be the sum of the titrant first one and then titrant and total volume also will increase. So, we are writing a slightly complicated expression; it is not very uncomplicated, but the actual volume will be different from if I take 10 ml of this and 10 ml of this, the total volume would be 20. So, we have to make small correction.

So, the actual conductivity would be the sum of the total volumes divided by volume that would be the concentration, total volume and observed conductivity. So, where v is the volume of the titrant or reagent added, capital V is the initial volume and v plus V is the final volume. So, with this kind of information we will go towards commercial apparatus, it is available in the shop in the market, in scientific shops. The commercially available equipment is fairly accurate for routine conductometric titration. The important advantage of such equipment is that it is convenient.

We see normally what happens is we have to buy the wire, we have to buy the conductance, we have to make the specific surface etcetera to make an experiment in the laboratory on our own. But, a readymade equipment is available and what I am trying to tell you is a readymade equipment is fairly comfortable, you can buy one and use it and it is not very high end research equipment that is what I am trying to tell you, ok. So, it is convenient, it can be set up and used without the knowledge of electronics or electricity, do not worry about it. So, what you are interested is in the titration, is not it.

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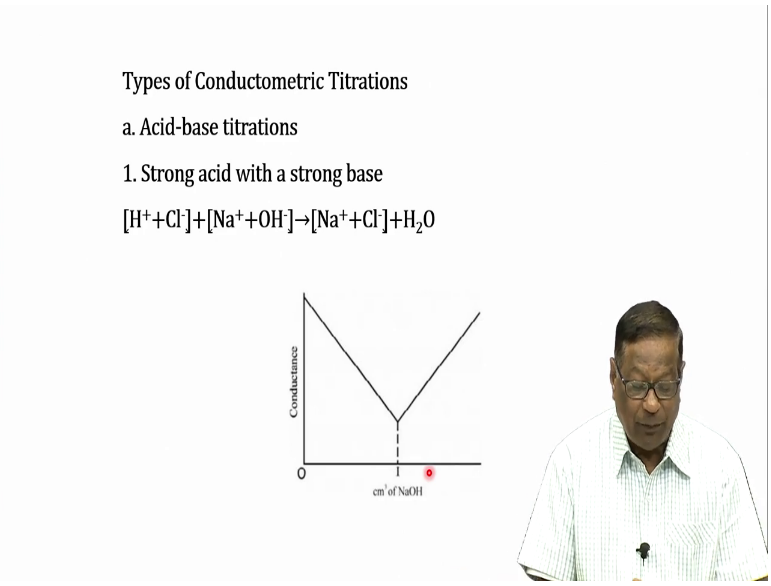

Types of Conductometric Titrations

a. Acid-base titrations

1. Strong acid with a strong base

$[H^+ + Cl^-] + [Na^+ + OH^-] \rightarrow [Na^+ + Cl^-] + H_2O$

So, we have different types of titrations; one is I can do acid base titration a strong acid with a strong base. Here we are going to talk about many of these systems what we had earlier discussed and what is the strong acid H Cl I can titrate it with a strong base. This is done conduct using conductivity as well as in the laboratory using at phenolphthalein indicator.

So, with conductivity I do not have to use the indicator phenolphthalein or methyl orange or whatever it is. So, the basic reaction is written as H plus Cl plus; Cl minus plus we are going to add the titrant that is Na plus and OH minus what we are going to get is Na plus and Cl minus and H 2 O, ok.

So, as the titrant HCl as you keep on adding Na OH, the water will be formed ok, after the water is formed the conductivity of water is very less compared to Na plus and Cl minus. H and OH minus ions are being removed. H plus is approximately 349, OH minus is 198 and sodium and chloride are approximately 60s maybe 30s, 55 etcetera water is almost nil 10 raise to minus 14.

So, initially as the, you add Na OH only sodium and chloride ions will form. So, the conductivity will keep on coming down. After the addition of the after the equivalence point they are going to have suddenly excess of Na OH, and Na will remain 60, contribution of Na plus will remain 60 and contribution of OH minus will be very high. So, the titration curve will zoom. So, this is volume of the Na OH added, this is conductivity very simple.

So, the beauty is you do not have to worry about where is the conductance, you just record plot 2 graphs and the intersection is we will tell you what is the concentration; equivalent concentration, what is the concentration of the acid.

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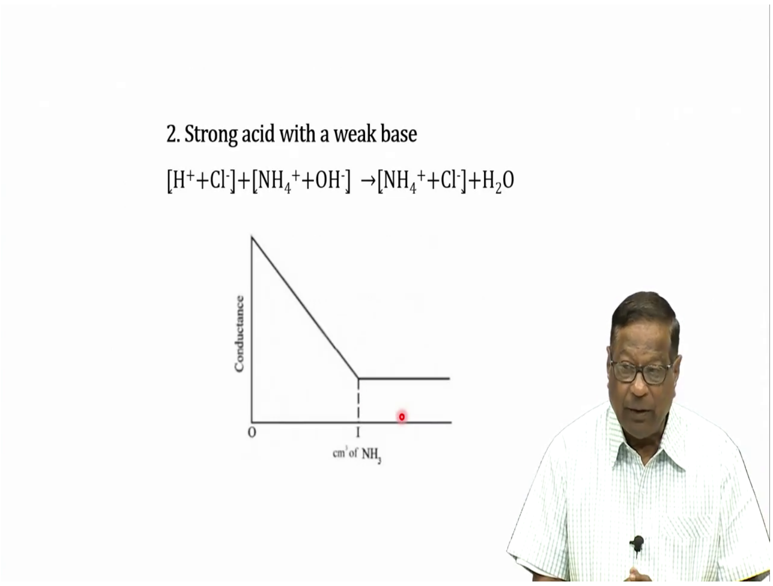

2. Strong acid with a weak base

$[H^+ + Cl^-] + [NH_4^+ + OH^-] \rightarrow [NH_4^+ + Cl^-] + H_2O$

We can also say a strong acid with a weak base that is NH 4 OH, here after the equivalence point what happens the, you are going to add NH 4 and OH minus ok, excess will be there or you can take NH 4 OH with H Cl. So, conductance will keep on coming down. So, long as water will water will be formed as one of the products here and excess NH 4 OH it will remain conductance, will remain essentially same. So, the intersection is again available for the interpretation of the neutralization.

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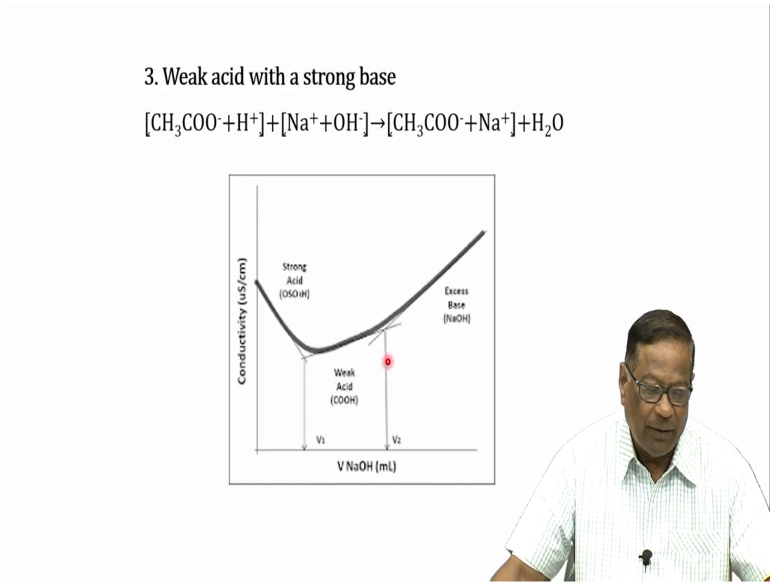

3. Weak acid with a strong base

$[CH_3COO^- + H^+] + [Na^+ + OH^-] \rightarrow [CH_3COO^- + Na^+] + H_2O$

So, suppose I take weak acid and strong base then what happens? Here, I have weak acid very less ionization CH 3 COO minus H plus and the weak acid, here I have a strong acid SO 3 OH etcetera and weak acid is somewhere here end point and then excess base will be here. So, the if I take strong acid it will end point will be here, if I take weak acid end point will be somewhere here. So, excess base is highly concentrated and base has got a better Na OH. So, after the equivalence point it will keep on increasing.

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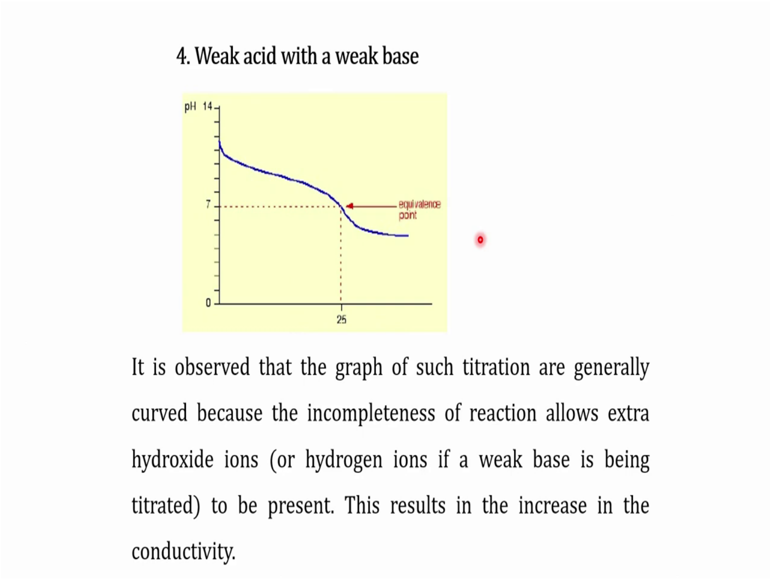

4. Weak acid with a weak base

It is observed that the graph of such titration are generally curved because the incompleteness of reaction allows extra hydroxide ions (or hydrogen ions if a weak base is being titrated) to be present. This results in the increase in the conductivity.

So, weak acid with a weak base, it is observed that the graph of such titrations are generally curved because the incompleteness of the reaction in especially in weak acids and weak basis, ok. So, the extra hydroxide ions need to be present to see the end point of the reaction more clearly, ok; if I want to do weak base titration then I need extra acid.

So, this results in the increase in the conductivity. Here weak acid with a weak base, curve will come like this and at the after the end point again excess reagent is again a weak base or weak acid. So, it will keep on coming down.

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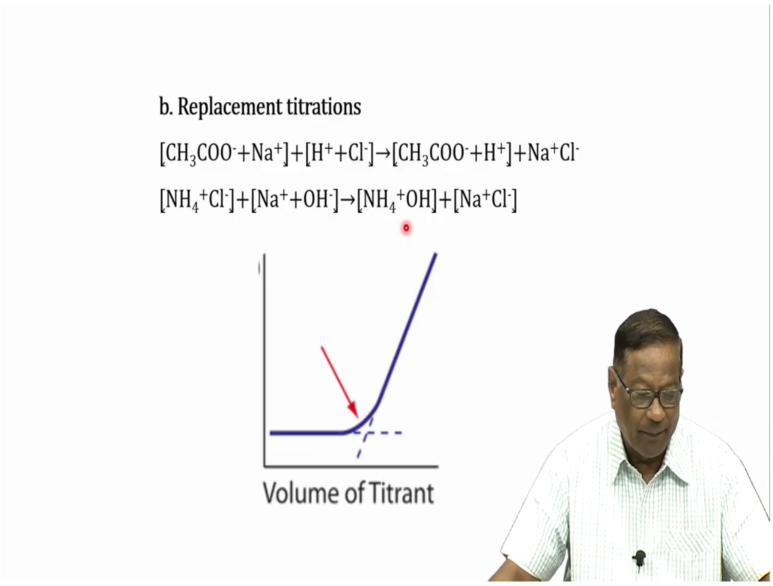

b. Replacement titrations

$[CH_3COO^- + Na^+] + [H^+ + Cl^-] \rightarrow [CH_3COO^- + H^+] + Na^+Cl^-$

$[NH_4^+Cl^-] + [Na^+ + OH^-] \rightarrow [NH_4^+OH] + [Na^+Cl^-]$

So, replacement titrations I can replace CH 3 COO Na plus with H Cl and CH 3 COO minus plus H plus; these are the products in the ionized form, we are not going to write water here. So, if I do it like this then volume of the titrant and increase later that is how it will be volume titration.

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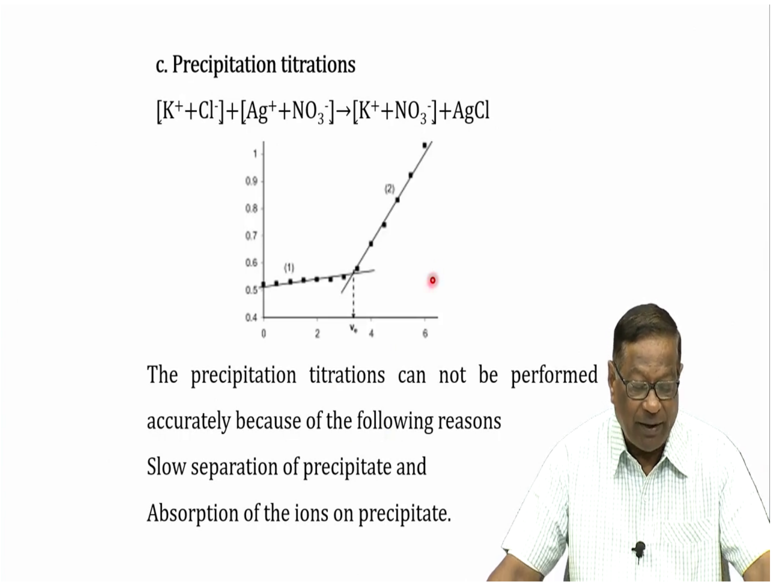

c. Precipitation titrations

$[K^+ + Cl^-] + [Ag^+ + NO_3^-] \rightarrow [K^+ + NO_3^-] + AgCl$

The precipitation titrations can not be performed accurately because of the following reasons

Slow separation of precipitate and

Absorption of the ions on precipitate.

So, precipitation reactions, they cannot be performed very accurately because of the following reasons. One could be slow separation of the precipitate it will not settle down immediately and absorption of the ions on the precipitate. This is a very a serious concern because quite often whenever we do a precipitation titration just like salvation what I had explained to you earlier with water molecules orienting themselves around H plus and OH minus ions.

Here also they precipitate, even though it is neutral it has got electrons and ions will be attached positive and negative ions will be attached around the precipitate. So, they will also settle down to some extent. So, the actual analysis will be slightly different. So, this is one complication we expect especially in the precipitation reactions. So, that is known sometimes they do get adsorbed on the ions.

That is why on the precipitate; that is why whenever we do a precipitation titration precipitation reaction in normal gravimetry, what we do is we wash it with lot of water especially barium sulfate. If you precipitate from hydrochloride solutions barium; sulfate precipitate barium chloride precipitate sorry, barium sulfate precipitate will be associated with lot of sulfate ions and the we have to wash to remove the excess sulfate ions otherwise the weight will be wrong.

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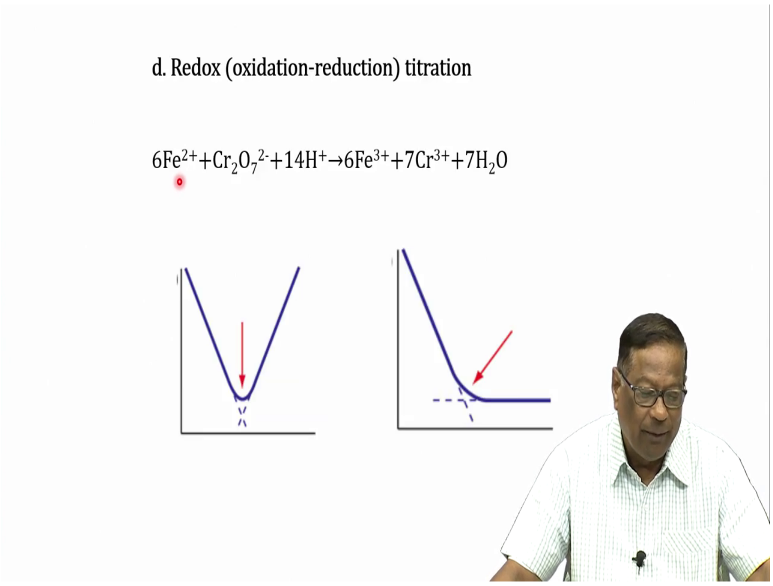

d. Redox (oxidation-reduction) titration

$6Fe^{2+}+Cr_2O_7^{2-}+14H^+ \rightarrow 6Fe^{3+}+7Cr^{3+}+7H_2O$

So, a redox reaction I can continue to do by titration very simple; what is redox reaction it is oxidation and reduction titration. Example I am giving you here iron and potassium dichromate in presence of acid that will give you ferric and chromium 3 and 7 H 2 O. This would be the kind of titration curve what you would be expecting this or this depends upon different kinds of reactions.

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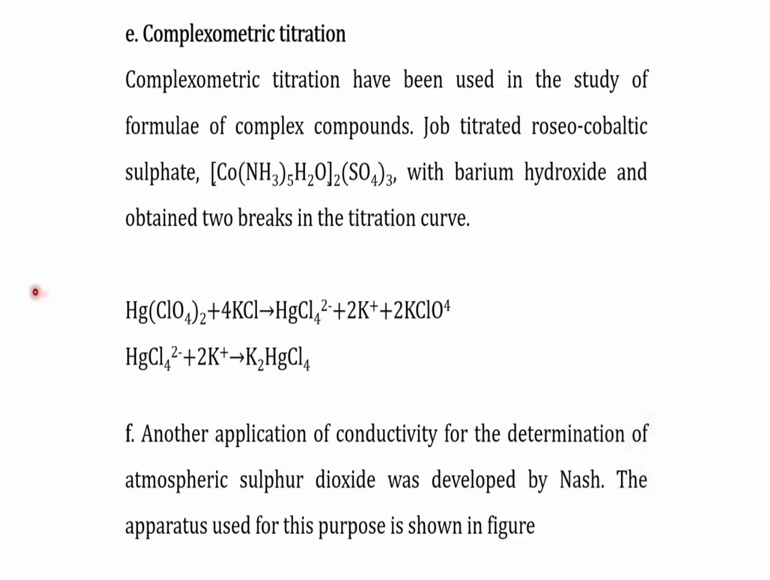

e. Complexometric titration

Complexometric titration have been used in the study of formulae of complex compounds. Job titrated roseo-cobaltic sulphate, $[Co(NH_3)_5H_2O]_2(SO_4)_3$, with barium hydroxide and obtained two breaks in the titration curve.

$Hg(ClO_4)_2+4KCl \rightarrow HgCl_4^{2-}+2K^++2KClO^4$

$HgCl_4^{2-}+2K^+ \rightarrow K_2HgCl_4$

f. Another application of conductivity for the determination of atmospheric sulphur dioxide was developed by Nash. The apparatus used for this purpose is shown in figure

So, we will continue our discussion for another 5 or 6 slides and then I am going to describe to you complexometric titration. So, in complexometric titrations and they have been used in the study of formula of formulation of the complex compounds. Job is the name of the scientist he titrated roseo-cobaltic sulfate, CO NH 35 times water. This is a complex here in the cobalt is associated with 5 molecules of ammonia and one molecule of water, it is a hexadentate ligand and cobalt this is the anionic part. He titrated it barium hydroxide and obtain 2 breaks in the titration curve.

So, another application is mercuric per chlorate, titration with the 4 potassium chloride will give you HgCl 4 2 minus, this is a complex as well as anion and then 2 K plus plus 2 KClO 4. So, HgCl 4 2 minus can react with 2 ions of potassium to give you K 2 HgCl 4 this is the another complex. So, it can be determined by titration. Another application of conductivity for the determination of atmospheric sulphur dioxide was developed by Nash. The apparatus used for this is shown here.

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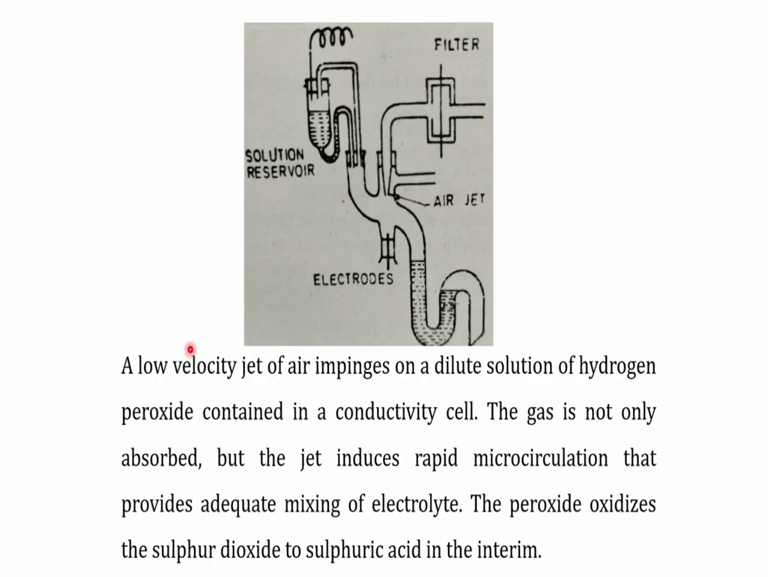

A low velocity jet of air impinges on a dilute solution of hydrogen peroxide contained in a conductivity cell. The gas is not only absorbed, but the jet induces rapid microcirculation that provides adequate mixing of electrolyte. The peroxide oxidizes the sulphur dioxide to sulphuric acid in the interim.

And very simple apparatus we have to sub extract Sulphur dioxide from the top, from the atmosphere and then that will give rise to H 2 SO 3 which can be titrated. So, a low velocity jet of air impinges on a dilute solution of hydrogen peroxide contained in a conductivity cell. The gas is not only absorbed, but also it induces rapid microcirculation because you are bubbling and that provides adequate mixing of the electrolyte. So, the peroxide oxidized the sulfur dioxide to sulfuric acid which can be titrated just like any other sodium hydroxide acid base titration.

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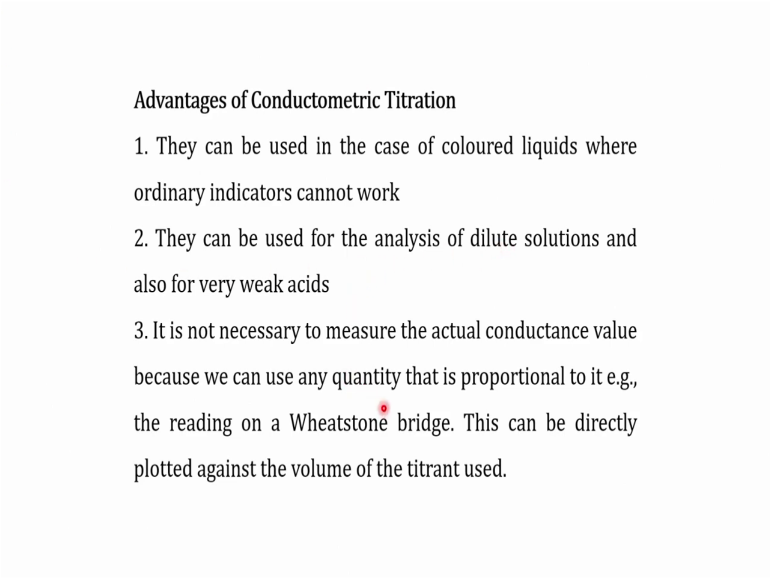

Advantages of Conductometric Titration

1. They can be used in the case of coloured liquids where ordinary indicators cannot work
2. They can be used for the analysis of dilute solutions and also for very weak acids
3. It is not necessary to measure the actual conductance value because we can use any quantity that is proportional to it e.g., the reading on a Wheatstone bridge. This can be directly plotted against the volume of the titrant used.

So, the what I am trying to do is, I am trying to give you different kinds of application of conductometry as an analytical technique for pollution monitoring. One is hydrolysis of organic acids, another is conductance measurements, another is complexometric reactions, another is titration reactions. The typical titration reactions that is acid base, weak acid weak based, a weak acid strong base, strong acid weak base etcetera, etcetera. And now, I will enumerate a little bit about the advantages of conductometric titrations they can be used in case of colored liquids.

You do not have to bother if the substances are colored because unlike ordinary titrations where you have to watch the color change, here you do not have to watch the color. So, you need not worry about indicators working or not. They can be used for the analysis of dilute solutions and very weak acids. It is not necessary to measure the actual conductance value because we can use the quantity that is proportional to it and reading for example, reading on a Wheatstone bridge this can be directly plotted.

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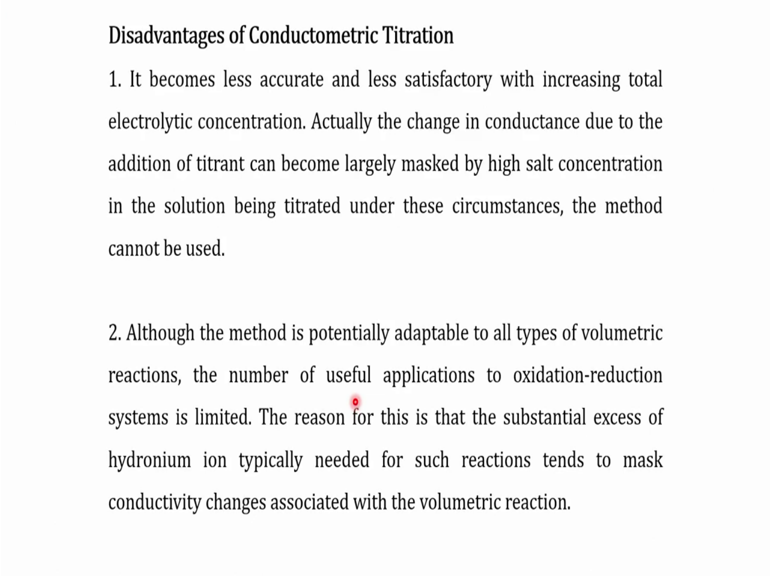

Disadvantages of Conductometric Titration

1. It becomes less accurate and less satisfactory with increasing total electrolytic concentration. Actually the change in conductance due to the addition of titrant can become largely masked by high salt concentration in the solution being titrated under these circumstances, the method cannot be used.

2. Although the method is potentially adaptable to all types of volumetric reactions, the number of useful applications to oxidation-reduction systems is limited. The reason for this is that the substantial excess of hydronium ion typically needed for such reactions tends to mask conductivity changes associated with the volumetric reaction.

And this, there are couple of disadvantages of conductometric titration. It becomes less accurate, less satisfactory with increasing electrolytic concentration, if there are more ions it becomes a little tricky. Actually the change in the conductance due to the addition of the titrant can become largely masked by high salt concentration, this is the problem.

So, the, then the method cannot be used and although the method is potentially adaptable the number of useful applications is limited. The reason for this is that substantial excess of hydronium ion typically needed for such reaction tends to mask conductivity changes especially for acids and other things, there will be some problem with that.

So, we stop here and in our next class we will study the electrochemical methods known as potentiometer.

So, thank you very much have a nice day.