Electrochemical Technology in Pollution Control

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Lecture – 12
Potentiometry 3

Greetings to you; welcome to the next class. We are having different types of electrodes for comparison and there are different types of electrodes; one is a metal in equilibrium with it is ions ok.

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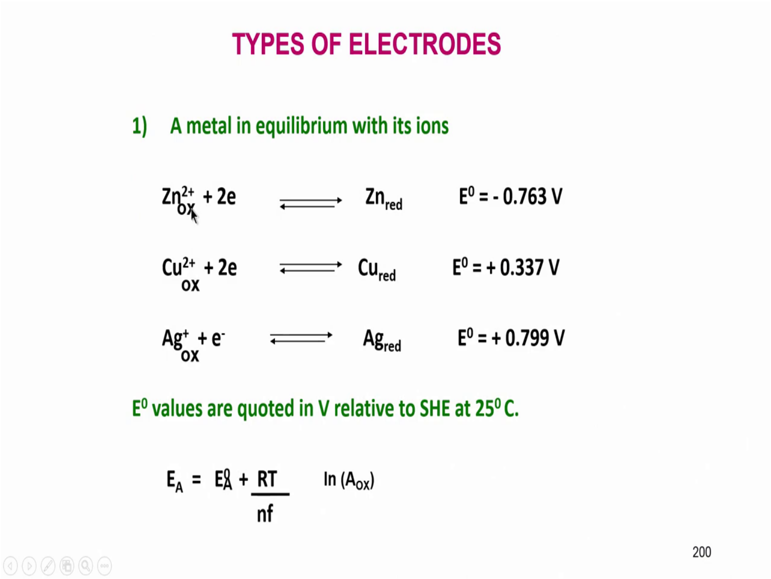

TYPES OF ELECTRODES

1) A metal in equilibrium with its ions

$Zn^{2+}_{ox} + 2e \rightleftharpoons Zn_{red}$ $E^0 = -0.763$ V

$Cu^{2+}_{ox} + 2e \rightleftharpoons Cu_{red}$ $E^0 = +0.337$ V

$Ag^{+}_{ox} + e^{-} \rightleftharpoons Ag_{red}$ $E^0 = +0.799$ V

E^0 values are quoted in V relative to SHE at 25^0 C.

$$E_A = E^0_A + \frac{RT}{nf} \ln(A_{ox})$$

So, here I have a zinc metal, I have a zinc metal in the oxidized state ok, that is carrying plus 2 charge that can react with 2 electrons, it can pick up 2 electrons and become zinc metal that is reductant.

So, oxidant plus electrons gives you reductant, I should write 2 e minus here ok. But it is not there. Please make a note; Z n 2 plus plus 2 e minus should give you 2 plus and 2 e minus should give you 0. So, we do not write 0 here, but it is zinc reductant. So, E naught is equal to the when I compare with hydrogen as a inert electrolyte, I get a voltage of minus 0.763. So, hydrogen is a reductant ok, so zinc is also a reductant because it is minus ok. So, zinc metal is a reductant, zinc 2 ions are oxidized species.

Similarly, I can take copper ion copper solution and then radius copper using an inert electrolyte ok that is standard hydrogen electrode. and what reaction takes place in that case? Cu 2 plus in the oxidized state that is ions cupric ions will react with 2 electrons and that goes to cupric metal copper metal and the potential what I get is 0.337 volts when I compare it with hydrogen. So, we by convention we get assign hydrogen as 0, so I measure 0.337 volts.

Similarly, I can take silver ions silver nitrate in solution react it with an electron. So, it gives me silver reductant and E naught is equal to 0.799 volts. So, E naught values are quoted in voltage relative to SHE; Standard Hydrogen Electrode at 25 degrees. The expression what I write is EA is equal to E naught A plus RT by nf ln A oxidant, here you should see that I am not writing reductant here at the bottom correct. So, but I theoretically I should write, but the convention is whenever an ion is reduced to it is material, it is activity is 0 ok, so log 0 is 1.

So, instead of writing log activity of the reductant, as 1 I simply write ln A ox that is the ion in solution. So, what does it mean? The actual potential what you get when compared with the SHE is nothing but the standard reduction potential plus RT by nf ln of log of concentration, I am not writing activity also now, actually I should write activity But activity and concentration if they are almost same if the solutions are dilute, so, I am writing a concentration term of the concentration of the solution; A oxidant is the concentration of the solution, when it is getting reduced I do not write the denominator.

So, this is a very standard practice you should all remember this. I am many quite often in the in my future this thing I will not be writing this.

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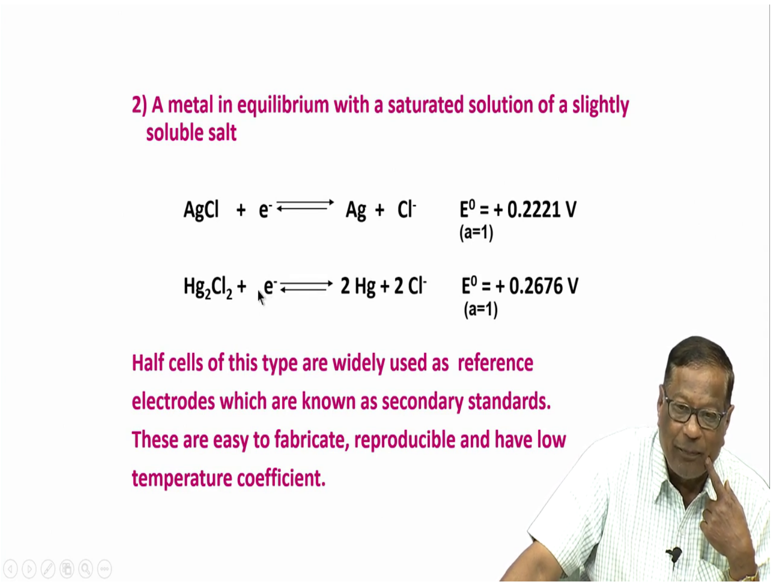

2) A metal in equilibrium with a saturated solution of a slightly soluble salt

$AgCl + e^- \rightleftharpoons Ag + Cl^-$ $E^0 = +0.2221\ V$ (a=1)

$Hg_2Cl_2 + e^- \rightleftharpoons 2\,Hg + 2\,Cl^-$ $E^0 = +0.2676\ V$ (a=1)

Half cells of this type are widely used as reference electrodes which are known as secondary standards. These are easy to fabricate, reproducible and have low temperature coefficient.

So a metal has ion, that is one kind that is a metal in equilibrium with it is own solution ok, in equilibrium with it is own solution a metal to wire rod electrode in equilibrium with it is own solution couple to standard hydrogen electrode.

So, whatever EMF value potential value I get, I list. So, that is how I got for zinc it is 0.763, for copper it is 0.337 and for silver it is 0.799, for zinc it is negative that means, with the hydrogen electrode becomes positive in this case here it is negative ok. Then I have another type of electrode that electrode we define like this, a metal in equilibrium with a saturated solution of a slightly soluble salt. That means, I have a metal wire as an electrode that is dipped in a solution and that substance a solution contains a sparingly soluble salt solution.

The best example I can give you is silver chloride. You take silver chloride put it in water. So, silver a little bit of silver chloride will dissolve, remaining will be settling at the bottom and I dip a silver electrode in that solution. So, a silver electrode dipped in a solution of silver chloride is an electrode of the second type ok, because it is a sparingly soluble salt, it is a saturated solution ok. So, in this case again, it is connected to standard hydrogen electrode that I am not writing here ok.

So, the what is the reaction now? I have a silver chloride salt, that can pick up an electron that is Ag plus plus electron; this AgCl will give you Ag plus and Cl minus ok. So, this silver will react with one electron to give you silver metal and chloride ion. So, the potential for this at activity is equal to 1 that means very dilute concentrations. E naught is equal to 0.2221 volts. So, similarly I can pick up other sparingly soluble salts, for example Hg 2 Cl 2; mercuric mercurous chloride this is known as mercurous chloride that is also sparingly soluble salt.

If I take mercurous chloride in water and put a mercury electrode, I have a electrode of the second kind, that is metal in equilibrium with a saturated solution of slightly soluble salt and Hg 2 Cl 2 plus e minus I can write an equation 2 Hg plus 2 Cl minus. So, I should have 2 here, we are not writing stoichiometric equation. So, but I can you can write 2 here; Hg 2 Cl 2 plus 2 e minus will be will give you 2 Hg plus 2 Cl minus, but it does not alter the voltage ok.

So, E naught remains the same whether it you write 2 or 1, because we are writing only an equation. So, E naught is equal to 0.2676 volts at activity of 1, that is very dilute solutions. So, half cells of this type are used as reference electrodes and known as secondary electrode standards.

I will explain to you a later just give me a few minutes I will explain. These are easy to fabricate and reproducible and have low temperature coefficient. Now imagine how do I prepare the secondary electrode of this type? Take a solution; put a little bit of silver chloride and put one silver electrode that is it. But it gives me an exact voltage with respect to hydrogen that is 0.2221. But standard hydrogen electrode we make by first taking a solution and then putting a platinum electrode passing the hydrogen gas that should be at 1 atmosphere and then it should have certain amount of acid etcetera to keep the reaction going.

So, instead of that this I can use it as a reference electrode instead of hydrogen electrode, very easy to make with respect to hydrogen; you need a gas cylinder open it operate it and all those things. And people are not comfortable, writing preparing a having a standard gas electrode in the laboratory, because you need hydrogen cylinder any time it may explode if people are not careful. So, it is a little tricky to have standard hydrogen electrode only for very accurate work

R and D labs research labs, yes, it can be done. But if I know that this silver silver chloride electrode is having a potential of 0.2221, I can connected to any other system instead of standard hydrogen electrode and subtract 0.2221. Then that gives me the standard electrode potential, not standard electrode, but actual electrode potential.

So, this is used to replace standard hydrogen electrode that is the electrodes of the second kind. First kind is a electrode with it is own solution, but that salt is soluble in large quantities that is number 1. Number 2 a metal ion with a sparingly soluble salt with precipitate below and the electrode metal electrode.

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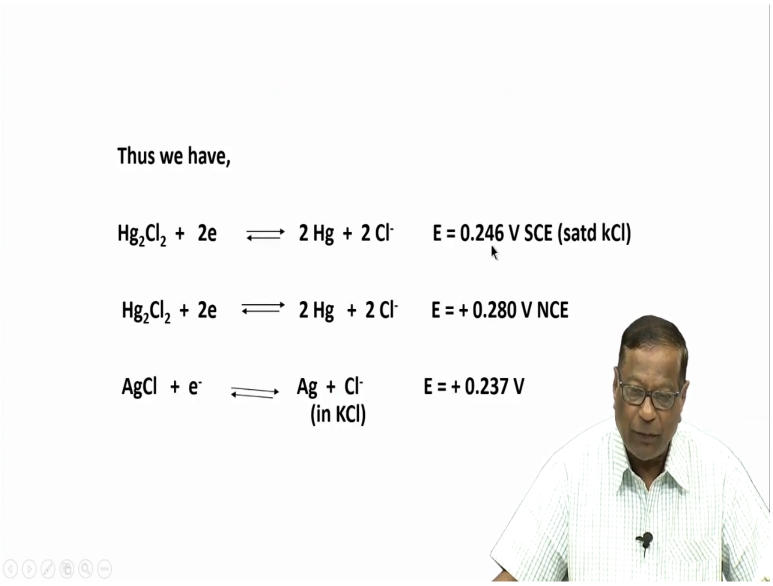

Thus we have,

$Hg_2Cl_2 + 2e \rightleftharpoons 2\,Hg + 2\,Cl^-$ E = 0.246 V SCE (satd kCl)

$Hg_2Cl_2 + 2e \rightleftharpoons 2\,Hg + 2\,Cl^-$ E = + 0.280 V NCE

$AgCl + e^- \rightleftharpoons Ag + Cl^-$ (in KCl) E = + 0.237 V

Third one is we can prepare this half cell you know before I go to the third one, we can have 2 types of reactions with respect to Hg 2 Cl 2, that is I can write something like this; Hg 2 Cl 2 plus 2 electrons goes to 2 Hg plus 2 Cl minus that goes to 0.246 versus saturated kCl electrode. This is a reference electrode now. This saturated kCl saturated calomel electrode it is called as Hg 2 Cl 2 plus 2 e and if it is saturated it will give me voltage of 0.2446, but if it is not saturated then it gives me 0.222, saturated will give me 0.246 ok.

So, Hg 2 Cl 2 plus 2 e is also give me 0.280 versus NCE national standard, AgCl also will give me 0.237 in KCl solution; 1 molar KCl solution. It gives me 0.237, again it is a sparingly soluble salt of the second type and it gives me reproducible value every time I put silver chloride in a solution and put a silver (Refer Time: 13:13). So, the first 2 type this type is known as standard calomel electrode and this is silver silver chloride electrode ok.

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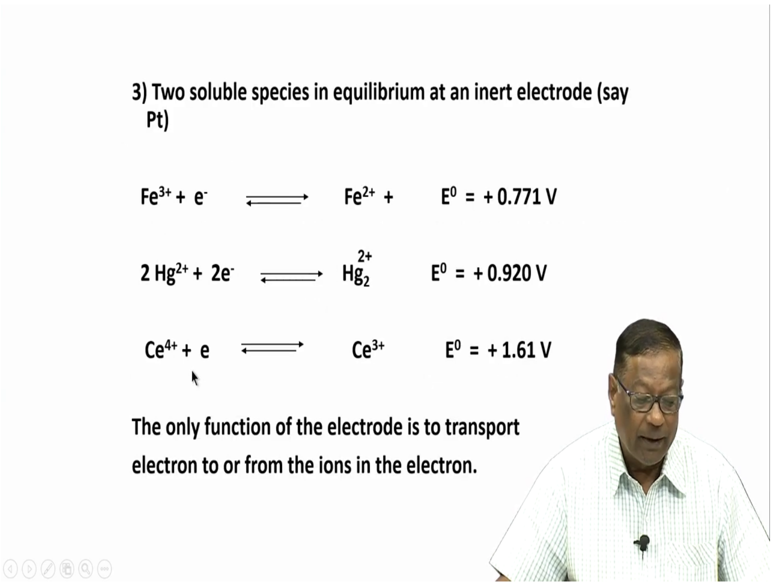

3) Two soluble species in equilibrium at an inert electrode (say Pt)

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} +$ $E^0 = +0.771$ V

$2\,Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+}$ $E^0 = +0.920$ V

$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ $E^0 = +1.61$ V

The only function of the electrode is to transport electron to or from the ions in the electron.

And then I have another kind that is third one that is 2 soluble species in equilibrium at an electrode at an inert electrode, say platinum. So, here I have a small problem, the oxidized state and the reduced state both are in solution, we can imagine iron. Iron can be in ferric state it will dissolve quite a like in large quantities that will be brown in color and iron solution can also be in ferrous state plus 2 oxidation state that is light green in color. So, if you take iron ferrous that is green color oxidize it will become brownish color ok. So, both the oxidized state as well as reduced state is in equilibrium are in equilibrium, but they are in of different color, they are in solution.

So, when so far I had explained to you that any oxidation state to reduction state when it is reduced it should go to metal, that is not always true. What is true? It can go to reduced state and that also can be a solution. In such cases I cannot have a reduced species metal ion metal electrode I cannot have Fe 2 plus I can have only iron electrode ok. So, in such cases I can write an expression when such systems are examined with respect to electrode standard electrode potential, I get Fe 3 plus e minus going to Fe 2 plus and e naught is equal to 0.77 volts with respect to standard hydrogen electrode. But then if what kind of cathode I should have here, the question comes what kind of cathode we will have here.

The point is we can have the platinum electrode platinum electrode to pick up electrons from ferric to ferrous, ferrous to ferric equilibrium in the solution, whenever the released electrons will be picked up by the platinum electrode and transfer to the outside circuit. So, that is the kind of third electrode electrodes of the third kind. So, first is electrodes of the first kind is a metal electrode with it is own solution which is quite soluble, second is a metal electrode with a sparingly soluble salt that is second kind and third is a metal electrode a platinum electrode with 2 species in solution which are not platinum they are and they could be anything ferrous ferric iron that is cerus ceric or it can be manganese manganic, it can be anything.

So, I can also write another equation is Hg 2 plus going to Hg 2 plus Hg 1 plus it should be 1 plus here. So, 2 Hg 1 plus plus 2 e going to Hg 2 2 plus ok, this is mercurous and mercury here, there is an error here it should be it at 1 that is mercurous to mercuric this is ferric to ferrous ok. So, here it is mercuric to mercurous other way round sorry. So, 0.920 and here it is ceric to cerus I told you know we are going to write everything as reduction potential. So, ferrous ceric to cerus is reduction, cerus to ceric is oxidation. So, here we are going to write everything as a reduction reaction and the standard electrode potential what with respect to NHE National Standard Electro she standard hydrogen electrode is 0.771 0.920 and 0.161 the only function of the electrode is to transport electron to or from the ions in the electron ok.

So, these are the three kinds of electrodes normally who employ in our electrochemical studies. So, we have described three types of electrodes and one is metal in it is own solution metal in a equilibrium with it is sparingly soluble salt and a redox species in the solution with 2 platinum electrodes or one platinum and one hydrogen electrode ok.

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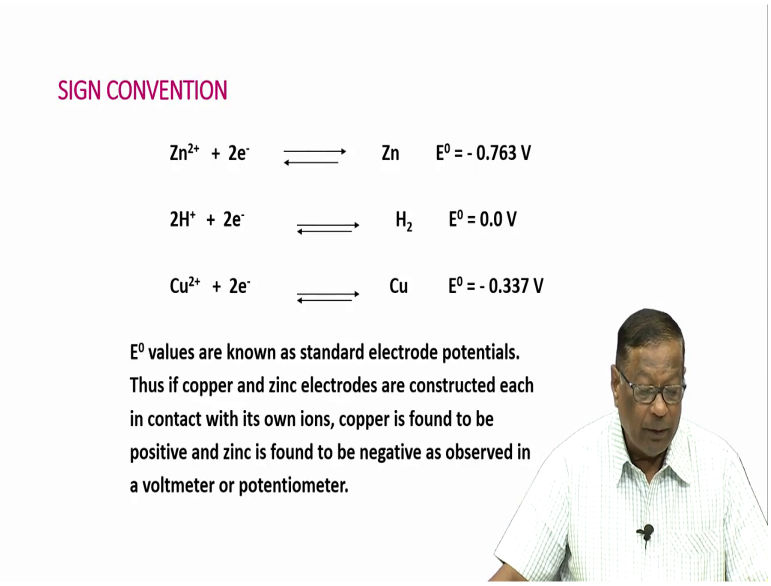

SIGN CONVENTION

$Zn^{2+} + 2e^- \rightleftharpoons Zn \quad E^0 = -0.763\ V$

$2H^+ + 2e^- \rightleftharpoons H_2 \quad E^0 = 0.0\ V$

$Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^0 = -0.337\ V$

E^0 values are known as standard electrode potentials. Thus if copper and zinc electrodes are constructed each in contact with its own ions, copper is found to be positive and zinc is found to be negative as observed in a voltmeter or potentiometer.

So we now I talk about the sign convention, as I said earlier we e naught values are known as standard electrode potential and if copper and zinc electrodes are constructed look at the data here now. Here I am writing zinc 2 plus plus 2 e minus as zinc this is one half cell reaction and e naught is 0.763 with respect to the SHE and hydrogen electrode is H 2 H plus plus 2 e minus going to H2 and that is e naught is equal to 0.0.

In all these cases we assume that concentration activity coefficient is one and concentration is equal to equivalent is equivalent to activity. Then I can write another equation Cu 2 plus plus 2 e minus goes to Cu and e naught is minus 0.337 volts. So, if copper and zinc electrodes are constructed in, if I take one copper electrode and one zinc electrode put them in a in 2 beaker put 2 electrode copper electrode and zinc electrode and connect them from outside, copper ion is found to be positive with respect to zinc why copper is minus 0.337 volts where as zinc is minus 0.763. You construct a scale minus 0.763 minus 0.337 and then come to 0 then positive values.

So, 33 minus 0.337 is positive with reference to zinc. So, if I have copper and zinc solutions with their electrodes I connected from outside zinc is found to be negative compared to copper and that will be reflected in the potentiometer voltmeter whatever it is ok. This is so this is the convention, so even if I know that copper is going to be deposited on zinc ok. So, the writing is only on the as a reduction reactions, I am not writing both of them one has positive reaction actually I should write Zn 2 plus plus 2 e minus going to plus Zn 2 plus plus Cu 2 plus going to Zn and zinc ok.

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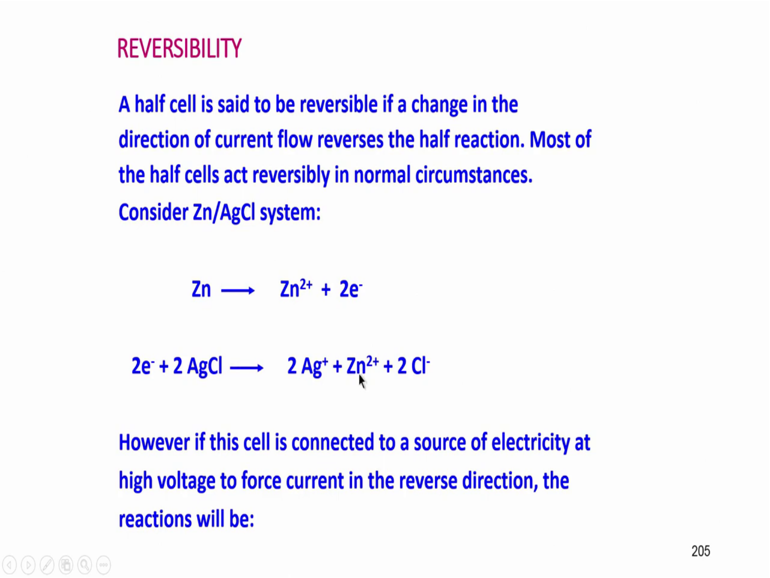

REVERSIBILITY

A half cell is said to be reversible if a change in the direction of current flow reverses the half reaction. Most of the half cells act reversibly in normal circumstances.

Consider Zn/AgCl system:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$2e^- + 2\,AgCl \longrightarrow 2\,Ag^+ + Zn^{2+} + 2\,Cl^-$$

However if this cell is connected to a source of electricity at high voltage to force current in the reverse direction, the reactions will be:

So, the half cell reaction if I connect this I will get a difference of about 0.763 minus 0.337 that is approximately 0.3 volts 0.4 volts ok.

So, that is the utility of sign convention, henceforth please right all electrochemical reaction as reduction reaction that is the message ok. So, we define a term what is known as reversibility, a half cell is said to be reversible half cell not full cell half cell is said to be reversible. If a change in the direction of current flow that is I changed from outside the switches positive to negative and negative to positive I just exchange them, then the reaction proceeds in the opposite direction.

So, most of it the half cell reaction also should reverse, so that is if oxidation is taking place on one side I change the polarity outside, then the reduction will be taking place in the solution. So, such a system is known as reversible reaction. So, most of the half cells act reversibly in normal circumstances, so consider zinc and AgCl system again zinc going to Zn 2 plus plus 2 e minus is the reaction this is we are writing as reduction potential reduction reaction and 2 e minus plus 2 Ag goes to 2 Ag plus plus zinc 2 plus plus 2 Cl minus ok.

So, this is the reaction and I am combining this reaction also here. So, zinc 2 on my on the right hand side I have zinc ions and silver ions and chloride ions. And if the cell is connected to a source of electricity at high voltage to force current in the wrong direction in the reverse direction, that means I change the polarity.

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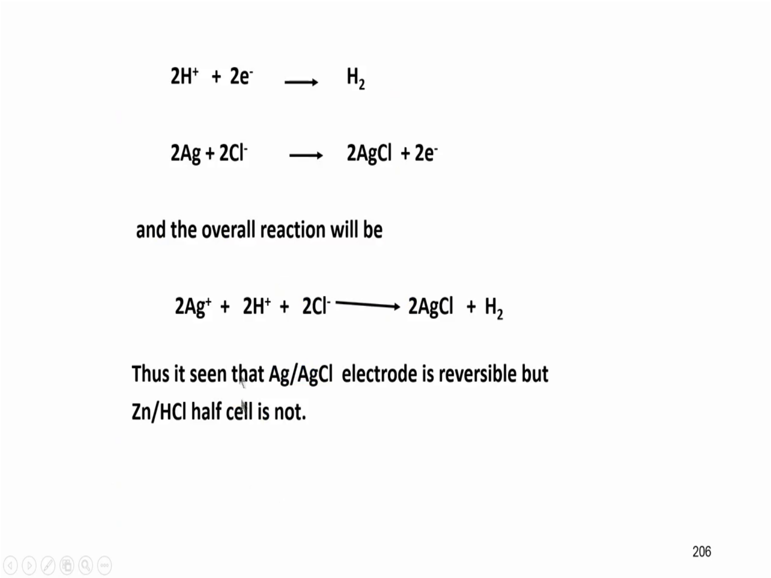

$2H^+ + 2e^- \longrightarrow H_2$

$2Ag + 2Cl^- \longrightarrow 2AgCl + 2e^-$

and the overall reaction will be

$2Ag^+ + 2H^+ + 2Cl^- \longrightarrow 2AgCl + H_2$

Thus it seen that Ag/AgCl electrode is reversible but Zn/HCl half cell is not.

The reaction is going to be 2 H plus plus 2 e minus going to H 2 and 2 silver plus 2 Cl minus this is going to precipitate as silver chloride. So, the overall reaction is nothing, but 2 Ag plus plus 2 H plus plus plus 2 Cl minus that is already there. So, this will form AgCl silver chloride and hydrogen.

So, instead of deposition we are going to have release of hydrogen. So, it is seen that silver silver chloride is reversible, but not zinc HCl solution ok. So, what happens if zinc HCl solution I change the polarity hydrogen will be released, if I change the polarity again zinc will be deposited. So, this you should understand about the reversibility, but most of the reactions are reversible in electrochemical science.

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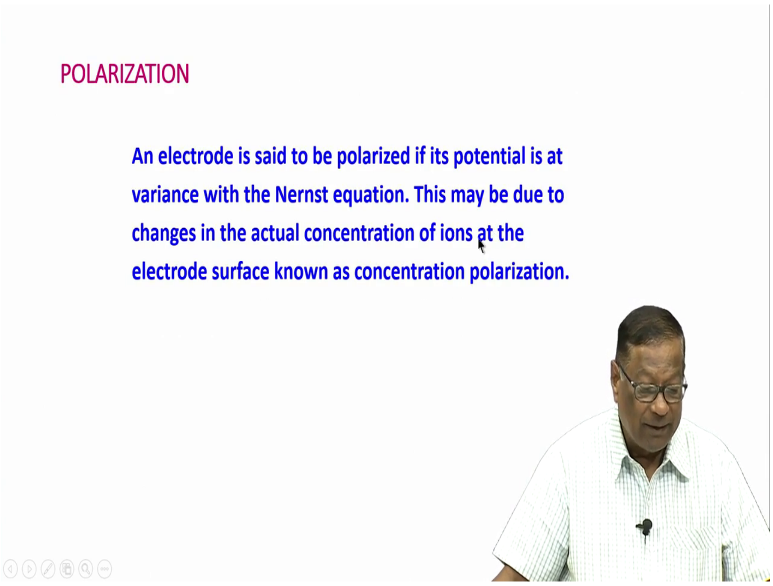

POLARIZATION

An electrode is said to be polarized if its potential is at variance with the Nernst equation. This may be due to changes in the actual concentration of ions at the electrode surface known as concentration polarization.

So, an electrode this I have already explained to you that in electrode is said to be polarized, if it is potential is in variance. But now we are talking about the potential not the voltage and we are talking about the electrode.

So, electrode is said to be polarized if it is potential is in variance with the Nernst equation. So, what does Nernst equation say e is equal to e naught minus RT by nf plus RT by nf ln oxidant divided by ln reductant. So, ln reductant is 1 so ln oxidant e is equal to e naught plus RT by nf ln A oxidant ok. Now the whatever is the value depends upon e naught is fixed constant ok.

So, the potential will be should be proportional to the concentration, I will go back just momentarily for your convenience for that reaction. Here EA is equal to e naught A plus RT by nf ln A oxidant, for any reaction for assume that this is for the electrode zinc and zinc Zn 2 plus electrode I write e naught zinc zinc zinc 2 plus Zn by Zn 2 plus this is constant with respect to standard electrode potential with respect to SHE.

But then what will be EA EA is we depends upon the concentration of the solution is not it. So, R; R is constant T is constant number of electrons are constant Faraday is constant. So, only thing that can vary is concentration of the solution. So, actual potential depends upon the concentration of the solution and if the concentration, if the actual potential is indifference it is it variance with the calculated value like this they were taking into account concentration. What I should get if I do not get it then I say electrode is polarized ok, so that is the concept of polarization. So, a an electrode is said to be polarized if it is potential is at variance with the Nernst equation, that means you calculate with respect to concentration add e naught and if it is not the same actual potential what you measure in the voltmeter, then it is electrode is polarized. This happens quite often whenever there is poisoning of the electrode and then sometimes depositions. So, many other reasons are there we will go into that later.

So, this polarization of the electrode may be due to changes in the actual concentration of the ions at the electrode surface that is known as concentration polarization. Sometimes changes occur due to actual concentration not at of the activity at the electrode surface, then it is known as concentration polarization. If the concentration is the reason then it is known as concentration polarization.

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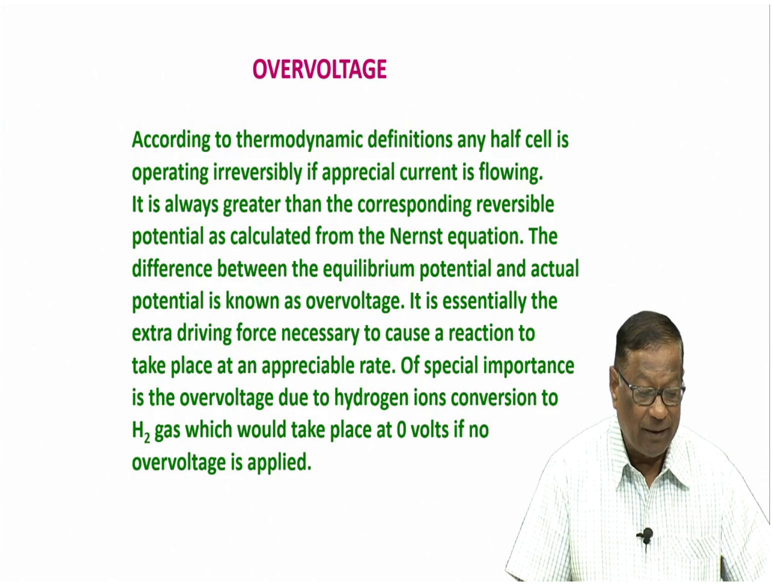

OVERVOLTAGE

According to thermodynamic definitions any half cell is operating irreversibly if apprecial current is flowing. It is always greater than the corresponding reversible potential as calculated from the Nernst equation. The difference between the equilibrium potential and actual potential is known as overvoltage. It is essentially the extra driving force necessary to cause a reaction to take place at an appreciable rate. Of special importance is the overvoltage due to hydrogen ions conversion to H_2 gas which would take place at 0 volts if no overvoltage is applied.

So, over voltage again I had to defined it number of time and according to thermodynamic definitions any half cell that is operating irreversibly, if appreciable current is flowing. It is always greater than the corresponding reversible potential as calculated from the Nernst equation. The difference between the equilibrium potential and the actual potential is known as overvoltage that is the difference. Whenever we say an electrode is polarized what is the quantity of voltage that is different how much it is different it is so that potential is known as overvoltage.

It is essentially the extra driving force necessary to cause a reaction to take place at an appreciable rate. So, of special importance is the over voltage due to hydrogen ions conversion to hydrogen gas which would take place at 0 volts, if no overvoltage is applied ok. That means, conversion of hydrogen ions to hydrogen gas should take place at 0 volt, but it has to be it has to happen when there is no overvoltage. But if you have to apply overvoltage; that means, the other electrode is polarized. So, you have to apply that much of extra voltage to get the hydrogen gas ok.

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Fe^{3+} and Zn^{2+} can be reduced to free metals at a mercury cathode even though their standard potentials (E^0) are more negative than SHE because the high overvoltage of H_2 ion on mercury pressure liberalization. At a platinum cathode these ions cannot be reduced from an aqueous solution as the potential cannot exceed that required for H_2 liberation.

So, ferric and zinc 2 plus can be reduced to free metals at mercury cathode, even though their standard potentials are more negative than standard hydrogen electrode. Now a little bit of chemistry because ferric and zinc ions can form amalgams with mercury. So, they can many elements can form amalgams with mercury. So, we can use them with mercury cathode many elements.

So, they their standard potentials are more negative than standard hydrogen electrode of because, hydrogen electrode is 0 nothing can be less than 0 in real life. So because the high overvoltage of hydrogen ion on mercury pressure liberation that is the reason, so at a platinum cathode these ions cannot be reduced from an aqueous solution, as the potential cannot exceed that required for hydrogen liberation.

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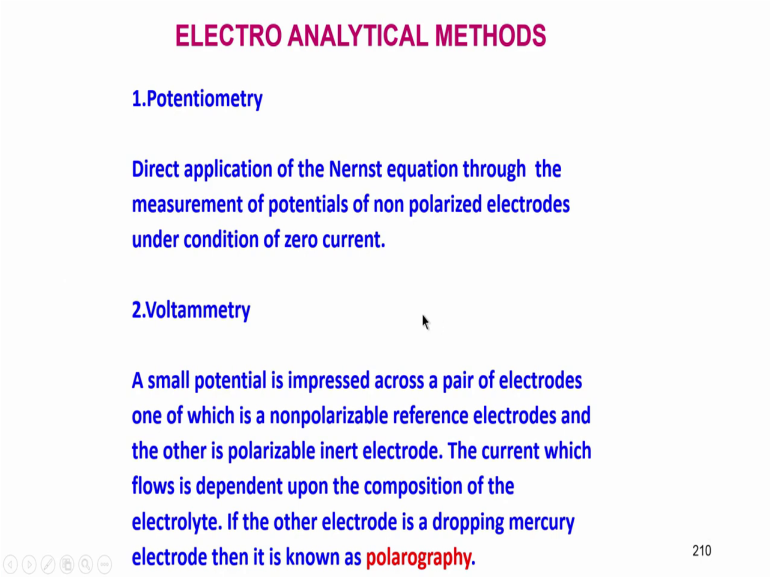

ELECTRO ANALYTICAL METHODS

1.Potentiometry

Direct application of the Nernst equation through the measurement of potentials of non polarized electrodes under condition of zero current.

2.Voltammetry

A small potential is impressed across a pair of electrodes one of which is a nonpolarizable reference electrodes and the other is polarizable inert electrode. The current which flows is dependent upon the composition of the electrolyte. If the other electrode is a dropping mercury electrode then it is known as polarography.

So, based on this information on this information we have different kinds of Electro Analytical techniques, one is potentiometry that is direct application of the Nernst equation through the measurement of potentials of non polarized electrodes under condition of 0. We equate concentration and potential when there is no current is passing ok. That is a 0 that is known as potentiometry, voltamery I do apply a potential across a pair of electrodes one of which is a non polarizable electrode that is reference electrode.

The other one is polarizable inert electrode the current that flows must be dependent upon the composition of the electrolyte and I determine the composition of the electrolyte depending upon the current that is being produced. So, if the other electrode is a dropping mercury electrode then we call it as polarography, this is part of voltammetry only.

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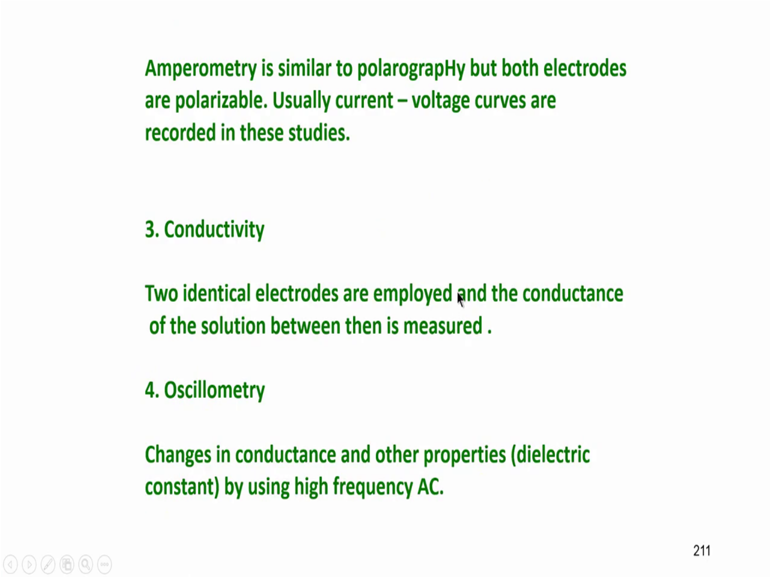

Amperometry is similar to polarograpHy but both electrodes are polarizable. Usually current – voltage curves are recorded in these studies.

3. Conductivity

Two identical electrodes are employed and the conductance of the solution between then is measured .

4. Oscillometry

Changes in conductance and other properties (dielectric constant) by using high frequency AC.

So Amperometry is similar to polarography, but both electrodes are polarizable usually current voltage curves are recorded in these studies. Then conductivity we have already studied a little bit and oscillometry changes in the conductance and other properties by using high frequency like AC.

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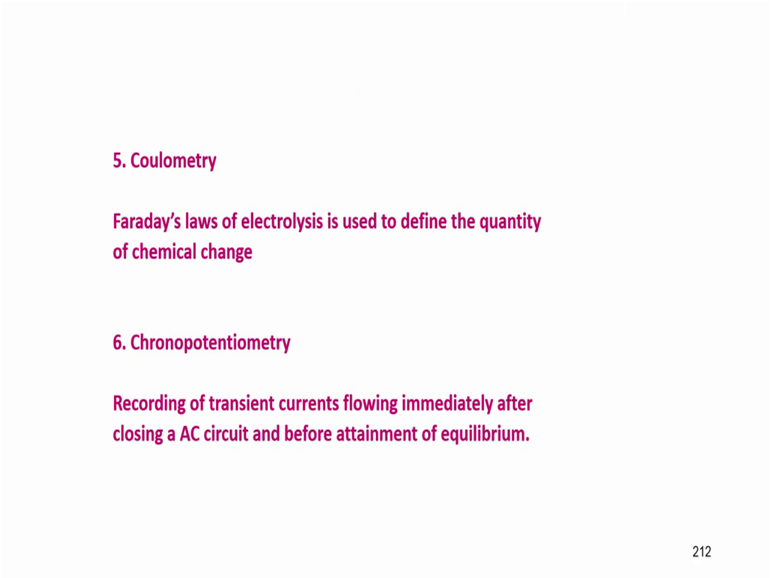

5. Coulometry

Faraday's laws of electrolysis is used to define the quantity of chemical change

6. Chronopotentiometry

Recording of transient currents flowing immediately after closing a AC circuit and before attainment of equilibrium.

And then Coulometry is Faradays laws of electrolysis, applied to electrode deposition that is electroplating. Chronopotentiometry is recording of the transient current movement flowing immediately after closing an AC circuit before it attains equilibrium that is chronopotentiometry.

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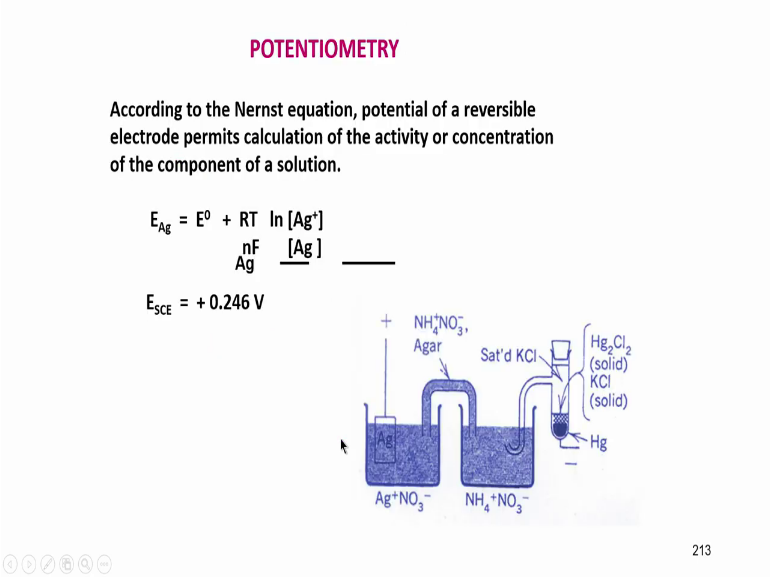

POTENTIOMETRY

According to the Nernst equation, potential of a reversible electrode permits calculation of the activity or concentration of the component of a solution.

$$E_{Ag} = E^0_{Ag} + \frac{RT}{nF} \ln \frac{[Ag^+]}{[Ag]}$$

$$E_{SCE} = +0.246\ V$$

All these things are different types of Electro analytical techniques and we will be studying them in detail not all ut potentiometry and voltammetry and then we will move on to other subjects that we will study in our next class.

Thank you very much.