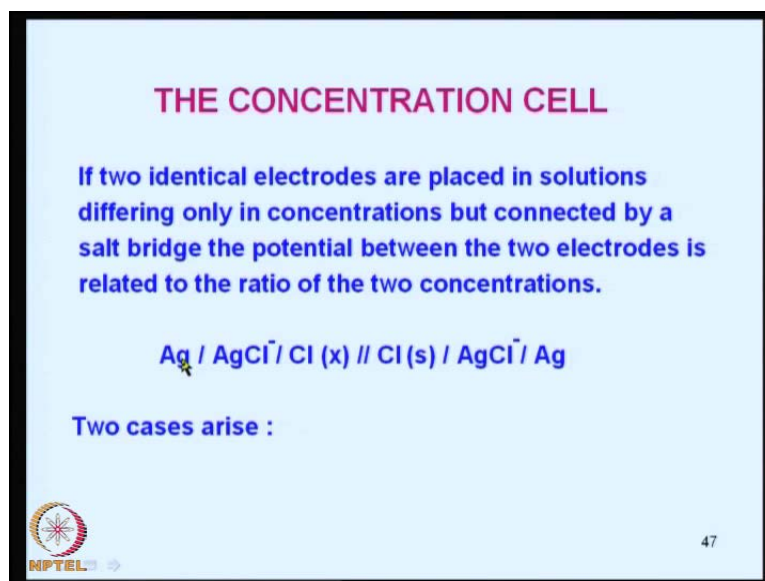


Modern Instrumental Methods of Analysis
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Lecture No. # 37
Fundamentals of Electrochemical Techniques-2 Introduction (continued)

Welcome to the next class, we will continue our discussions on the concentration cell. Earlier we had discussed about the electrodes of the first kind, second kind, and third kind etcetera. Now, we are going to discuss about the concentration cell. So, in the previous **in the previous** cell discussions we had put same electrodes, but solutions of different kinds solution concentrations.

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THE CONCENTRATION CELL

If two identical electrodes are placed in solutions differing only in concentrations but connected by a salt bridge the potential between the two electrodes is related to the ratio of the two concentrations.

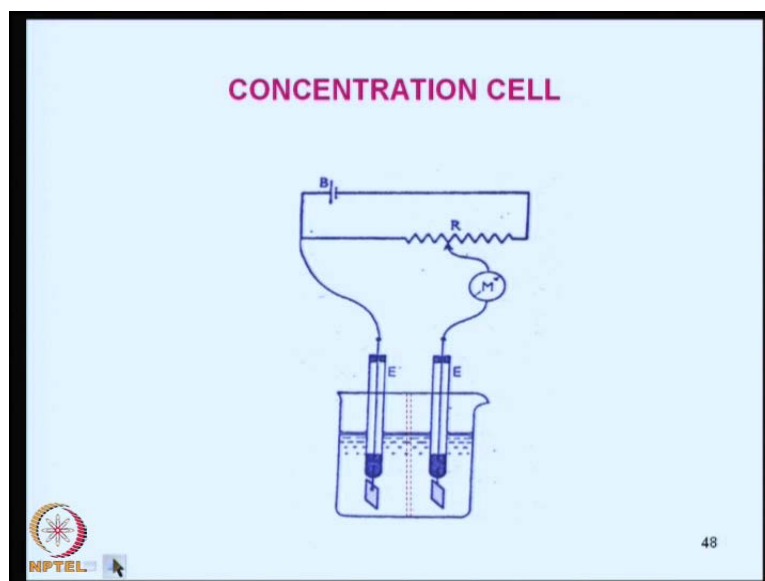
$\text{Ag} / \text{AgCl} / \text{Cl} (x) // \text{Cl} (s) / \text{AgCl} / \text{Ag}$

Two cases arise :

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So, now I am putting it in the form of this expression silver, silver chloride that is the electrode part and it is dipped in a solution of chloride solution of unknown concentration x, and chloride concentration of a, known volume that known concentration that is standard, again connected with the silver chloride, silver electrode. So, you can see that except the two, except this part that is chloride concentration all other side, all other parts of these left hand side and the right hand side are same. So, the only differences if we can get any EMF it has to come from the differences of the chloride concentrations.

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Now, let us this is how the arrangement goes, that is I have a chloride concentration here separated by a salt bridge; that means, there is no direct contact with the ions except through the salt bridge and then I have another electrode connected to a resistor and the power supply. So, this is the cell I am defining now.

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Case 1

Suppose the standard is 0.1000 M. Its single electrode potential is given by,

$$E_s = + 0.222 - 0.0591 \log 0.1000 = + 0.281 \text{ V.}$$

If the unknown is more concentrated say 0.1500 M then

$$E_x = + 0.222 - 0.0591 \log 0.1500 = + 0.271 \text{ V.}$$

Thus $E_{\text{cell}} = E_s - E_x = + 0.010 \text{ volt.}$

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Now, suppose the standard is 0.1000 molar it is a single electrode potential I can write E is equal to E° minus $\frac{RT}{nF} \ln \frac{\text{oxidant}}{\text{reductant}}$; instead of oxidant by

reductant, I am going to write the numbers now. So, the silver **silver silver** chloride electrode E_{naught} is equal to 0.222.

So, because it involves only one single electron, I write 0.0591 by 1; that means one only. So, the logarithm of this only and the reduced form is always one, if it is a metal. So, I delete that and then solve this I get 0.281 volts. If the unknown is more concentrated say 0.1500 molar than the standard 0.100 then E_x , I can write half cell is equal to 0.222 minus 0.591 logarithm of 0.15 that works out to 0.271 volts.

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Case 2

Suppose the unknown is 0.0680 M then

$$E_x = 0.222 - 0.0591 \log (0.0680) = 0.291 \text{ volt and}$$
$$E_{\text{cell}} = E_x - E_s = + 0.010 \text{ V}$$

Thus any measured potential is open to ambiguous interpretations which may be avoided by noting that the interpretation corresponds to more positive of the two.

The concentration cell provides a convenient tool for analysis of pH.

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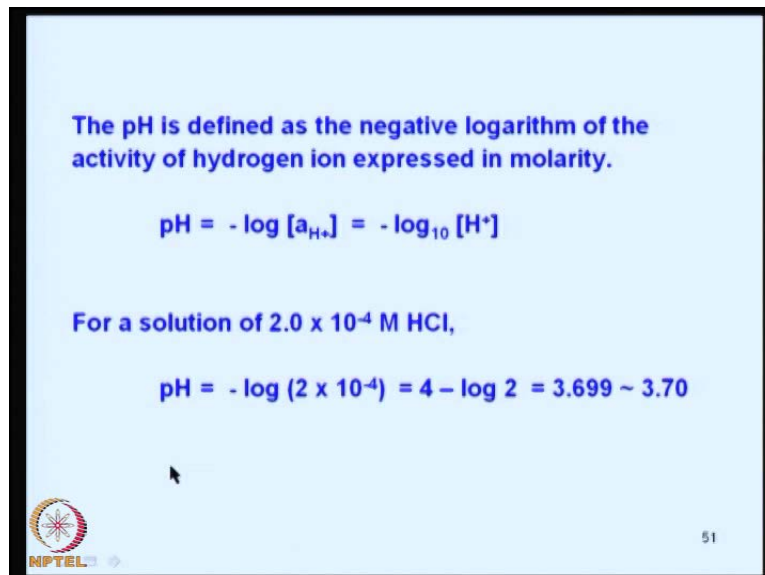
Now, what is the EMF you are going to see, in this case; that is E_{standard} , minus E_x this is 0.281, minus 0.271 is 0.010 volt. Now, suppose the unknown is 0.680 instead of 0.1500 **instead of 0.1500** this is 0.680 molar then I can write a similar expression and I get 0.291 volts.

And E_{cell} what you actually measure is 0.010 volts, you will be surprised now, which one to take be unknown concentration; that is if the concentration is 0.1500 still you are going to observe only 0.10 volts. If the concentration of the unknown is 0.680 molar still the difference what you are going to observe is 0.100, 0.010 volts.

So, any measured potential could correspond to two different concentrations and the different ambiguous interpretations are possible. So, you can avoid this ambiguous interpretation by noting that the interpretation corresponds to more positive of the two.

So, the concentration cell provides a convenient tool for the analysis of pH, if I replace the chloride solutions by hydrogen ion solutions

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The pH is defined as the negative logarithm of the activity of hydrogen ion expressed in molarity.

$$\text{pH} = -\log [a_{\text{H}^+}] = -\log_{10} [\text{H}^+]$$

For a solution of 2.0×10^{-4} M HCl,

$$\text{pH} = -\log (2 \times 10^{-4}) = 4 - \log 2 = 3.699 \sim 3.70$$

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So, similar process should happen with respect to hydrogen ions. So, how do we define the pH? pH is defined as the negative logarithm of the activity of the hydrogen ion expressed in molarity; that is pH equal to negative log of a H plus that is equal to negative log of H plus. Here, we are going to neglect the activities, because the solutions are very dilute and activity coefficients are expected to be one. So, I am going to simply replace the activity terms by H plus.

So, suppose you have a solution of 2 into 10 raise to minus 4 molar hydrochloric acid. Then you can calculate the pH of this solution as negative log of 2 into 10 raise to minus 4; that is equal to 4, minus log of 2 and then 3.699; which is approximately equal to 3.7 volts. That means given any concentration of p hydrogen ion concentration you should be able to determinate its pH.

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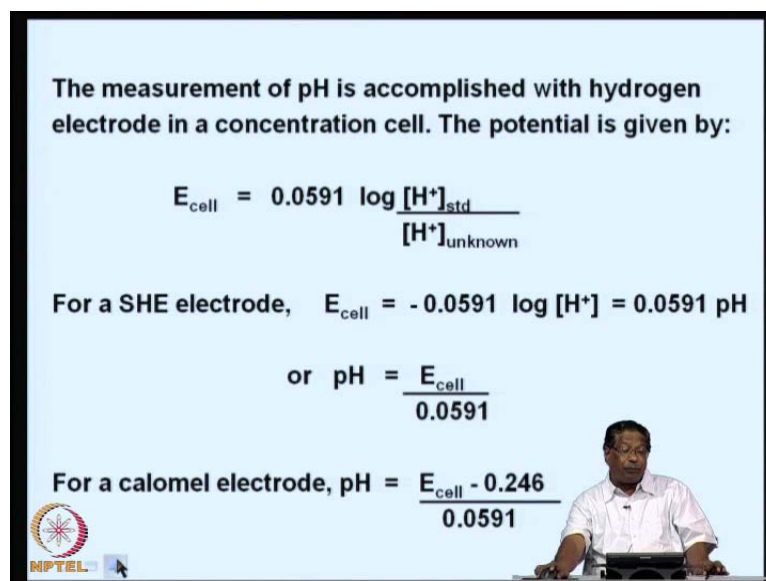
The measurement of pH is accomplished with hydrogen electrode in a concentration cell. The potential is given by:

$$E_{\text{cell}} = 0.0591 \log \frac{[\text{H}^+]_{\text{std}}}{[\text{H}^+]_{\text{unknown}}}$$

For a SHE electrode, $E_{\text{cell}} = -0.0591 \log [\text{H}^+] = 0.0591 \text{ pH}$

or $\text{pH} = \frac{E_{\text{cell}}}{0.0591}$

For a calomel electrode, $\text{pH} = \frac{E_{\text{cell}} - 0.246}{0.0591}$



So, the measurement of pH is accomplished with hydrogen electrode, as I had told you earlier in a concentration cell; that means, I must have a standard hydrogen ion concentration and then an unknown concentration of hydrogen.

So, the potential of such a system is given by E is equal to E_{cell} **E cell** is should be equal to 0.0591 logarithm of the concentration of standard divided by the concentration of the unknown. So, for a standard electrode higher standard hydrogen electrode E_{cell} is nothing but minus 0.0591 logarithm of H plus divided by oxidant divided by reductant; reductant activity in zero. So, it is log of 0 is 1. So, minus 0.591 negative log of H plus is pH. So, I am going to get 0.0591 p H or p H is nothing but actual EMF divided by 0.0591; that is the RT by nf value

So, if I use a calomel electrode instead of a standard hydrogen electrode, I must be write E_{cell} minus that of the calomel electrode that is 0.246 divided by 0.591 **0.591** volt, why do I go for a calomel electrode? That is, because standard hydrogen electrode is difficult to set up. So, calomel electrode is very simple.

So, if I use a calomel electrode it gives reproducible values and I can measure the pH very simply just by connecting still better option would be to use a glass electrode. So, what is a glass electrode? A glass electrode is a thin membrane of a certain variety of a very thin membrane of in the form a bulb, in which I am going to put some solution and seal it at the top with a wire in between and then I put another solution outside the glass


bulb; that means, the glass membrane is in contact with the solution of standard solution which is sealed inside the membrane and another solution which is outside the membrane. Therefore it is essentially a concentration cell. So, I can represent the concentration cell like this that is inner SCE that is look at this slide please.

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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:

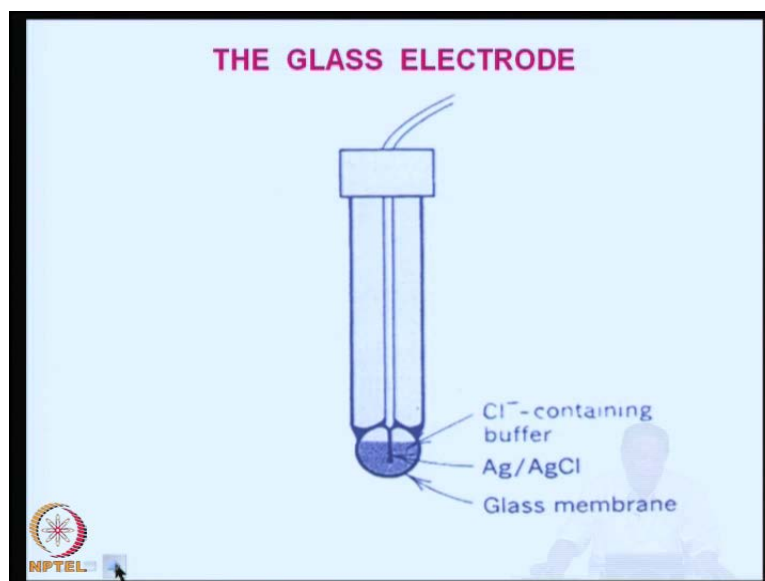
Inner / pH 7 / Glass membrane / test solution / External
SCE / buffer / SCE

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And this inner is calomel electrode, the electrode instead of standard I put pH 7 buffer then I have a glass membrane, then I have a test solution which is connected again to external SCE, the EMF corresponding to this and this will be cancelled because one is positive and another is negative.

So, the only difference in EMF should come from the test solution and pH 7 buffer that is a standard concentration.

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So, this is how a glass electrode will look like, I have a silver **silver** chloride electrode with a connection outside this is a glass tube and it is a small bulb here and then in the bulb. I have silver **silver** chloride electrode that is this one and then I have a solution chloride containing buffer.

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

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.

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So this, if I dip in a solution of unknown concentration it sets up a concentration cell. So, for such a cell pH is given by E_g that is asymmetry of EMF of the glass cell, minus E_{cell} divided by 0.059 volts. E_g is a constant that includes the potential of reference

electrodes and some additional small spurious potentials called as asymmetry potential; it arises out of unequal strain in the glass.

Because, every glass membrane is unique therefore, the strains are asymmetry potential would be different for each glass therefore, though it is included in a as a constant in this equation. So, the glass electrode is a routine analytical tool in any laboratory, in highly alkaline solutions you may not get very good results, very correct results of pH especially above pH 10 and the error may be as high as one pH.

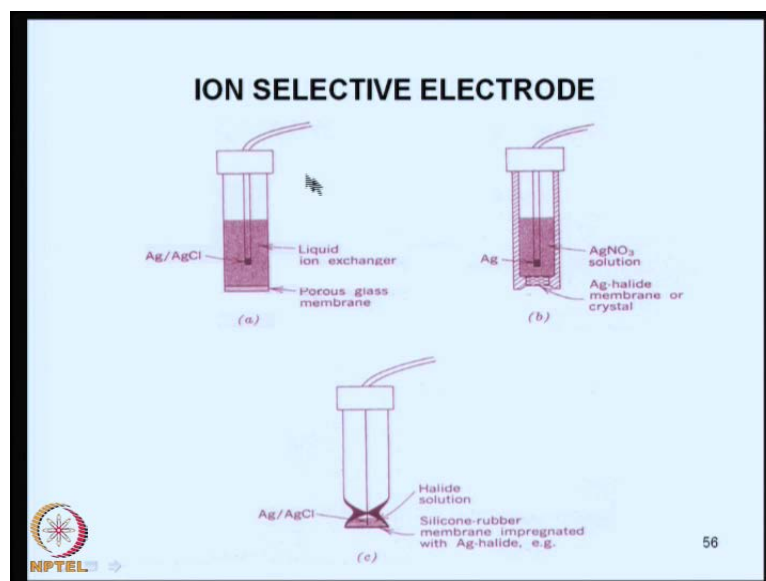
The glass surface can also absorb some specific ions which may cause erroneous results that is apart from hydrogen it may absorb some other ions also. And great branch of electro chemistry has been electro sensor technology has been built up around this property of the membranes, capable of exchanging the ions and these are known as specific ion electrodes.

So, apart just like hydrogen ions you can construct a glass electrode or a an electrode which is responsible to fluoride ions, ammonia, cyanide and then carbon monoxide, carbon dioxide like that several systems you can design by providing a ion specific membrane and such electrodes are known as ion selective electrodes.

We are not going into details of the ion selective electrodes as such, but this is the point where the theory of ion selective electrodes starts. So, the glass surface since you can absorb specific ions it is a very good way of controlling the concentrations. Therefore, it is essential to rinse, because once you have a solution and then you dip your glass electrode in that it is already set up equilibrium and you want to measure the pH of another solution

Now, the glass surface is having a concentration of the previous ions; that is memory. So, you had to keep on washing it number of times, until all the memory effect goes away and then you are going to introduce your solution into that. That is why? We always say, wash a glass electrode with copious amounts of water before you proceed with the measurements that is a good laboratory practice.

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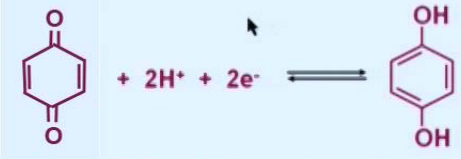
Now, these are some of the ion selective electrodes, what I was talking about, this is a silver **silver** chloride electrode and this is a porous glass membrane, this is liquid ion exchange and similarly, I can have silver **silver** nitrite solution and if I have a silver halide membrane here. And which is permeable to halide then I can determine chloride ions and nitrate ions like that different. This part which is the membrane or a crystal is going to play a very important role and then I can have a silicone rubber membrane impregnated with silver halide different constructions of the electrode ion specific electrodes.

And several ion selective electrodes are marketed routinely in the **the** analytical determination of the specific substances in water or soil or air or any other matrix specific ion selective electrodes are being marketed by several reputed companies.

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QUINHYDRONE ELECTRODE

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



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

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

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Now, let us look at Quinhydrone electrode, it is nothing but variant of the glass electrode which can be used to measure the pH. Now, in Quinhydrone electrode, I have a platinum wire and it contains Quinhydrone that is 0.4 keto graph at one for position benzoquinone and quinone and then in presence of hydrogen ions it can reduced to OH.

So, the EMF is given by $E = E^{\circ} + 0.0591 \log [H^+]$ plus again I am going to neglect the reduced species and then this is E° is 0.699 and then two hydrogen two electrons are there. So, I had to take twice and this is a another similar electrode with glass like glass electrode, but it is not useful for pH is above 9. And in presence of strong oxidizing and reducing agents it would not work, because the hydroxyl groups can get converted to ketonic groups in presence of the oxidizing agents and ketonic groups can get reduced to hydroxyl groups in presence of strong reducing agents.

So, it has got somewhat limited applications, but we do have a metal wire like a antimony, they can take antimony electrode coat it with antimony oxide and then make an electrode out of that.

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ANTIMONY ELECTRODE

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

$$2\text{Sb} + 3\text{H}_2\text{O} \rightleftharpoons \text{Sb}_2\text{O}_3 + 6\text{H}^+ + 6\text{E}^-$$

⚠

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.



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And the reaction is given by 2 antimony plus 3 H₂O going to Sb₂O₃ plus 6 H plus plus 6 e minus. This electrode is not as fragile as a glass electrode nor would it show variations of 3 H depending upon the presence of oxidizing and reducing species. So, the potential of this electrode depends on the method of preparation and on the nature of the solution, but I can use such an electrode.

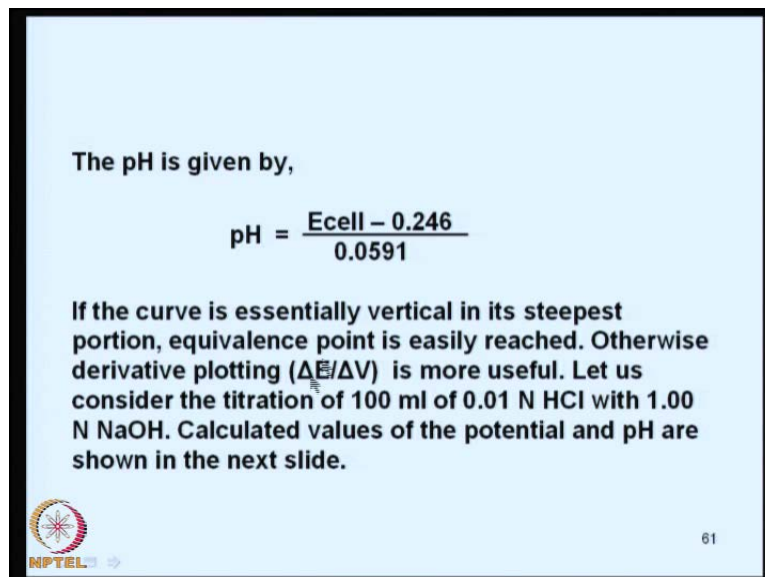
I can use such an electrode in process solutions where the process solutions are moving at a very fast velocity; that means, if there, if I insert a glass electrode in a fast moving solution it may not be able to show, the correct pH or it may get broken or something like that can happen, but if I have an antimony antimony oxide electrode then I can measure the pH under harsher conditions that is the idea.

So, a great many reactions may be followed by potentiometric titrations provided there is addition or removal of some ions for which an electrode is available. Thus, acid based titrations hydrogen ions are being removed or OH ions are being added. So, one ion is being removed, another ion is being added, if one of them is responsive to EMF changes that is potential changes the reaction can be followed by potential method.

So, you can do you can have different kinds of reactions like acid based reactions, precipitation reactions, redox reactions, complexation reactions, etcetera all these things can be followed by potential metering only thing is, what you need is a pH electrode or a reference electrode, specific electrode and a reference electrode; reference electrode

could be pH electrode, glass electrode or a calomel electrode one of the two would be fine. And then the potential can be measured and you can plot the pH versus the amount of the titrant added or you can plot the potential also.

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The pH is given by,

$$\text{pH} = \frac{E_{\text{cell}} - 0.246}{0.0591}$$

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.


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So, if you take a look at this figure, at this slide the pH is given by E cell minus 0.246 that is the reference electrode potential divided by 0.0591.

And if the curve is essentially vertical in its steepest portion equivalence point is easily reached otherwise derivative plotting is more useful. Let us consider, the titration of 100 ml of 0.01 normal HCl with 1 normal NaOH; that means, the NaOH is already 10 times or 100 times more concentrated than the titrant this is 0.01 this is 1.

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Volume added (ml)	[H ⁺]	pH	E (vs SCE) V
0.00	10 ⁻²	2	0.364
0.50	5 x 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 x 10 ⁻¹²	11.7	0.936
2.00	10 ⁻¹²	12.0	0.954



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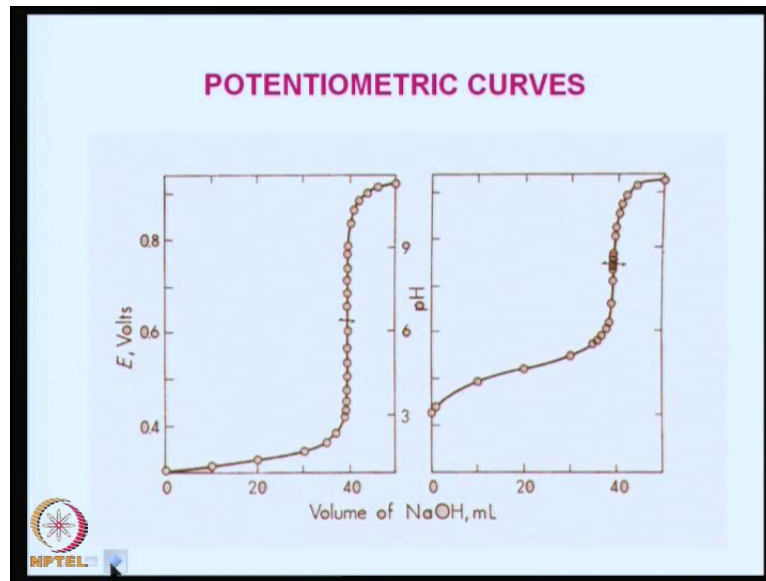
So, that we can calculate the values of the potential and pH this is a very simple calculation and I have put it in the table. So, when you have not added anything the hydrogen ion concentration is same as 0.01 normal that is it is a strong acid 100 percent ionized. So, the H plus is 10 raise 2 minus 2 and pH is 2 and potential is 0.364.

Suppose you add 0.5 ml the following the 50 percent of this would be reduced would have reacted and the concentration would have come down by half. So, 5 into 10 is minus 3 the pH would change to 2.3 and 0.372 similarly 0.9 you get pH 3 and 0.423 you will get, and then 0.99 if you go pH would be 4 and 0.472.

We can work out these numbers yourself and satisfy that, the pH changes and the EMF changes are accurate. Now, when I add 1 ml of this, because it is 100 times more concentrated there is complete neutralization and we know that, at new random neutralization conditions pH is 7. So, I have a pH 7 here and the EMF is given by 0.659. Now, I add 0.0001 volume milliliter of the NaOH excess.

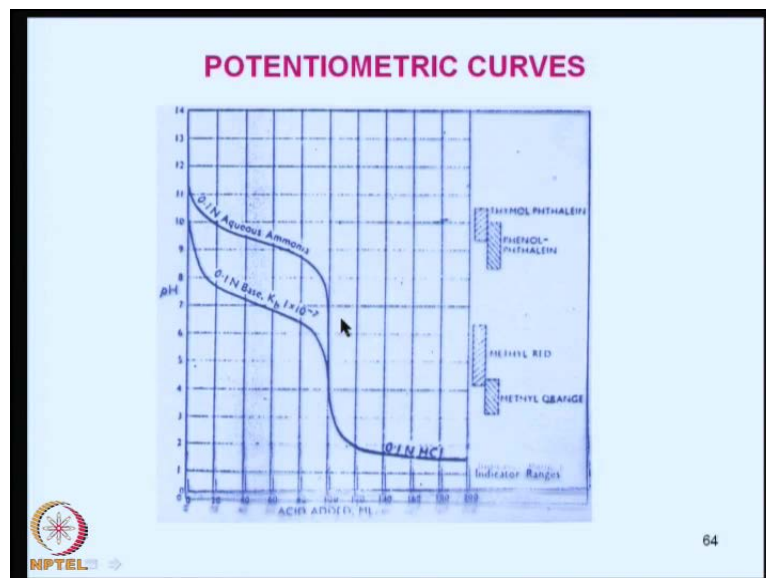
Now, what happens? pH will become 8 and the EMF will become 0.718 and similarly, if I had 0.001. I will have pH 9, 0.777 and then 1.1 ml , 0.1 ml extra. If, I had, I will have 0.895 and 2 ml, I will I will have 0.954. So, if I plot EMF versus the concentration, I would end up with a figure like this what is there on the left side. So, a very sharp peak you will get a sharp inflection point.

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So, similarly I can go for a other systems; these are the potentiometric curves. What you would see, with the titration of NaOH and Hcl on the left side very sharp inflection point you will see that, the within a fraction of a milliliter you are going to end up from one end to the other end; that means, you will get a very beautiful end point, somewhere in the middle here and if you plot pH you would see that changes from 3 to 9 or 10 would be visible with again a very sharp end point.

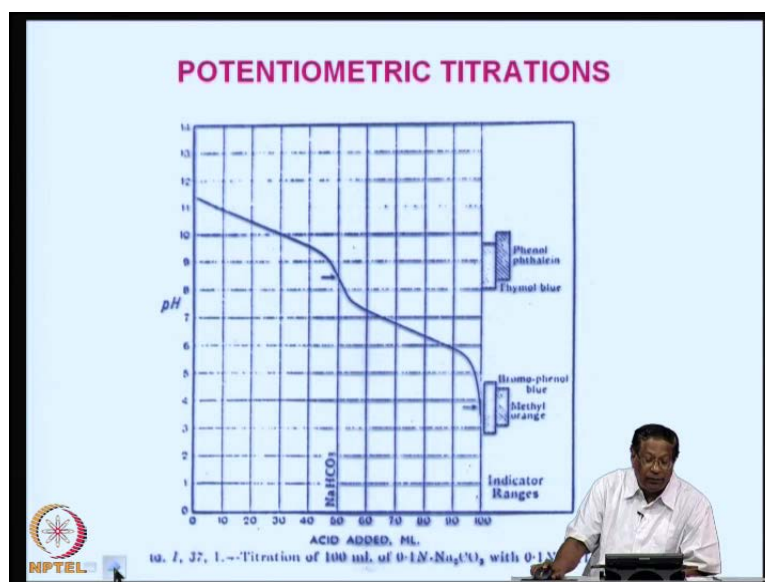
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Usually the midpoint of this vertical portion is the end point of the reaction, now these are some of the potential curves the potentiometric curves this will be top one is 0.1 normal aqueous, ammonia titrated with HCl here, you can see the sharp point is one point is here and another point is somewhere here, the inflection point. So, I can have an indicator which can change color in this region as well as in this region.

So, if I have only one end point strong acid and strong base, I will have a very sharp end point single with a dibasic I will get 2 inflection points, tribasic I get 3 inflection points like that you can see different kinds of potentiometric curves in this for example, this is sodium bicarbonate titrated with the acid.

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Here, you will see that the inflection point is not so well defined, but still you can see it because this is the area where the inflection point and phenolphthalein thyme blue will change color in this range to this range; that means, inflection point is covered. So, you can there is another inflection point somewhere here that is corresponding to pH 3 or. So, and then there is another indicator.

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Titration 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 AgNO₃ titrated by 1.00 N NaCl.

The potentials can be calculated by the Nernst equation

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

At the equivalence point, $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1 \times 10^{-10}$

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



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So, we can carry out the reactions like this without involving much problem. So, what are we saying is acid based titrations can be followed by measuring the EMF and you can get accurate end point. Now, is it possible only for acid based the answer is no the titrations involving the precipitations are also conducted using potentiometric, what is the need for conducting potentiometric titrations for precipitation reactions, because the end point is not easily detectable especially in presence of precipitate. So, you may overshoot the end point at any time.

So, they you will not be able to stop the reaction at the exact point that, in such a case you should go for potentiometric titrations and then involve in precipitation, but such titrations can be performed very easily. Consider the reaction of silver ion with chloride ion, now we are going to consider 0.01 normal silver nitrate against one normal sodium chloride that is again there is a 100 percent difference in the concentrations of the titrant and the titrand.

So, the potentials can be calculated by using the Nernst equation, E_{cell} is equal to 0.553 minus 0.059 P Ag I am writing this, because it is negative log of Ag silver concentrations I am going to write at the equivalence point what happens is silver ion and chloride ion are equal and the product of this works out to 1 into 10 raise to minus 10. That means the silver ion concentration should be square root of this. So, if I take the square root I can calculate that this silver ion concentration, in a precipitation reaction would be 10 raise to

minus 5 molar at the equivalence point, now take the titration look at this I have made a similar table like acid based titration.

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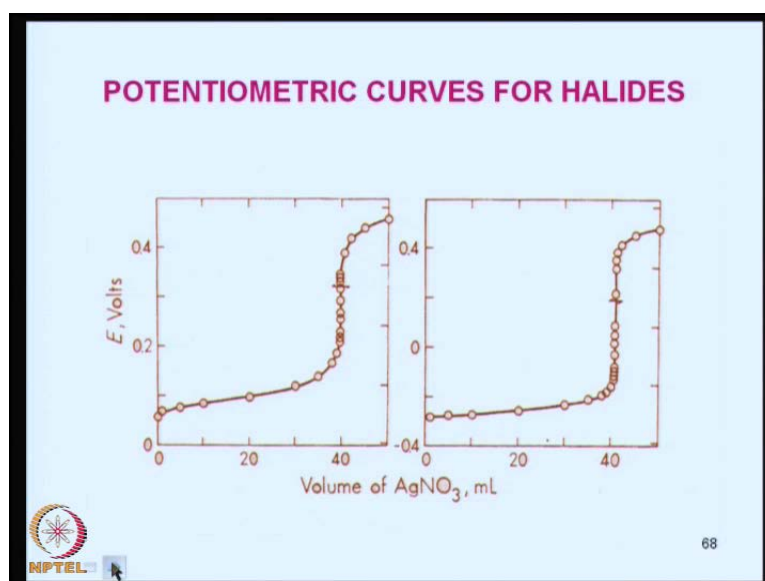
Titration of 0.01 N AgNO₃ with 0.1 N NaCl

Volume	[Ag ⁺]	pAg	E
0.00	10 ⁻²	2.0	0.435
0.50	5 x 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 x 10 ⁻⁵	4.8	0.270
1.000	10 ⁻⁵	5.0	0.258
1.001	6.4 x 10 ⁻⁶	5.2	0.246
1.01	x 10 ⁻⁶	6.0	0.199
1.1	x 10 ⁻⁷	7.0	0.140
1.50	2 x 10 ⁻⁸	7.7	0.098
2.00	10 ⁻⁸	8.0	0.081

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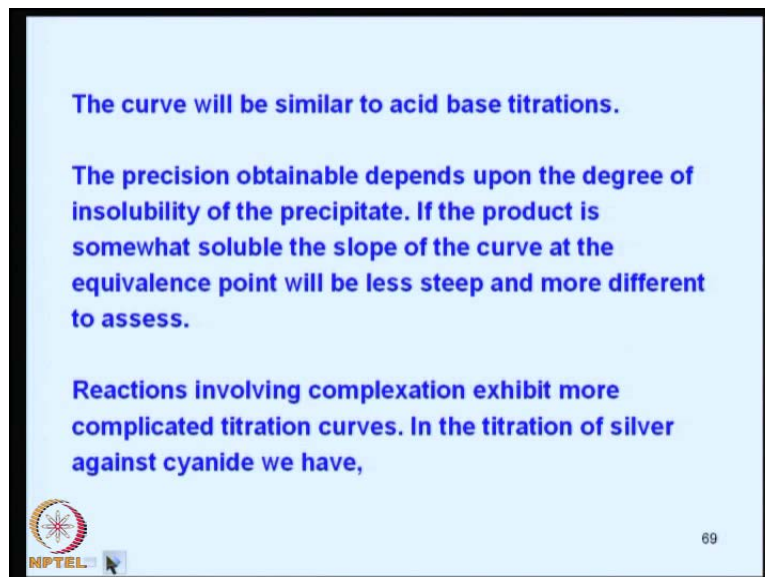
I have put Ag plus and p Ag that is negative log of Ag plus and E and then I have put 0.00, 0.50, 0.90, 0.99, 1.001, 0.192, etcetera and 0.435, 0.417 you are going to get 0.376, 0.317 and 0.270, at 0 exactly equivalence point you will get 0.258 after that the decreases starts and you will end up with 0.081.

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Now, what happens, if you plot these things the you will see a beautiful curve here, similarly for other halides this is the titration for silver nitrate and the curve will be similar to acid based titrations.

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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,

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And the precision obtainable depends upon the degree of insolubility of the precipitate, if the precipitate is highly insoluble the precision would be very good; if the precision solubility is more or if the substance behaves amphotericly the end point will not be sharp. So, if the product is somewhat soluble, the slope of the curve at the equivalence point would be less steep and more different, difficult to access also. So, reactions involving complexations exhibit more complicated titration curves in the titration of silver against silver cyanide.


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$\text{Ag} \rightarrow \text{AgCN} \rightarrow \text{Ag}(\text{CN})_2^-$

Near the start of this titration $\text{Ag}(\text{CN})_2^-$ 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 examples include titration of cyanide, iodide, bromide, chloride, SCN with silver.

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



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If we consider, you will see that we have a reaction going like this silver forming cyanide AgCN precipitate followed by again it dissolves forming $\text{Ag}(\text{CN})_2^-$. That means, if you start the reaction take the cyanide and add silver plus more of cyanide is at the bottom, less of silver is there, first it will form $\text{Ag}(\text{CN})_2^-$. So, there it will be dissolving and then as you increase the addition of silver all the $\text{Ag}(\text{CN})_2^-$ would be formed, but then the cyanide it will form a precipitate. So, AgCN will be forming.

So, near the start of this titration we have $\text{Ag}(\text{CN})_2^-$ at the conference, at the completion of this reaction, the potential of silver shows a sudden decrease after which the insoluble silver cyanide will start precipitating when all the cyanide is used up another jump in the potential will occur. Other examples of such precipitation titrations involve, the substances whose solubility products are very low that is iodide then bromide then chloride and thiocyanate etcetera, is it possible? To determine all the mixtures of chloride, cyanide, bromide and iodide, etcetera, the answer is yes.

And the first equivalence point will correspond to silver cyanide and the second one will correspond to the next highly insoluble precipitate among the halides iodide is having lowest K_{sp} . So, the next one will correspond to iodide next to inflection point in the correspond to iodide, next one would to bromide next one would be to cyanide, I mean chloride etcetera.

So, it is possible for us, to determine the various end points like this on the right hand side. I am showing you first inflection point will correspond to cyanide and then iodide then bromide then chloride, etcetera. So, all these reactions are easily followed by potentiometric titrations. Now, you can look at oxidation, reduction reaction, titrations these are followed by simple platinum indicator electrode and saturated calomel electrode, one reference you will need anyway that is reference electrode, it can be SCE or silver **silver** chloride electrode or any of the known electrodes.

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OXIDATION – REDUCTION TITRATIONS

These are followed by a simple platinum indicator electrode and SCE. Consider the reaction of stannous chloride with ceric sulphate. The reaction is represented by

$$\text{Sn}^{2+} + 2\text{Ce}^{4+} \rightleftharpoons \text{Sn}^{4+} + 2\text{Ce}^{3+}$$

and the equilibrium constant is given by

$$K = \frac{(\text{Sn}^{4+})(\text{Ce}^{3+})^2}{(\text{Sn}^{2+})(\text{Ce}^{4+})^2}$$

At the start, the ratio of $\text{Sn}^{4+}/\text{Sn}^{2+}$ is nearly zero and $\log [\text{Sn}^{4+}]/[\text{Sn}^{2+}]$ has a large negative potential value.

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And when we consider, the reaction of stannous chloride with sulphate, ceric sulphate the reaction we can write it as Sn 2 plus **plus** ceric going to Sn 4 plus that is tannic and 2 moles of cerous.


And the equilibrium constraint of this reaction is given by the products divided by the reactants; that is Sn 4 plus I am writing here, Ce 3 plus whole square I am writing here, and divided by Sn 2 plus and ceric 4 plus ceric. At the start the ratio of stannic to stannous is nearly zero; that means, before I add any ceric then most of it would be in the stannous; that means, the tannic to stannous would be zero. And log of Sn 4 plus Sn divided by Sn 2 plus that is stannic to stannous log value would have a large negative value, because the concentration of the denominator is almost near zero. So, it will have a very large negative value.

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After the first addition of the oxidant of some Sn^{2+} is converted to Sn^{4+} and the potential is given by,

$$E = E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 + \frac{0.0591}{2} \log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]}$$

Also some cerium is present and hence,

$$E = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + 0.0591 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$


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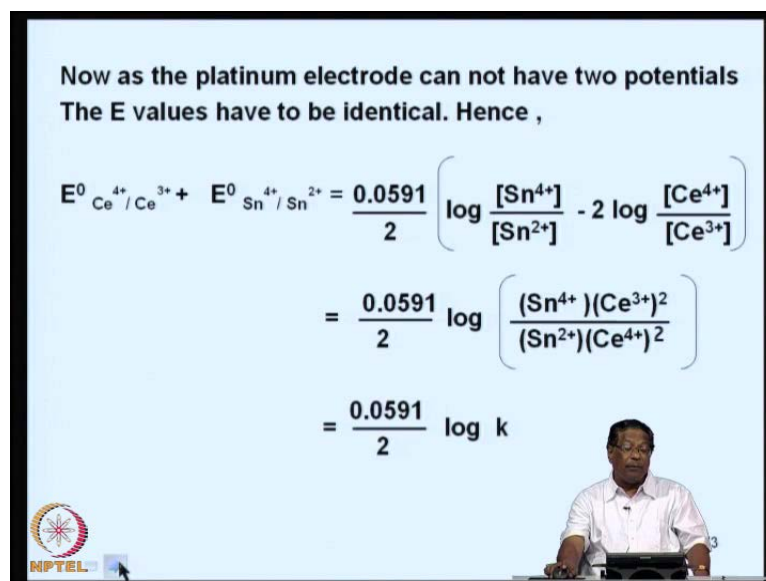
You know after the first addition of the oxide some of the stannic gets converted to stannous, the moment we have stannic and stannous we can write Nernst equation that is E is equal to E naught stannic by stannous plus 0.0591 divided by 2; that is RT by nf value divided by 2, because n is 2 here, and logarithm of the oxidant divided by the reductant, remember that both the oxidant and the reductant are in solutions now.

So, they will have a definite concentration. So, some ceric **ceric** is also present now. So, we can write another equation the Nernst equation for ceric cerous system; that is E is equal to E naught ceric cerous plus 0.0591 only single electron is required and ceric 2 cerous plus ceric 2 cerous.

But the EMF, if you are using one electrode and one reference and one standard the EMF value cannot be two different values for ceric and cerous and stannic and stannous, because all the four species are in the same solution, it has to show only one EMF value therefore, we can compare these equations **we can compare these equations** and reorganize.

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Now as the platinum electrode can not have two potentials
The E values have to be identical. Hence ,

$$E^0_{\text{Ce}^{4+}/\text{Ce}^{3+}} + E^0_{\text{Sn}^{4+}/\text{Sn}^{2+}} = \frac{0.0591}{2} \left(\log \frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]} - 2 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \right)$$
$$= \frac{0.0591}{2} \log \left(\frac{(\text{Sn}^{4+})(\text{Ce}^{3+})^2}{(\text{Sn}^{2+})(\text{Ce}^{4+})^2} \right)$$
$$= \frac{0.0591}{2} \log k$$


How we are going to do that, is like this put all E naughts on one side and solution terms, concentration terms on the other side. So, E naught Ce 4 plus by Ce 3 plus, plus E naught Sn 4 plus by Sn 2 plus should be equal to this 0.0591 by 2, logarithm of stannic to stannous minus twice logarithm of ceric to cerous.


And this is I can simplify this two will become square here, and take out the log and then Sn 4 plus into ceric 3 plus whole square divided by Sn 2 plus Ce4 plus. So, this value is nothing but, the equilibrium potential equilibrium of the value of the reaction. So, I simply write log K. So, instead of writing all this, I simply put it as 0.0591 by 2 logarithm of K.

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Substituting the known values of E^0 s we get

$$\frac{(1.61 - 0.15)}{0.0591} = \log k \text{ or } k = 2.5 \times 10^{49}$$

At the equivalence point it can be easily seen that

$$(\text{Ce}^{3+}) = 2 (\text{Sn}^{4+}) \text{ and } (\text{Ce}^{4+}) = 2 (\text{Sn}^{2+}) \text{ and}$$
$$\frac{(\text{Sn}^{4+})}{(\text{Sn}^{2+})} = \frac{(\text{Ce}^{3+})}{(\text{Ce}^{4+})} = \sqrt[3]{k} = 2.92 \times 10^{16}$$


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Now, substituting the known values of the E naughts for stannic to stannous and ceric to cerous we get 1.61 minus 0.15 divided by 0.0591 these values are obtainable from the standard reference table. I had shown in the last class ceric to cerous stannic to stannous etcetera and $\log K$ this value should be equal to or K should be equal to 2.5 into 10 is to 49.

So, at the equivalence point the concentration of ceric should be twice that of cerous; that means, twice stannic is equal to ceric and the twice stannous would be equal to cerous and we can write this stannic to stannous and ceric to cerous this is twice to 2 plus 1 is 3. So, the cube root of this corresponds to the concentration ratios of the stannic to stannous and ceric to cerous. So, the species you can concentrations you can easily calculate at the equivalence point. Now, we can now substitute that value that what did we calculate in the last this thing 2.92 into 10 raise to 16.

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We can now substitute this value of ionic ratios and calculate

$$E = 0.15 + 0.0591 \log (2.92 \times 10^6) = 0.64 \text{ volt}$$
$$E = 1.61 - 0.0591 \log (2.92 \times 10^6) = 0.64 \text{ volt}$$

Note that the same value is obtained both ways which is expected.

Many redox reactions especially those with permanganate, dichromate, nitrate and similar oxidants have a strong dependence on pH and the potential calculations become complicated.

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Now, we are going to substitute these values 0.15 into 0.0591 logarithm of 2.92 into 10 raise to 6 that becomes 0.64 volt. If, I substitute calculate with respect to other electrode that is other species then also I should get the same value, but it has to be with a negative value. So, 1.61 minus 0.0591 logarithms of 2.92 into 10 raise to 6 should be equal to 0.64 volt so; that means, we get exactly the same value; that means, our results are accurate.


So, note that the same value is obtained both ways this is expected any way. So, many redox reactions especially those of permanganate, dichromate, nitrate and similar other similar oxidants have a strong dependence on pH. So, the you could you can recall that the ceric to cerous reaction is no where we have written the pH or acid value; that means, it is independent of the pH, but several redox reactions are pH dependent. Some of them will proceed **some of them will proceed** in the right direction in presence of acids, some of them will proceed only in presence of alkalis. So, pH dependence also we had to factor in, if we want to talk about the complex reactions so; that is redox reactions, the potential calculations will also become subsequently complicated.

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For example, in the permanganate titration of iron the equilibrium constant is given by,

$$K = \frac{(\text{Fe}^{3+})^5 (\text{Mn}^{2+})}{(\text{Fe}^{2+})^5 (\text{MnO}_4^-) (\text{H}^+)^8}$$

and at the equivalence point,



$$K = \frac{(\text{Fe}^{3+})}{(\text{Fe}^{2+})} = \frac{(\text{Mn}^{2+})}{(\text{MnO}_4^-)} = K^{1/6} (\text{H}^+)^{8/5}$$


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One such example is, reduction of permanganate **reduction of permanganate** ion by ion. So, if you take ion ferric and add potassium permanganate, the ferrous will become ferric and permanganate ion will become monogamous ions.

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The reaction is as follows:

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e} \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
$$5\text{Fe}^{2+} \rightleftharpoons 5\text{Fe}^{3+} + 5\text{e}$$
$$E = E^0 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$
$$= 1.52 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$


So, we can write the equations like this that is MnO_4^- , plus 8 H plus, plus 5 e going to Mn^{2+} , plus 4 H_2O ; this is for the manganese. And 5 Fe^{2+} plus **plus** going to 5 Fe^{3+} plus 5 electron you add up both and this 5 electrons will get cancelled, you will

have a reaction of MnO_4^- plus 8 H^+ plus, 5 Fe^{2+} going to 5 Fe^{3+} , Mn^{2+} plus 4 H_2O these electrons will get cancelled.

Now, for this you can write an expression like this E is equal to E° plus 0.059 divided by 5, because 5 electron system, logarithms of the products divided by the reductants. So far, manganese I had to write like this and if I insert the value of E° I will end up with such an expression.

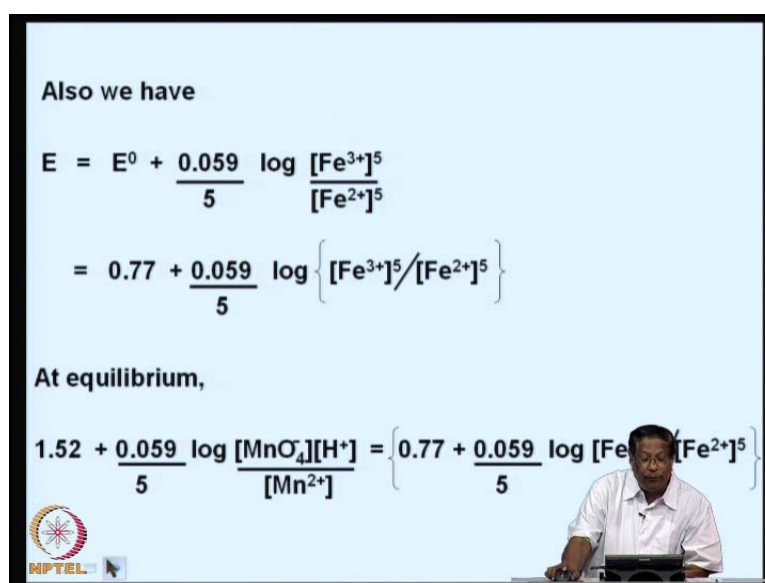
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Also we have

$$E = E^\circ + \frac{0.059}{5} \log \frac{[\text{Fe}^{3+}]^5}{[\text{Fe}^{2+}]^5}$$

$$= 0.77 + \frac{0.059}{5} \log \left\{ \frac{[\text{Fe}^{3+}]^5}{[\text{Fe}^{2+}]^5} \right\}$$

At equilibrium,

$$1.52 + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} = \left\{ 0.77 + \frac{0.059}{5} \log \frac{[\text{Fe}^{3+}]^5}{[\text{Fe}^{2+}]^5} \right\}$$


Now, we have a similar expression for ferric to ferrous. So, the reaction is 5 electron systems now. So, E is equal to E° of 0.059 divided by 5 logarithm of ferric to ferrous.


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or $\log \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8} = \frac{5(1.52-0.77)}{0.059} = 63.5$ or

$$K = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8} = 3 \times 10^{63}$$

The large value of K shows that the reaction is virtually complete. Suppose we titrate 10 ml of 0.1 KMnO_4 with 0.1 N FeSO_4 then $[\text{Fe}^{+++}] = 0.01$ N at equivalence point, [solution at eq pt is 100 ml].

$[\text{Mn}^{2+}] = 1/5 [\text{Fe}^{3+}] = 0.002$ N and $[\text{Fe}^{2+}] = x$.



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So, I can write like this and at the equilibrium both the manganous side, Mn side and ferric side, ion side should be can be equated and logarithm of by exchanging the terms on the left and right and rearranging. I get logarithm of manganese 2 plus, plus Fe 3 plus raise to 5 divided by MnO 4 minus multiplied by Fe 2 plus and H plus raise to 8 equal to 63.5 or K would be equal to 3 into 10 raise to 63.

The large value of K in this case, shows that the reaction is virtually complete; that means, you take ion ferric, you take ferric add permanganate, take ferrous add permanganate it will immediately go to ferric and manganese will get reduced; that means, very fast reaction because you can simply by knowing the value of K is equal to 3 into 10 raise to 63 you can simply predict that the whole reaction would be instantaneous.

So, suppose we take this further for titration, now if I do that, I can titrate 10 ml of 0.1 molar potassium permanganate with 0.1 normal ferrous sulphate and at the equivalence point ferric concentration I will know and manganese concentration I will know. So, at the equivalence point ferric would be 0.01 normal and manganese would be one fifth of this; that is 0.002 normal one fifth of this concentration and Fe 2 plus is unknown, because at that time most of the ferrous would have got converted to ferric and how much of ferric ferrous is there we do not know.

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Let excess of permanganate solution at the equivalence point be 1 drop or 0.05 ml which corresponds to:

$$\frac{0.05 \times 0.1}{100} = 5 \times 10^{-5} \text{ N} = [\text{MnO}_4^-]$$

Substituting these values in the equilibrium equation,

$$K = \frac{(2 \times 10^{-3})(1 \times 10^{-2})^5}{(5 \times 10^{-5})(x^5) \times 1^8} = 3 \times 10^{63}$$

or $x = 5 \times 10^{-15} \text{ N}$



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So, a little excess of permanganate solution at the equivalent point, if I add, how you will add? A little excess means one drop basically. So, if you add one drop that approximately corresponds to 0.05 milliliter. So, if I add one drop of the permanganate excess; that is 0.05 milliliter then I can write this expression 0.05 multiplied by 0.1 divided by 100 that is the volume I am taking. So, the concentration would be of the permanganate would be 5 into 10 raise to minus 5 you just solve this you will get this number.



So, substituting these values in the equilibrium equation, now let us substitute K is equal to if you go back Mn 2 plus, Fe 3 plus, MnO 4 all these things I am going to substitute now 2 into 10 raise to minus 3, 1 into 10 raise to minus 2 divided by these values and what I get, is x is equal to 5 into 10 raise to minus 15.

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Consider a redox reaction titration of 100 ml of 0.1 N ferrous ion with 0.1 N ceric ion in presence of sulphuric acid using ferric/ferrous electrode and ceric/cerous electrode.

$$\text{Ce}^{4+} + \text{Fe}^{2+} \rightleftharpoons \text{Ce}^{3+} + \text{Fe}^{3+}$$

Thus we have,

$$E_1 = E_1^0 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$
$$= +0.75 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$


So, the concentration of the ferrous at the equivalence point concentration of ferrous at the equivalence point without actually measuring, just by continuing the reaction I can calculate it to be 10^{-15} molar that is a beautiful thing a wonderful way of determining the concentration of a substance which you cannot see and potentiometric titration permits us to do this kind of tricks.

So, let us consider another redox reaction that is ceric to cerous corresponding reaction would be ferrous to ferric; that means, if I take ferrous add ceric ion, ferrous will get converted to ferric and ceric ion will get converted to cerous. This slide shows the actual reaction ceric 4 plus plus Fe 2 plus going to ceric 3 plus plus Fe 3 plus. So, we can write the expression Nernst equation E_1 is equal to E_1^0 and this I can replace with a known value that is 0.75 plus 0.0591, one electron system I do not bother log of Fe 3 plus by Fe 2 I had to write both these equations, because both the solutions are both the chemical species are in the form of solutions.

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$$E_2 = E_2^0 + \frac{0.0591}{1} \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$
$$= +1.45 + 0.0591 \log \text{Ce}^{4+}/\text{Ce}^{3+}$$

At equilibrium, the rate constant is given by,

$$\log K = \log \frac{[\text{Ce}^{3+}][\text{Fe}^{3+}]}{[\text{Ce}^{4+}][\text{Fe}^{2+}]} = \frac{1.45 - 0.75}{0.0591} = 11.84 \text{ or } K = 7 \times 10^{11}$$

Therefore the reaction is virtually complete.

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Now, similar reaction I can write 1.45 that is for ceric cerous, E naught value and ceric cerous I can write here, again you would remember that both the species are in solution. So, at the equilibrium the rate constant is given by I can put it, you know this value and this value **this value** this expression and the next expression I can equate.

And I can calculate the value of K is equal to log of ceric cerous, the ferric divided by ceric and ferrous products divided by reactants is given by 1.45 minus 0.75 that is the E naught differences divided by 0.591 volts that corresponds to 11.84 or K should be 7 into 10 raise to eleven negative log of this would be 7 into 10 raise to 11.



Again the value of the electrode potential shows us that the reaction is very complete otherwise you will not end up with values like 7 into 10 raise to 11, you would always it is a fantastic feeling, because if it is 10 raise to 1, 10 raise to 2, 10 raise to 2.5 like that.

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Upto the equivalence point all the ceric ions will be utilized to oxidise ferrous to ferric ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$).

When

10 ml $\text{Ce}(\text{SO}_4)_2$ is added,	$E_1 = 0.75 + 0.0591 \log 10/90 = 0.69 \text{ V}$
50 ml $\text{Ce}(\text{SO}_4)_2$ is added,	$E_1 = 0.75 + 0.0591 \log 50/50 = 0.75 \text{ V}$
90 ml $\text{Ce}(\text{SO}_4)_2$ is added,	$E_1 = 0.75 + 0.0591 \log 90/10 = 0.81 \text{ V}$
99 ml $\text{Ce}(\text{SO}_4)_2$ is added,	$E_1 = 0.75 + 0.0591 \log 99/1 = 0.87 \text{ V}$
99.9 ml $\text{Ce}(\text{SO}_4)_2$ is added,	$E_1 = 0.75 + 0.0591 \log 99.9/0.1 = 0.96 \text{ V}$



Then it may not be a virtually complete reaction, but 10 raised to the power of 11; it means, it is a virtually complete reaction. Now, up to the equivalence point all the ceric ions will be utilized to oxidize ferrous to ferric. So, we can write the ceric ferrous to ferric equations like this when 10 ml of ceric sulphate is added, 10 percent is oxidized, 90 percent is still in the reduced phase.

So, oxidized species divided by reduced species, if I put the value of 0.75 I will get 0.69 volts. Now, 50 ml when I add 50 percent will get oxidized and 50 percent remains unoxidized and this is 0.75. So, 90 ml if I add, 90 by 10, 99 by 10 similarly and then 99.9 divided by 0.01 volts; that is 0.69 volts.

If you had to remember, here that the values are changing almost in an arithmetic fashion that is 0.69, 0.75 that is 0.06 difference and then 0.75 to 0.81 is again 0.06 and 0.81 to 0.87 is 0.06 and 0.87 to near the end point is a big jump here, and you have to also remember that we are neglecting the dilution effects.

Otherwise it should be 10 by 100 then, but we are neglecting the dilution effects because that is why we are taking the concentrations concentration of one to other is at least 10 to 100 times.

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At 100 ml, $E = \frac{E_1 + E_2}{2} = \frac{0.75 + 1.45}{2} = 1.10 \text{ V}$

100.1 ml $\text{Ce}(\text{SO}_4)_2$ is added, $E_1 = 1.45 + 0.0591 \log 0.1/100 = 1.27 \text{ V}$
101 ml $\text{Ce}(\text{SO}_4)_2$ is added, $E_1 = 1.45 + 0.0591 \log 1/100 = 1.33 \text{ V}$
110 ml $\text{Ce}(\text{SO}_4)_2$ is added, $E_1 = 1.45 + 0.0591 \log 10/100 = 1.39 \text{ V}$
190 ml $\text{Ce}(\text{SO}_4)_2$ is added, $E_1 = 1.45 + (\log 90/100) 0.0591 = 1.45 \text{ V}$

The slide also features the NPTEL logo in the bottom left corner and a small inset image of a man sitting at a desk with a laptop in the bottom right corner.

So, that we do not have we can neglect the dilution effect. So, when I have 100 ml added to that the EMF would be average of the 2 that is E_1 plus E_2 by 2, because the concentration terms are going to cancel out, because all the reactants have reacted with all the and all the reactants have reacted and the products are formed.

So, the EMF would be corresponding to the only the E naught values that is E_1 by E_2 by 2 that corresponds to 1.10 volts. Now, when I add ceric extra 0.1 ml, I will have 1.27 volts and 1.0 then 101 ml, I will have 1.33 again 0.6 volts difference and 1.39 again 0.6 again 0.6 volt.

Now, we on the right side again it is assuming a very standard format except at the equivalence point from 1.27 to 1.10 this is an error where it should be 1.10, 1.1 and previous one would be 0.69, from 0.69 it jumps to 1.1 and then it jumps to 1.27 a big jump.

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At 99.9 ml, $\text{Fe}^{2+} = 0.1 \times 0.1/199.9 = 5 \times 10^{-5}$ or $\text{pFe} = 4.3$

At 100 ml, $[\text{Fe}^{2+}] = 0.05 \text{ N}$, $[\text{Fe}^{2+}] = 5 \times 10^{-2}/8.5 \times 10^5$
 $= 6 \times 10^{-8} \text{ N}$ or $\text{pFe} = 7.2$

At 100.1 ml $[\text{Fe}^{3+}]$ is practically unchanged at $5 \times 10^{-2} \text{ N}$ and

$$E = E_1 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.75 + 0.0591 \log \frac{5 \times 10^{-2}}{[\text{Fe}^{2+}]}$$

or $[\text{Fe}^{2+}] = 1 \times 10^{-10}$ or $\text{pFe} = 10$

Thus pFe changes from 4.3 \rightarrow 7.2 \rightarrow 10 within a volume change of 99.9 \rightarrow 100 \rightarrow 100.1. These values are important for the choice of indicators for the titration.

So, at 99.9 ml, I can calculate the pFe that is just like pH. I can calculate the pFe ferrous concentration would be 0.1 into multiplied by 0.1 divided by the total volume of the solution that is 199.9, that will be 4.3. At 100 ml, it will be 5 into 10 raise to minus 2 divided by 8.5 into 10 raise to 5 that would be 6 into 10 raise to minus 8 or pFe would be 7.2.

At 100.1 Fe 3 plus remains practically unchanged at 5 into 10 raise to minus 2 normal and if, I put this value Fe 2 plus can be calculated to be 10. Now, pFe look at the change of the pFe values 0.1 ml difference before the equivalence point it is 4.3, at exactly 100 it is 7.2, at 100.1 it is 10. So, 4.3 to 7.2 to 10 within a volume change of 0.00 then 99.9 to 100.1 that is 0.2 ml, 90 from 1 and 2 between 0.2 ml, the pFe changes from 0.43 to 10.

So, these values are important for the choice of indicators, these values also indicate like the reaction can be very easily followed. So, how we follow the reactions? Such reactions all redox reactions, complexation reactions, etcetera we will discuss in the next class; that is with the potentiometer.