Lecture – 13
Potentiometry

So, greetings to you. We will continue our discussion on Potentiometry. In the last class, I had taught you about electrodes of the first kind, second kind, third kind and hydrogen electrode.

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How we can use different kinds of electrode for different applications and because the standard hydrogen electrode is difficult to set up and handle every time, we go for reference electrodes and whose values have been determined very accurately which can be used for day to day purposes.

So, according to the Nernst equation, potential of a reversible electrode permits calculation of the activity or concentration of the component of a solution. So, using a Nernst equation if I have an electrode dipped in a solution, I can find out its concentration that is the analytical technique. So, I write Nernst equation something like this E Ag is equal to E naught Ag plus RT by nF l n Ag plus divided by Ag that is log of oxidant divided by reductant. And then it is connected to another electrode that is not hydrogen electrode, but a calomel electrode E SCE is calomel electrode that is standard calomel electrode.

So, standard calomel electrode that is electrode of mercury with in equilibrium with its sparingly soluble salt ok. So, here I have two beakers and one contains silver nitrate solution with a silver electrode and then I have a salt bridge here, the salt bridge will contain nitrate solution; potassium nitrate or something. That will permit the passage of NO nitrate ions and through this and silver ions will be transfer will be moving towards cathode here and nitrate ions will be moving towards anode here.

So, though what is the other electrode anode, that is calomel electrode. So a calomel electrode is constructed using a very simple system that is I have a tube here and do you see this small small area in this area here, it is the mercury here at the bottom and above mercury I have a small quantity of mercurous chloride that is Ag 2 Cl 2 and above that I have a saturated potassium chloride solution ok. This is saturated filled with saturated chloride solution and that is dipped here. So, the electrons can be in contact here I have an external connection. So this is plus, this is minus. So, if I have a system something like this and this is agar is nothing but a something like gelatin and that is the how the salt bridges are made.

So, I can write half cell equation reaction for E Ag is equal to E naught Ag plus RT by nF ln Ag plus by Ag and E SCE. I do not have to write the equation, but I know the value from the books.

$$E_{cell} = E_{Ag} - E_{SCE}$$

$$= E^0_{Ag} - E_{SCE} + \frac{RT}{nF} \ln (Ag^+)$$

$$\log (Ag^+) = \frac{E_{cell} - E^0_{Ag} + E_{SCE}}{2.303 (RT/nF)}$$

$$= \frac{+0.400 - 0.799 + 0.246}{0.0591}$$

$$= 2.59 \text{ or } [Ag^+] = 2.57 \times 10^{-3} M$$

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So, I can write E cell is given by E Ag minus E SCE, what is E Ag E Ag is E naught plus RT by nF l n Ag plus and minus E SCE this I am writing here. So, E naught Ag log of Ag l n log of Ag I can transfer it on the left side is nothing but that is equal to E cell minus E naught Ag. I am transferring retaining this side transferring everything on the left hand side.

So, E cell minus E naught Ag this comes here plus E SCE this minus sign becomes plus E SCE goes there and then divided by 2.303 RT by nF this 2.303 appears because I am converting that into log scale not natural logs. So, this value you should remember for all the time to come if you want to be an electrochemist 2.303 RT by nF is 0.0591 ok. So, if it is the n is equal to 2, then it will be different put n is equal to 2 and find out whatever comes out like that. And so I put the value E cell is measured on the potentiometer that is plus 400 and E naught Ag is minus 0.799 that I get it from the table standard table and E SCE is 0.246 volts

that I get it from the table from the textbooks. Available E is 0.0591 is the value of 2.303 RT by nF and so I what I get is 2.59.

So, if I know log Ag plus is equal to 2.59 I can find out what is Ag plus anti log of this, would be nothing but Ag plus would be 2.57 into 10 raised to minus 3 molar. So, what does it mean? If I have a solution of silver nitrate ok, I just connect it like this; connect it like this with ammonium nitrate as another solution, I do not have to do any experiment just connect it. Put a calomel electrode connect wires to plus and minus calomel is to negative silver to positive and note down the potential voltage. How much I am getting? ,2.59 take the antilog of this. So, that tells me the concentration of silver plus is 2.57 into 10 raise to minus 3. I do not have to do any experiment at all just by noting down the potential I can find out what is the concentration, that is the beauty of potentiometry ok.

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So, here you have to note down a few points for example, we always subtract more negative from the more positive. So, which is more negative more negative is 0.799 is not it 0.4 is positive 0.246 is positive more negative is 0.799. So, that we are subtracting from the more positive and 2.303 RT by nF, this I have already told you that it is a 0.591 at 25 degrees.

If you want very accurate values use the T value temperature of the solution as Kelvin ok. Then pAg; pAg is nothing but minus log of Ag plus that is just like pH negative log of hydrogen ion. Here it is negative log of Ag plus ions ok.

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As another example consider a cell of platinum electrode dipping in 0.1N $FeSO_4$ with SCE as a counter electrode. A potential differences is 0.395 volt is obtained. It is desired to obtain the percentage of Fe(II) which has been converted to Fe(III) by oxidation.

So, consider one more example now. I am taking a platinum electrode dipping in 0.1 normal for a sulfate with standard calomel electrode as a counter electrode ok. A potential difference I

just connect with a saturated calomel electrode or whatever it is, a potential difference is 0.395 is what I note down on my voltmeter.

So, I should know what is the concentration of ferrous and ferric and how much ferric ferrous has been converted into ferric by oxidation. I think you are all very familiar with ferrous ferric oxidation systems. Whenever you cut an apple within no time, you see a brown color on the cut side of the apple that is oxidation of ferrous to ferric. Anywhere in the world wherever there is ferrous solution where there is always a it always reacts with air to get oxidized to ferric. So, if even if you take ferrous sulfate as the as a medicine, you know ferrous fumarate is a B12 medicine tablet and you want to know how much of ferrous is there after some time, you want to know how good is the medicine; you have to find out how much of the ferrous is there.

So, if you want to find out what is ferrous ferric concentration in a given solution, what I am going to do is I will say do not do any experiment connected the solution to a platinum electrode. Put another calomel electrode measure the voltage, I will tell you how what is the concentration of the ferrous and ferric.

We write, $E_{Fe^{3+}/Fe^{2+}} = E^0_{Fe^{3+}/Fe^{2+}} + \dfrac{RT}{nF} \ln \dfrac{(Fe^{3+})}{(Fe^{2+})}$

$E_{cell} = E_{Fe^{3+}/Fe^{2+}} + \dfrac{RT}{nF} \ln \dfrac{(Fe^{3+})}{(Fe^{2+})}$

$\log \dfrac{(Fe^{3+})}{(Fe^{2+})} = \dfrac{E_{cell} - E^0_{Fe^{3+}/Fe^{2+}} + E_{SCE}}{0.0591}$

$= -2.20\ V$

$Fe^{3+}/Fe^{2+} = 6.3 \times 10^{-3}$ or 0.63 percent.

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How I am going to do that is very simple. I simply write E ferrous ferric to ferrous this is the redox system. The EMF of the ferric to ferrous solution is dependent upon the is the sum of E naught Fe 3 plus by Fe 2 plus this is the standard reduction potential of ferric ferrous plus RT by nF ln ferric to ferrous ok. This is oxidized state and reduced state and whenever oxidized state reduced state both are in solution the higher valancy would be in the oxidized state.

So it is very simple to write, you do not have to know a lot of chemistry to write it ok. So, the then measure the EMF. What is the E cell? EMF nothing is nothing but E cell potential of the cell, when you set up ferric ferrous solution with platinum electrode and calomel electrode. So, I write ferric ferrous EMF plus RT by here it should be E naught ok. I have forgotten there to right there plus RT by nF n l Fe 3 plus by Fe 2 plus. So, now I want to know what is

log of Fe 3 plus by Fe 2 plus and I keep this on the left hand side and transfer all other information this information on the right hand side.

So, RT by nF is nothing but the difference. So, is log of Fe 3 prior Fe in this E cell minus E naught Fe 3 by Fe 2 Fe 2 plus E SCE, because I am connecting the E cell. Remember here also we had done a similar exercise E SCE when I transfer it becomes plus ok.

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$$E_{cell} = E_{Ag} - E_{SCE}$$

$$= E^0_{Ag} - E_{SCE} + \frac{RT \ln (Ag^+)}{nF}$$

$$\log (Ag^+) = \frac{E_{cell} - E^0_{Ag} + E_{SCE}}{2.303 \, (RT/nF)}$$

$$= \frac{+0.400 - 0.799 + 0.246}{0.0591}$$

$$= 2.59 \quad or \quad [Ag^+] = 2.57 \times 10^{-3} \, M$$

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So, same thing happens here, so E cell is equal to a log of Fe 3 by Fe 2 is equal E cell minus this thing put the values and what I got is 2.20 volts ok, 2.20 volts when I get I can simply take the antilog of this value 2.20 and tell you that 6.3 into 10 raise to minus 3 is the value or what I get. That is approximately point six three into 10 raised to minus 2 that is 0.63 percent. So, without determining any doing any chemical analysis, I am going to find out what is the

concentration of ferric and ferrous. If you just give me a solution of ferric and ferrous in which you want to determine your ferric ferrous solution.

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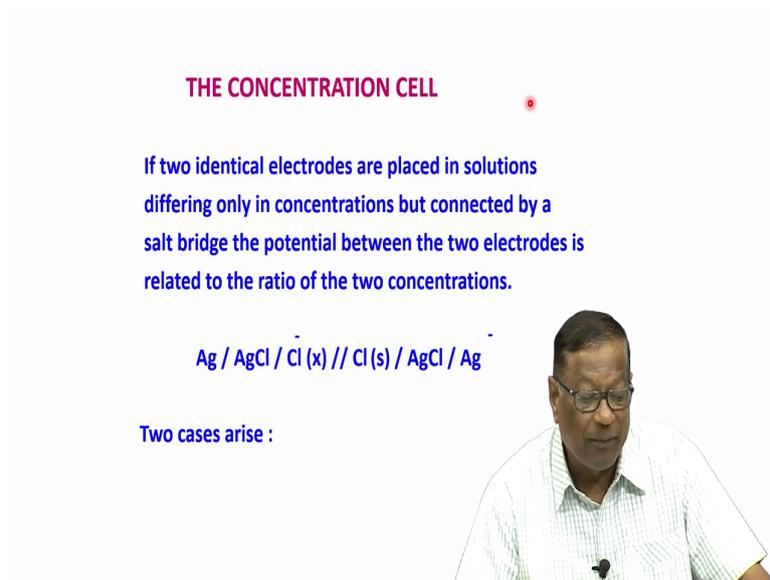
So, that is the beauty of potentiometry, you appreciate that good. So, now we will talk about concentration cell. What is a concentration cell? Very important concept, imagine I have two electrodes placed in solutions in the same kind of solution, but differing in concentration. I take two beakers; there are two solutions of different concentration, but same material ok. So, but they are connected with the salt bridge also. So, the potential between the two electrodes must be related to the concentrations, because it is the same electrolyte in the in both the beakers.

So, I can write something like this silver chloride electrode ok, silver electrode in contact this line represents a this line represents a contact single contact. Silver is in contact direct contact

with silver chloride solution a silver chloride precipitate here it is and no here it is liquid a solution and that is in contact with silver chloride ions in the solution of concentration x. And then I have a salt bridge in another and dipping in the other beaker in which the other part of the salt bridge is there, I have a chloride solution in contact with silver chloride and Ag plus. This concentration I know yes.

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Case 1

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

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

If the unknown is more concentrated say 0.1500 M then

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

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

So two cases arise, what are the two cases? Case 1 suppose the standard is 0.1 molar. It is a single electrode potential is given by E s is equal to 0.222 that is silver silver chloride as measured E naught, as measured against standard hydrogen electrode that is standard reduction potential minus 0.0591 log of oxidant divided by a reductant ok.

So, 0.0591 log of 1, log of 0.1 so this gives me 0.281 volts. You can calculate this and find out for yourself what is the voltage. So, if this concentration I already know, so I know how

much is the voltage I am going to get. Then I take the unknown concentration which you want to find out how much of silver is there. We need to find out lot of lot of silver analysis we need to analyze especially photographers and other people who have developed the photographs in actual print, they dip it in silver bromide solution and per sodium sulfite etcetera and silver gets consumed while printing. So, the concentration of silver goes down and they keep on changing and they want to know how much of silver is there in the solution.

So, I have a solution which I do not know, I want to find out how much of silver is there. So, if the unknown is more concentrated say 0.1500, then I can write E x is equal to 0.222 this is common because its E naught of silver silvers Ag Ag plus Ag plus by Ag minus 0.0591 log of 0.1500. Now I am assuming that it is 0.1500 concentration, then what I should get? This value is 0.271.

So, E cell is I have same electrode both of them cancel out. So, the only difference of potential should come from the solution. So, E cell is nothing but the difference of their two half cells. So, what is the first half cell 0.281, second half cell is giving me 0.271 because the concentrations are different. So, E cell is E s minus E x that is 0.010 volt ok so far so good no problem.

Now, consider another situation ok. So, look at the slide now suppose an unknown is having 0.680 moles molar silver solution unknown x, the other one is 0.1 volts ok. So, I write an expression 0.222 minus 0.0591 log of 0.0680 that gives me 0.291 volt and E cell is nothing but the difference between the two just like in the last slide and I am getting 0.010 volts and how much I am getting in the previous slide it is 0.010 volt. So, when the concentration is point 0.15, I get 0.01 volt and when the concentration is 0.680 also, I get 0.1 volt 0.01 volt. So, any measured potential is open to ambiguous interpretations that may we can avoid this by noting that the interpretation corresponds to the more positive of the two.

So, the concentration cell I can I should note down which is the polarity. So, if the polarity is positive I say yes this solution is 0.680; the other one is if the it is negative then the concentration could be 0.1500. So, any measured concentration, the same voltage if you get there could be two alternatives of the unknown composition one of that two. So, if you switch

you should get the character one ok. So, the concentration cell I have given you an example of silver silver chloride know.

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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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Now, I can give you concentration cell of hydrogen ion itself. Just look at it I have an inner calomel electrode I have a hydrogen ion solution of pH 7 as buffer. I have a glass membrane that is like a salt bridge and then I do not I have a solution whose pH I want to know and then I am connecting to external SCE. So, this is essentially like what we had talked about concentration cell now yes.

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.

$$Ag / AgCl / Cl^- (x) // Cl^- (s) / AgCl / Ag$$

Two cases arise :

This is Ag Ag Cl Cl minus in contact with Cl Ag Cl Ag. So, same thing I am writing here inner electrode saturated calomel electrode pH 7 buffer one membrane and one test solution and this concentration I know pH 7 buffer another is external. So, I can define a pH system like this, so by similar analogy I should be able to find out what is the concentration of hydrogen ions in the test solution, that is how we make our pH meters ok.

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

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

For a solution of 2.0×10^{-4} M HCl,

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

So, we go back how do we define a pH? So, pH is nothing but negative logarithm of the activity of the hydrogen ion concentration expressed in molarity. This definition you must by heart, but this is not correct because we should say it is yeah this is the correct definition thermodynamically correct definition of hydro pH. But in practical terms we say pH is the negative logarithm of the concentration of hydrogen ions expressed in molarity. Replace that term this activity with concentration that is practical ok. So, pH is we write like this pH is negative log of aH plus a is activity that is also equal to negative log of H plus ion logged to the base 10 and for a solution of 2.0 into 10 raise to minus 4 molar HCl.

If I have a solution of 2.0 into 10 raised to minus 4 molar hydrochloric acid solution, what would be the pH? Very simple apply this equation right pH is equal to negative log of instead of a H plus write 2 into 10 to the power of minus 4 like this and then solve this equation. This is a minus 4 will become 4 minus log 2 negative is there. So, log 2, so that will give me 3.699

and that is pH is 3.70. So, if I know the concentration of any acid strong acid it won't work for a dilute a weak acids. So, pH is nothing but negative log of hydrogen ion concentration that is available, a strong acid we know the concentration and if I prepare well and good. So, I can find out what is the pH of the solution if I know the concentrations ok.

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

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

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

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

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

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Now, the measurement of pH is accomplished with hydrogen electrode in a cell concentration cell. I have already explained to you calomel electrode, then H plus buffer versus in contact with glass membrane, in contact with a unknown solution in contact with calomel electrode. So, such a concentration cell the potential is given by this expression 0.0591 log of H plus standard divided by H plus unknown standard solution we know concentration. So, for a saturated calomel electrode its potential E 0 log 0 is 1.

So, E cell is nothing but point 0.0591 log of H plus that is point zero five nine one pH I am replacing minus log of H plus by pH ok. So, pH is nothing but E cell divided by 0.0591. So, for calomel electrode it is minus 0.246 if I use a calomel electrode instead of a standard electrode. So, calomel electrode shows minus 0.246 volts with respect to standard hydrogen electrode. So, if I have a cell of unknown solution of hydro unknown hydrogen ion concentration connected to a calomel, then my pH I should be able to define E cell would be actual E cell would be E cell minus 0.246 divided by 0.0591 I have to subtract, so that will give me the pH.

Commercial electrode pH meter can be conveniently made by using a calomel electrode ok. So, all the pH electrodes pH meter what you see around you are built on this principle, you take a solution of hydrogen chloride or any acid connected to a saturated calomel electrode measure the E cell, subtract calomel contribution divided by 0.0591 and the range is 1 to 14 they put a dial. So, the dial current generated would be used to move the needle across the dial from 0 to 14.

So, all these things were there until 1950's and 60's most of the pH meters that were available in the market were based on this principle the analog. Nowadays, we have digital pH meters as well as the more sophisticated ones and there are improvements in the electrodes also and that is known as glass electrode. So, what is a glass electrode? So, the glass electrode is a new invention of course, it is there since last since 1960's or 70 say yeah 60's approximately.

And now a days there are hundreds and thousands of beautiful glass electrodes in the market and the same version, but the same principle. So, thin membranes of certain varieties of glasses are permeable to hydrogen ions across the glass membrane. That means, if you take a solution an acid solution put it in a special glass membrane it will allow the passage of hydrogen ions on both sides.

So, essentially what I am doing is I am creating a concentration cell with one solution in inside the glass membrane, another solution outside the glass membrane which will permit a movement of hydrogen ions and across. So, a thin membrane of certain varieties of glasses are

permeable to hydrogen ions and a glass electrode is reversible. It contains a solution of known and unchanging pH that is a chloride containing buffer it should be known pH and it should have it should not change over a period of time. So, that is how a glass electrode is made and a reference electrode. Again reference electrode I can make calomel electrode or a silver chloride electrode.

So, the tube is permanently sealed at the top, because I do not want a known concentration buffer to spill out and loose its concentration or evaporate. So, a glass electrode, what I am going to do silver-silver chloride electrode and glass membrane and a platinum solution external mercury solution. So, the tube is permanently sealed at the top and this is dipped into an unknown a concentration cell results like this. This I already shown you and inner calomel pH 7 glass membrane test solution external SCE I can put silver-silver chloride electrode here and silver-silver chloride electrode here and measure their pH.

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

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.

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So, for such a cell the pH is given by E cell. What is E cell? Now it is glass and the so I write E g minus E cell divided by 0.0591. So, E g is a constant that includes the potential of reference electrodes and additional small spurious potentials called as asymmetry potential. That arises out of unequal strains in the glass and the glass electrode is special for each manufacturer. So, the glass electrode you have to standardize every time and whenever you buy a glass electrode that needs to be standardized with respect to standard solutions of pH 7, pH 4, pH 9 like that buffers and then you should use it because this E g water what you had. So, you referred earlier the asymmetry potential will not be the same for all types of glass membranes ok.

So, the glass electrode is a routine analytical tool in any laboratory in highly alkaline solutions. It gives certain error because sodium ions alkaline solutions sodium ions will also move a little bit this side that side and there will be an error of plus or minus 1 pH in it. But it can also absorb some specific ions some erroneous results. But in general from 1 to 9 1 to 12 pH you would not have any problem. Nowadays glass electrodes are pH meters with glass electrodes are available. They are known as combined electrode, combined glass electrode a single cell containing both the electrodes one reference. And one standard and they are available in the market with digital output and storage and nowadays you know with microprocessor you can do a lot of things.

So therefore, it is essential to use buffers for standardization and every time when you use a buffer you have to wash it number of times to make it memory independent, it should not remember the previous measurement ok.

QUINHYDRONE ELECTRODE

A platinum electrode in equilibrium with an equimolar mixture of quinine and hydroquinone.
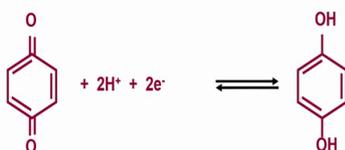
$$E = E^0 + 0.0591 \log [H^+] = \frac{(0.699 - E_{cell})^2}{(0.0591)}$$

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

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So, that is about the glass electrode. What we will do is we will continue our discussion about other types of electrodes for some time and then we will look up some of the potentiometric titrations etcetera in our next class.

So thank you very much. Have a nice day.