Electrochemical Technology in Pollution Control
Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 14
Potentiometry 5

Hello students, greetings to you. Let us begin where we stopped in the last class. I was discussing about the different types of electrodes, we had discussed about electrodes of the first kind, second kind, third kind, and then we discussed about the combined glass electrode, and then we discussed about the calomel electrode and we had discussed about the glass electrode.

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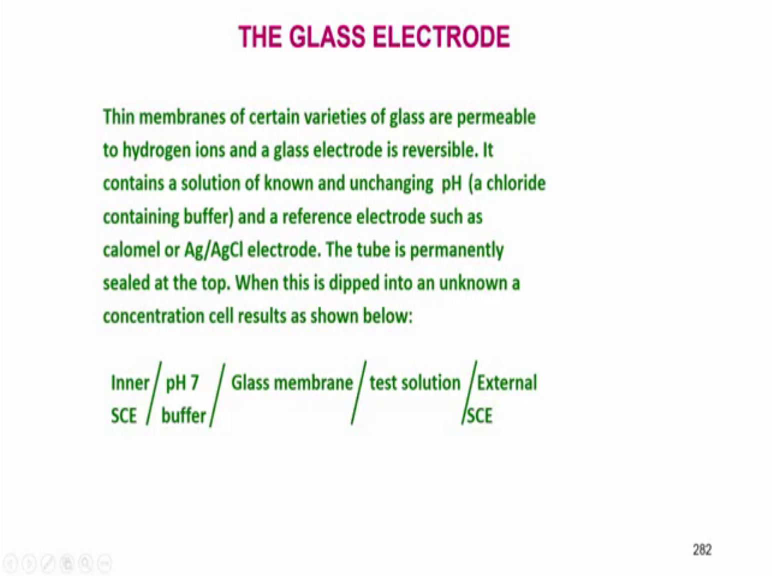

THE GLASS ELECTRODE

Thin membranes of certain varieties of glass are permeable to hydrogen ions and a glass electrode is reversible. It contains a solution of known and unchanging pH (a chloride containing buffer) and a reference electrode such as calomel or Ag/AgCl electrode. The tube is permanently sealed at the top. When this is dipped into an unknown a concentration cell results as shown below:

Inner SCE / pH 7 buffer / Glass membrane / test solution / External SCE

I had told you that glass electrode is something like a concentration cell only, that means, there is an inner reference electrode and then pH 7 buffer and then we have a glass membrane and test solution and external SCE. I can replace this inner saturated calomel electrode with silver-silver chloride electrode also ok. So, this is here you can see except a glass membrane, everything else is same. For example, inner cell here if this end is one electrode, this other end is same electrode.

So, it is like a concentration cell. In concentration cells, so we will have platinum electrodes or carbon electrode depending upon what do you want to work. And then pH 7 buffer, this is also a some sort of acidic solution. So, one is buffer, one is test solution. The other one is glass membrane that separates the pH 7 buffer and test solution.

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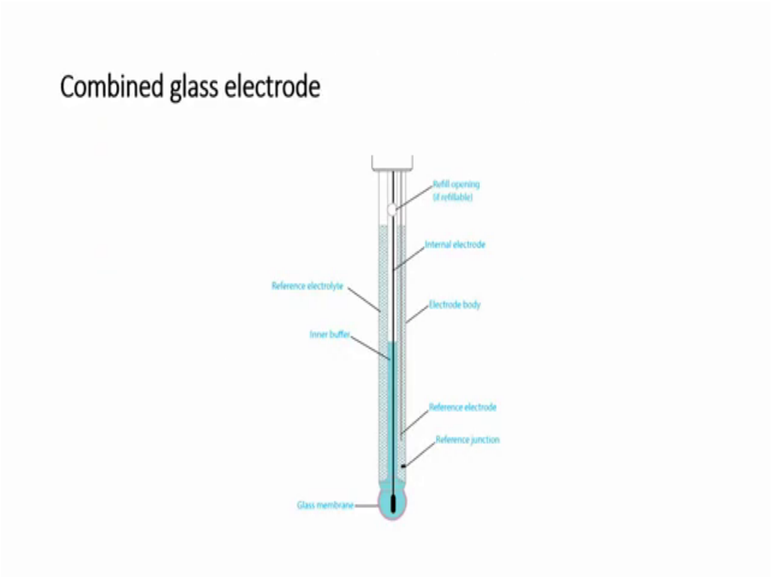

Combined glass electrode

So, such things have become commercially available. And you can see this figure, this is a modern readymade electrode available in the market. Here what we have, I have a glass tube here, and then I have a glass membrane here ok, this pinkish one. And inside that I have an electrode, and this electrode is an known as internal electron here. So, the internal electrode, and then I have refilling I have a small hole here to fill the solution, this green solution is an inner buffer that is about pH 7 buffer or something or pH 1 buffer whatever I want to put ok. So, through this hole I fill the solution in the inner chamber, and outer chamber you again it contains a reference electrode ok. So, this is a complete cell by itself.

Here I have one more electrode that is the electrode body, this one is electrode body. So, reference electrode is here this is the actual electrode, and this is the combined glass electrode what you can buy from a shop, scientific shop in your town. So, this electrode is known as combined glass electrode it costs about 2000 rupees currently in the current market. And this electrode is dipped in a solution of which you want to find out the pH, so that a test solution is outside this membrane. And this glass membrane is the one which is permeable to hydrogen ions from outer test solution to inner buffer. So, the pH of the outer solution will be determined by the emf difference between the reference electrode, internal electrode and the reference electrode here – this one, so that is glass electrode for you.

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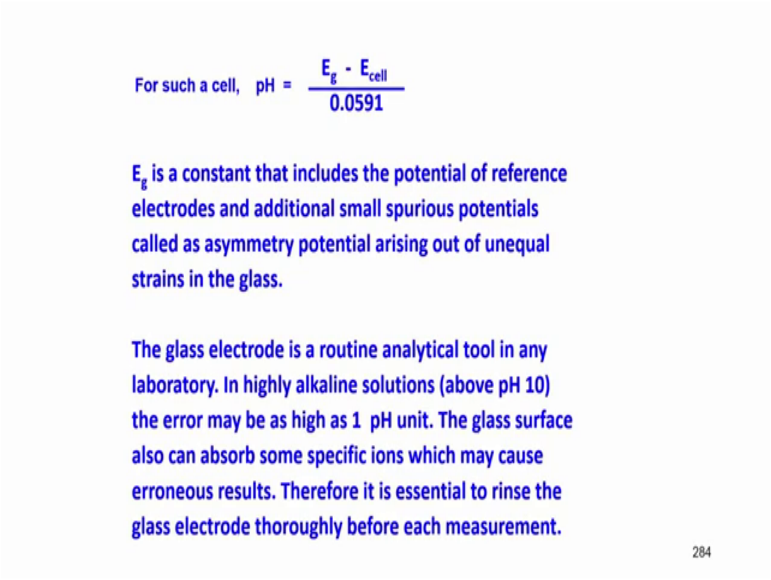

For such a cell, $pH = \frac{E_g - E_{cell}}{0.0591}$

E_g is a constant that includes the potential of reference electrodes and additional small spurious potentials called as asymmetry potential arising out of unequal strains in the glass.

The glass electrode is a routine analytical tool in any laboratory. In highly alkaline solutions (above pH 10) the error may be as high as 1 pH unit. The glass surface also can absorb some specific ions which may cause erroneous results. Therefore it is essential to rinse the glass electrode thoroughly before each measurement.

And for such a cell, pH is given by this equation that is E g that is potential generated for the glass membrane, and the potential generated by the cell, so that is the difference and divided by 0.0591 that is as usual. So, in this case, E g is the constant that includes the potential of reference electrode and additional small spurious potentials called as asymmetric potential. This I have explained to you earlier, this is only a repetition, so that arises out of unequal strains in the glass membrane. Usually in the glass membrane it is not possible to make a glass membrane of uniform quality over a period of time etcetera, every time you make a glass membrane there will be the asymmetry potential would be different for each glass membrane. In for every glass electrode, the asymmetry potential will be different, so that we should remember.

And the glass electrode is a routine analytical tool in any laboratory. So, nobody bothers to determine the asymmetry potential every time, but the manufacturer would have determined and calibrated the pH instrument for you, so that you do not have to worry about the asymmetry potential generated out of the glass membrane, but it would have been done by the manufacturer. So, in the what for you can use a glass electrode, it is a very convenient tool, just one electrode, you dip it in the solution, you get the reading. So, the pH of a solution can be simply obtained by dipping the glass electrode connected to a meter of course that is they understood.

So, it in highly alkaline solutions above pH 10, the there may be error because we are measuring the hydride hydrogen ions not the OH ions. So, the pH will we call it pH electrode, so hydrogen ions only we are measuring, but the concentration of hydrogen in alkaline solution will be higher than 10 raise to minus 7, minus 8, lower than 10 raise to minus 7 that would be minus 8, minus 10, minus 9, minus 10 like that that will be highly alkaline because hydrogen ion concentration is very less.

So, the error of hydrogen ion measurement could be as high as plus or minus 1 unit, that means, if you are measuring pH 11, it may be a pH 10 also, the actual pH. We have unable to determine the pH for such highly alkaline solutions. So, what we normally do is we standardize the glass electrode using a pH of buffer 9. So, from pH of buffer 9, we measure the alkaline solutions. And for acidic solutions, we can go for pH 4 as the standard buffer and then measure with respect to that.

So, for every glass electrode what you want to use depending upon the pH, you have to change the buffer for standardization. And you should do it every day because there because of the asymmetry potential and all, the pH will be the electrical response will be changing. So, every day if you adjust the pH and the slope that is 0.0591, you should be a glass electrode would be ready for use. Usually what people do is they come to the laboratory put on the pH meter for that day standardize it, and use it for the whole day, unless it is to be changed into alkaline solutions.

So, the glass surface can also absorb some specific ions which may cause erroneous results. Therefore, it is essential to rinse the glass electrode thoroughly before each measurement. Every time you want to make a measurement, you must wash it with minimum 10 ml, 20 ml of the solution if you are working in acidic solution ok, acidic range, you want to wash it with distilled water whose pH should be approximately 7 with about 10 to 15 ml. What we normally do is, we wash it, take a tissue paper, wipe the glass surface – not too hard, and then again wash, again wipe, like that three-four times if you do, glass electrode would be giving you a nice response. Same thing is true with alkaline conditions also all right.

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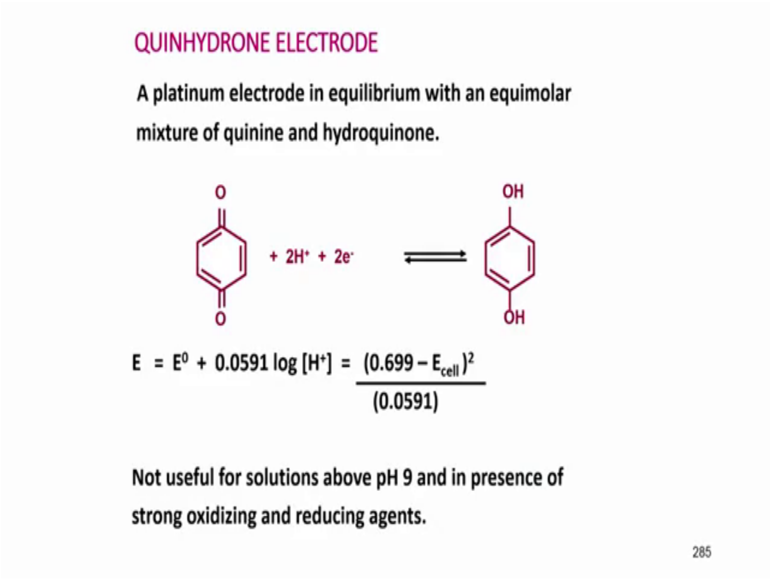

QUINHYDRONE ELECTRODE

A platinum electrode in equilibrium with an equimolar mixture of quinine and hydroquinone.

$$E = E^0 + 0.0591 \log [H^+] = \frac{(0.699 - E_{cell})^2}{(0.0591)}$$

Not useful for solutions above pH 9 and in presence of strong oxidizing and reducing agents.

So, apart from this, we can discuss about the quinine hydrogen electrode, quininehydron electrode is nothing but a platinum electrode in equilibrium with an equimolar mixture of quinine and hydroquinone quinone. So, this is quinone and this is hydroquinone that is OH, here it is OH. It is not quinine, it is quinone, there is an error please correct that. And it is quinone is nothing, but a benzene ring with two CO groups, and the reduced species is known as hydroquinone.

So, the pH of this the electrode would be platinum electrode in which what I do is I just take a beaker, put some quinone ok, and then add water, it will form hydroquinone. So, the quinone and hydroquinone will be in equilibrium in the solution in my beaker, and then I put two plate, apply one platinum electrode and another is reference electrode ok. So, quinone hydride electrode is used the other part would be another cell of the which was sample for which we want to determine the pH.

So, for such a situation potential is given by E is equal to E naught of quinone quinone and quinine hydron followed by 0.0591, and then this is a 2 H the logarithm of H plus and this would be the value of E naught is known 0.0699 a minus E cell whole raised to 2 divided by 0.0591. So, here it should be 2, point zero, there is an error here, please note 0.0591 by 2 - it should have been, and log H plus. So, electrode potential is nothing but 0.699 minus E cell divided by 0.0591 raised to 2. This is not useful for solutions above pH 9. And in presence of strong oxidizing and reducing agents, it is not very effective. Nowadays, nobody uses quinone electrode, because it is a like a cumbersome to use, you need a reference electrode. Instead of that, glass electrode to a lot of people regularly use ok.

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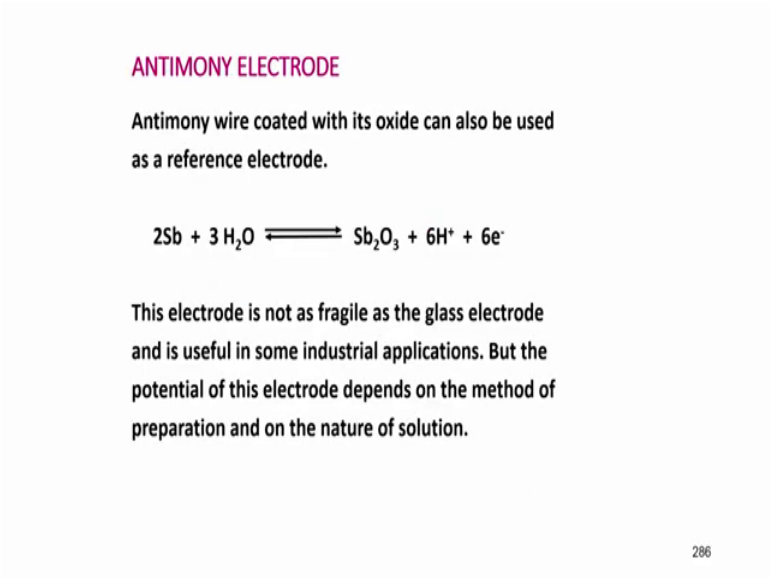

ANTIMONY ELECTRODE

Antimony wire coated with its oxide can also be used as a reference electrode.

$$2Sb + 3H_2O \rightleftharpoons Sb_2O_3 + 6H^+ + 6e^-$$

This electrode is not as fragile as the glass electrode and is useful in some industrial applications. But the potential of this electrode depends on the method of preparation and on the nature of solution.

Then we have another electrode known as antimony electrode. So, there are situations for example, when we do not want to use the glass electrode in highly alkaline solutions, no point, because the error will be more than plus or minus 1 unit. But still you want to know what is the pH or POH. And then sometimes in highly acidic solutions also pH is not defined ok, we can define pH up to 1, 0.1 we can, but 0 pH is not defined. So, if an acid is having more than 1 molar, there is no point in determining the pH of that because pH is negative and 0, negative log of concentration.

So, concentration if it is 1, it is 0; if it is 2, again it should give you one molar solution should give you 0 pH, and two molar solution also should give you 0. So, highly concentrated solutions cannot give you the pH. We do not define pH for two molar solutions, only up to one molar solution yes.

So, 0.1, pH we can define, but 1 to 0 pH, we get and for higher concentrated solutions you cannot get the pH. And in a highly acidic and alkaline solutions, you cannot use the glass electrode. So, what to do you need a metal electrode, quinone hydrone is cumbersome, and again it would not work with alkaline solutions. So, we do manage with a metal electrode that is antimony. Antimony wire coated with its oxide also can we just like silver cloak, silver wire coated with silver chloride Ag, Ag Cl, we can use antimony, antimony oxide coated wire as a reference electrode.

So, this is just like colonial electrode. The, this electrode is not as fragile as the glass electrode. You see glass electrode whenever you want to shake, a substance etcetera glass will membrane may break. If the membrane breaks, the glass electrode is useless you have to throw it and buy another one. So, in the harsh conditions, it is not practical to keep on breaking the glass membrane and buying another one. So, we use antimony, antimony chloride electrode. But the potential of this electrode depends on the method of preparation, how we prepare the antimony oxide and on the nature the solution ok.

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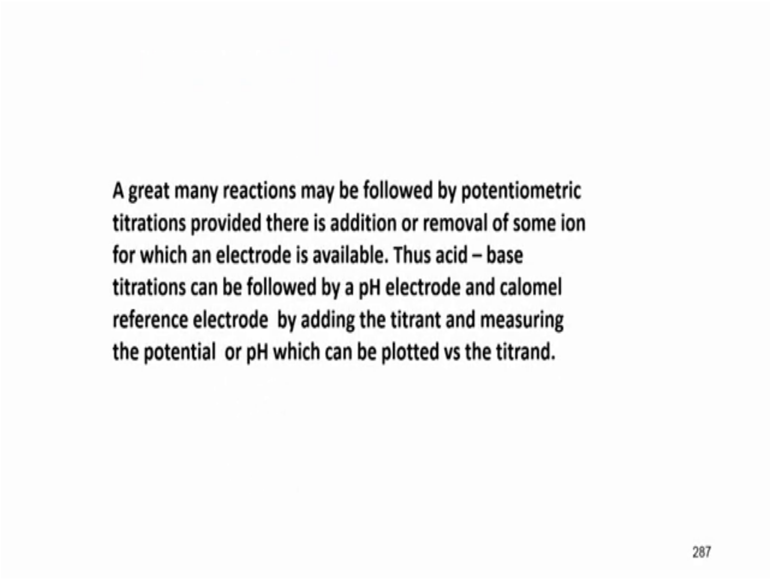

A great many reactions may be followed by potentiometric titrations provided there is addition or removal of some ion for which an electrode is available. Thus acid – base titrations can be followed by a pH electrode and calomel reference electrode by adding the titrant and measuring the potential or pH which can be plotted vs the titrand.

So, a great many reactions, the, this, this is the discussion we have about the electrode, different kinds of electrode. Now, we will discuss about what we can do with these electrodes in our day-to-day life. So, in day-to-day life we actually carry out titrations and follow the chemical reactions. We can follow the chemical reaction by the products or reactants, that is chemical kinetics etcetera, but electrochemically also we can follow the chemical reaction we can do the titrations etcetera. So, a great many reactions can be followed by potentiometric titrations provided, there is addition or removal of some ion for which electrode is available. You cannot have an ion of ammonia. If you to measure ammonia, you need an ammonia electrode; to measure cadmium you need a cadmium electrode.

So, any react chemically reaction where cadmium ion appears as a product or disappears as the reaction proceeds, you can follow that reaction by measuring the potential of the cadmium, similarly for any other material. So, among these things, we can count we can count several kinds of reactions, one is acid base titration just like what you do in your college, the first year PU, second year PU, you do acid base titration with phenolphthalein indicator or methyl orange indicator.

So, such reactions without indicators can be followed by the pH electrode, I can replace the indicator with pH electrode, keep on adding the alkali and keep on measuring the reference pH of the solution using a calomel electrode or combined glass electrode whichever is convenient. And then by adding the titrant and measuring the potential, then you have to plot put potential versus volume of the sample added.

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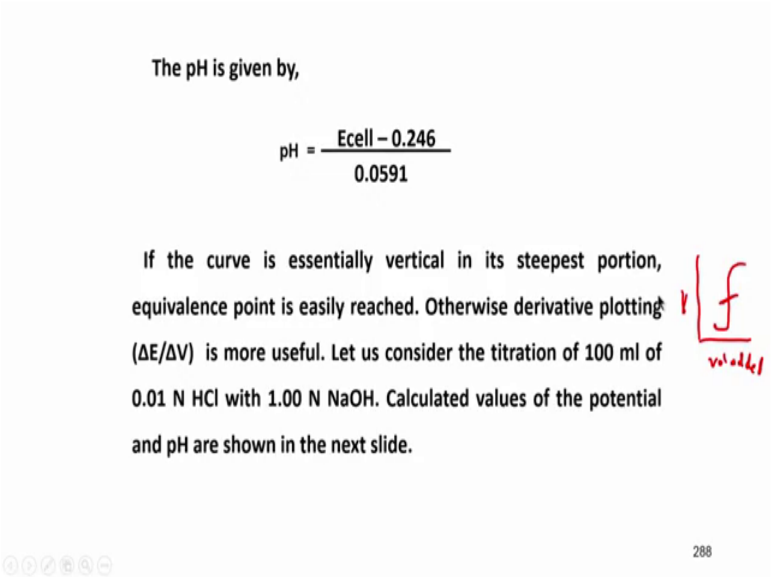

The pH is given by,

$$pH = \frac{Ecell - 0.246}{0.0591}$$

If the curve is essentially vertical in its steepest portion, equivalence point is easily reached. Otherwise derivative plotting ($\Delta E/\Delta V$) is more useful. Let us consider the titration of 100 ml of 0.01 N HCl with 1.00 N NaOH. Calculated values of the potential and pH are shown in the next slide.

So, a potential pH is given by E cell minus 0.246 divided by 0.0591. This equation is valid if you use a calomel electrode, saturated calomel electrode if you can measure if you can use, then the pH is given by this reaction, this equation E cell minus 0.246 divided by 0.0591. So, if the curve is essentially vertical in its steepest portion, the equivalent point is easily reached.

So, just like any other titration, I will have a curve like this, this is volume added, this is a potential voltage. So, the initially the curve will be like this. And then at the steepest portion we will have a separate reaction. Once if the reaction is over, I can always find out the equivalence point by the curve by the volume added where the change is maximum. So, this is a very simple procedure. So, if the curve is essentially vertical in the steepest portion, equivalence point is very easily reached. So, within plus or minus 0.1 ml, you should be able to get the titration.

So, let us consider the titration of 100 ml of 0.1 normal HCl with one normal NaOH. Assume that you do not have phenylalanine indicator and you want to find out what is the concentration of the acid. So, we can actually calculate the values of the potential against the volume of the alkali added.

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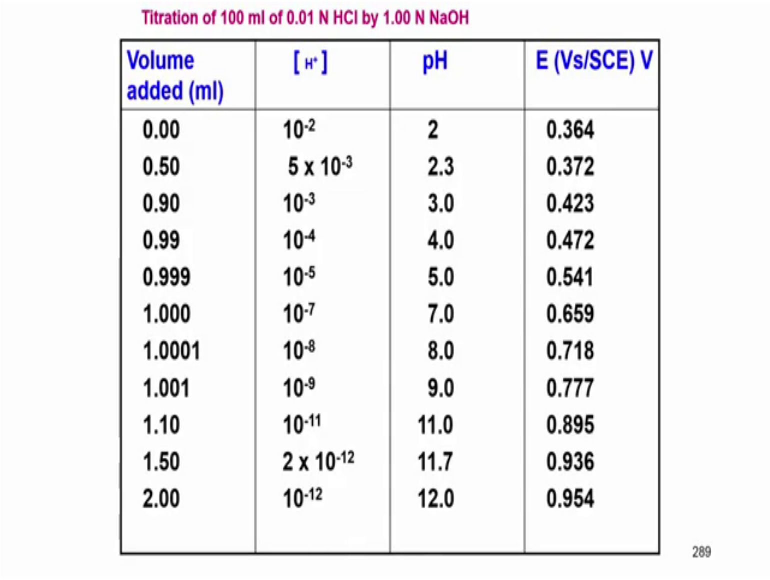

Titration of 100 ml of 0.01 N HCl by 1.00 N NaOH

Volume added (ml)	[H^+]	pH	E (Vs/SCE) V
0.00	10^{-2}	2	0.364
0.50	5×10^{-3}	2.3	0.372
0.90	10^{-3}	3.0	0.423
0.99	10^{-4}	4.0	0.472
0.999	10^{-5}	5.0	0.541
1.000	10^{-7}	7.0	0.659
1.0001	10^{-8}	8.0	0.718
1.001	10^{-9}	9.0	0.777
1.10	10^{-11}	11.0	0.895
1.50	2×10^{-12}	11.7	0.936
2.00	10^{-12}	12.0	0.954

So, here I am trying to titrate 100 ml of 0.01 normal HCl by 1 ml of by 1 ml of by 1 normal NAOH. You can remember this is 0.01 normal HCl, and this is 1 normal NAOH. So, the alkali is 10 times more concentrated than the titration than the acid. So, when I am not adding any alkali, my concentration is concentration of H plus would be negative log of 10 raise to minus 1 that is 10 raise to minus this 0.01 is 10 raise to minus 2 H plus and pH should be 2 and they if you measure the emf, you will get 0.364 versus saturated calomel electrode. So, you can have then I am adding 0.5 ml of NAOH to this ok, so the concentration of this is 50 percent radius. Do you remember this is 10 times more concentrated?

So, 0.5 ml means I am adding almost 50 ml ok. So, concentration would be half of the acid that will be 5 into 10 raise to minus 3, for this I can calculate the pH 2.3, and you can measure the e m f that will read 0.372. Now, I add 0.9 ml theoretically how much I should add, the equivalence point 100 m l of 0.01 normal HCl will should require correctly 1 ml of 1 normal

NAOH. So, I am going to add 0.5 ml, 0.9 ml, 19.99, 0.999, and then 1 ml. When I add 1 ml, it becomes neutral.

So, when I add a 90 percent, it will be 0.9 ml H plus will reach 10 raise to minus 3, pH will be 3 corresponding potential would be 0.243. When I add 99, it becomes 4, 0.472; 999, it becomes 5 and 0.541. And if it is 1 ml, it should be totally neutralized and the pH should be 7, H plus should be 10 raise to minus 7, and this would be a potential would be 0.659. And then I add point 1.0001 ml of excess NAOH, then my pH will be 8, and H plus would be 10 raise to minus 8, this will be 0.718.

And similarly if I proceed 1.001, it will become pH 9, and concentration would be 10 raise to minus 9, and the voltage potential would be 0.777. Suppose, I add 1.1 ml that is 10 percent extra, pH would be 11, H plus would be 10 raise to minus 11. This would be 0.895, 1.5 will become 0.936. 2 ml would become simply 100 percent extra, so that will be p H plus would be 10 raised to minus 12, and pH would be 12 and this should be 0.954.

Now, I want you to concentrate on the e m f values. Remember when nothing is added 0.364; 50 percent is added I get 0.372, what is the difference 0.008. Here what is the difference 0.372, 90 percent is added, it becomes 0.473. So, this will be 23 plus 23 about 56. Now, 3 minus 2 is 1, and 42, 32.51. And here it would be 0.47, you can see the difference this is 0.36, 0.37, 0.42, 0.47, 0.45, what is the difference 0.05 will give you 42, another 0.05 – 47, and another 0.05 should be 541, 47 plus 7. But immediately with 0.0001 ml excess the at the equivalence point it jumps from 0.54 to 0.659 huge jump ok.

So, this huge jump will show you a figure something like this. It will be slowly increasing suddenly there is a big jump, and then next jump is again very high 0.65 to 0.71. So, within 0.001 less to 0.001 excess, and the potential is changing from 0.541 to 0.718, this is not very regular. So, only for acids strong acids you will see a curve like this and you will get a nice equivalence point. After that it is 71 to 77 that is about 0.7 that will be 77 to 89 is another 0.08, 12 know 77 to 89 is 12.

71 to 77, forget the last number, round it off, 72 to 78. So, small changes will be very small, in this case except near the equivalence point. So, what is the moral, the moral of the story is you can follow the titrations of acid base titrations with by measuring the potential, and you will get a steep curve, and you can easily determine the equivalence point. You can make a table like this like this. So, previous one I had shown you in the previous slide and that is the end of the reaction ok.

So, what about titrations involving precipitation reaction? Sometimes it is very difficult to see the endpoint whenever we are doing precipitation titrations. So, some if they are there are colored indicators well and good, but if there are no colored indicators, it is difficult to follow when to determine when the precipitation reaction ends in a solution because our eye is not sensitive enough to determine the changes in the precipitation pattern. So, quite often we missed the endpoint.

A very simple example is silver ion with chloride ion. When the moment you add chloride ion, it will start precipitating you will see white precipitate next drop, you add you do not know whether precipitate is occurring or not it will be white only there a white turbids solution. So, there would not be any change in the turbidity because you are dealing with very fairly low concentrations, your eye is not sensitive.

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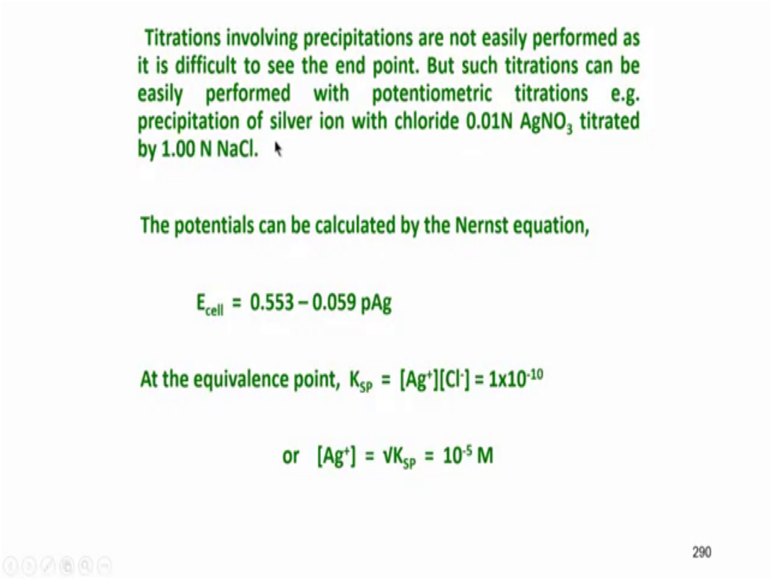

Titrations involving precipitations are not easily performed as it is difficult to see the end point. But such titrations can be easily performed with potentiometric titrations e.g. precipitation of silver ion with chloride 0.01N $AgNO_3$ titrated by 1.00 N NaCl.

The potentials can be calculated by the Nernst equation,

$$E_{cell} = 0.553 - 0.059\,pAg$$

At the equivalence point, $K_{SP} = [Ag^+][Cl^-] = 1x10^{-10}$

or $[Ag^+] = \sqrt{K_{SP}} = 10^{-5}\,M$

So, consider such a reaction in which silver ion is being titrated with chloride ion that is precipitation reaction, they assume that chloride ion silver ion is 0.01 normal silver nitrate and that is titrated by 1 normal NaCl – sodium chloride ok. So, the potentials can be calculated by the Nernst equation, and E cell is given by zero point five three 553, this data I get it from the database ok, any text book or Google will tell you what is the potential of a silver-silver chloride reaction E naught.

So, e is e naught minus 0.0591 ok, 1 I am neglecting divided by n, n should be 1 because silver chloride and silver-silver to silver chloride reaction is 1 electron reaction. So, I get a 0.0591 divided by 1, I can choose not to write, and then negative log of silver divided by negative log of the oxidant divided by reductant. Here I am changing the sign, so it will be negative log of the silver solution and that is nothing like nothing that is something equivalent to pH. Instead of pH for hydrogen we call it pAg for silver that means, the concentration of silver expressed in logarithmic scale pAg. Similarly, I can write pK for acid, pAg, p p p copper like that we can change the concentrations in log terms.

So, at the equivalence point, now I want you to consider equivalence point and what I had taught you about the precipitation sparingly soluble salts. Remember silver-silver chloride is a sparingly soluble salt, and I can write at the equivalence point K sp equal to Ag plus into Cl minus that is nothing but 1 into 10 raised to minus 10. This E data is also available from the database that is Google or whatever you want to search for so, but whenever a salt is ionized the cation concentration must equal anion concentration. So, A g plus should be equal to Cl minus.

So, I can write a g plus is equal to square root of this concentration. I am going back from log scale to log scale to concentration scale. So, it is the concentration of silver plus would be half of would be square root of this because the product a g into c l if they are equal. So, Ag plus would be K sp divided by Cl minus. So, k a Ag plus would be K sp divided by this 1 into 10 raise to minus 10 square root of that would give you 10 raise to minus 5 molar concentration. So, at the equivalence point, I know the concentration of silver in the in my beaker ok.

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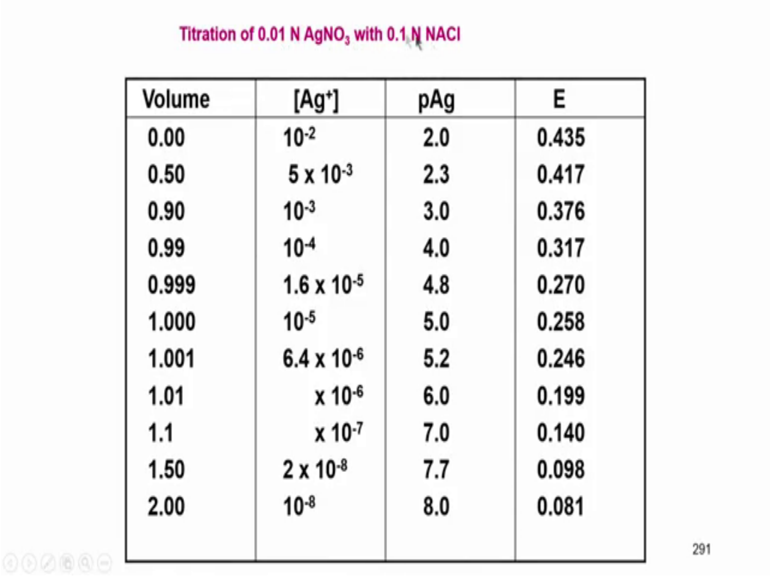

Titration of 0.01 N $AgNO_3$ with 0.1 N NACl

Volume	$[Ag^+]$	pAg	E
0.00	10^{-2}	2.0	0.435
0.50	5×10^{-3}	2.3	0.417
0.90	10^{-3}	3.0	0.376
0.99	10^{-4}	4.0	0.317
0.999	1.6×10^{-5}	4.8	0.270
1.000	10^{-5}	5.0	0.258
1.001	6.4×10^{-6}	5.2	0.246
1.01	$\times 10^{-6}$	6.0	0.199
1.1	$\times 10^{-7}$	7.0	0.140
1.50	2×10^{-8}	7.7	0.098
2.00	10^{-8}	8.0	0.081

So, let us do the titration same exercise like what we did earlier. I am taking titration of 0.01 normal Ag NO 3 0.1 normal again 10 times z at the 0 level, no ionization. So, Ag plus would be concentration of this 0.01 that is 10 raise to minus 2 p Ag would be 2. This would be 0.435. At when I add 0.5 ml solution is already reaction is already 50 percent complete and then I have this would be half of this concentration Ag plus 5 into 10 raise to minus 3, pAg would be 2.3, and the electrode potential would be 0.417.

Then again I do the same exercise 0.90, 0.99, 0.999, and then 1.000, and then again excess after the equivalence point whatever I add is excess, so that will remain unreacted. So, no precipitate no further precipitation. So, 0.001 10 times, and then 1 time, and then for 1.1, this is a 100 percent, and then 150 percent and 200 percent.

So, concentrations will change like this pAg also will change like this 2, 2.3, 3, 4, 4.8, like that, but here you can see 0.435, it is coming down 41, 0.43 to 41, then 0.37, then 0.31, 0.27. Here the difference between this and this is 0.02 here, and then here it is 41, 0.04, here it is 37 to 31 – 0.06; 31 to 27 is again 0.06, 0.04, suddenly it becomes 0.258 at the equivalence point.

And then if I add, there is no further addition that will become 246, and 0.19, 199 and, 0.140, 0.098, because the there is no reaction further. So, the equivalence point I can say that from 0.435, it becomes 0.258, and that is somewhere there, there is an equivalence point. After that it is 0.25, 0.24, 0.199 very small change that is occurring ok.

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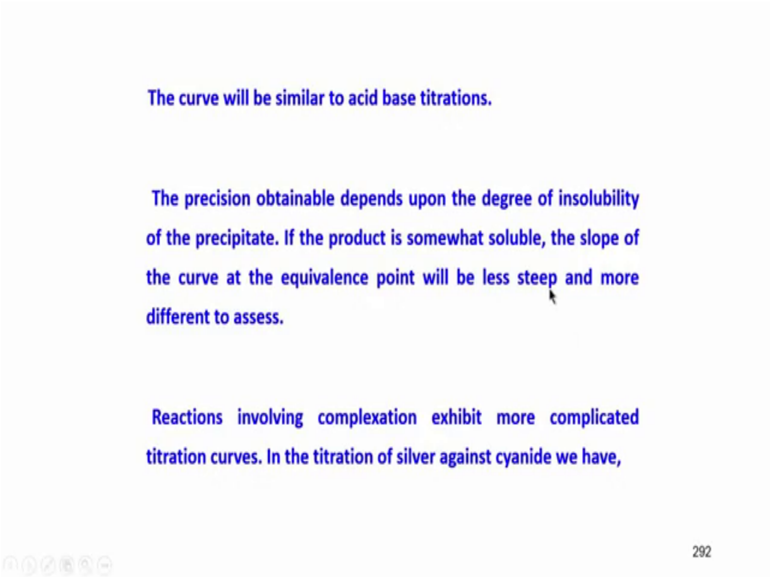

The curve will be similar to acid base titrations.

The precision obtainable depends upon the degree of insolubility of the precipitate. If the product is somewhat soluble, the slope of the curve at the equivalence point will be less steep and more different to assess.

Reactions involving complexation exhibit more complicated titration curves. In the titration of silver against cyanide we have,

So, the curve will be similar to acid base titrations. The precision obtainable depends upon the degree of in solubility of the precipitate. If the solution is very dilute very sparingly soluble, the precision will be extraordinary. If the product is somewhat soluble the slope of the curve at the equivalence point will be less steep, it would not be so sharp, and more it will be more difficult to assess. So, reactions involving complexation exhibit much more complicated titrations, but they can be followed by potentiometric titrations. In the titration of silver against cyanide is a best example.

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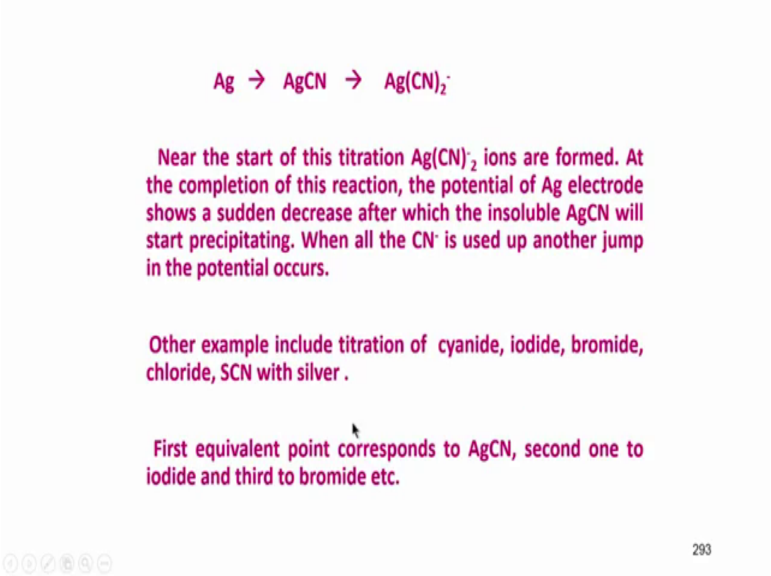

Ag → AgCN → $Ag(CN)_2^-$

Near the start of this titration $Ag(CN)^-_2$ ions are formed. At the completion of this reaction, the potential of Ag electrode shows a sudden decrease after which the insoluble AgCN will start precipitating. When all the CN^- is used up another jump in the potential occurs.

Other example include titration of cyanide, iodide, bromide, chloride, SCN with silver .

First equivalent point corresponds to AgCN, second one to iodide and third to bromide etc.

And that would be the formation of silver, I add cyanide, silver will form silver cyanide precipitate. If you add more cyanide, it will dissolve, the precipitate will dissolve itself forming silver cyanide ions. We will study that a in our next class.

Thank you very much.