Modern Instrumental Methods of Analysis

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Lecture no. # 36

Fundamentals of Electrochemical Techniques-1 Introduction

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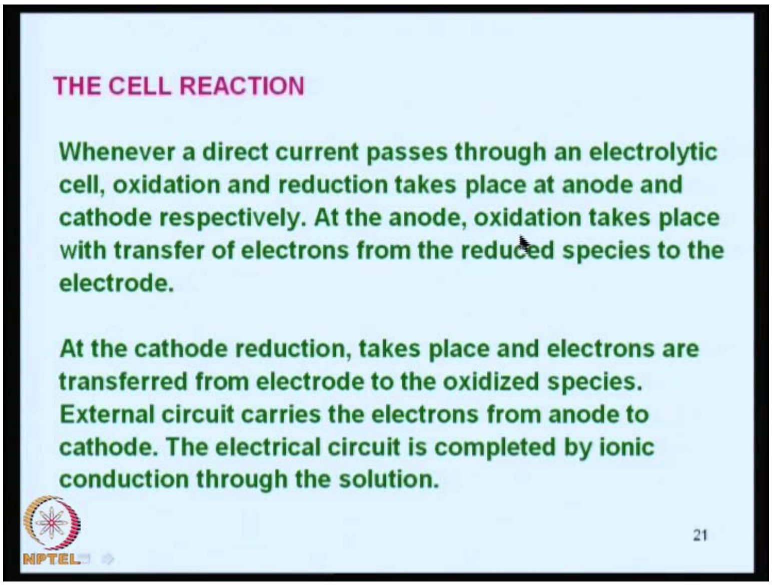

THE CELL REACTION

Whenever a direct current passes through an electrolytic cell, oxidation and reduction takes place at anode and cathode respectively. At the anode, oxidation takes place with transfer of electrons from the reduced species to the electrode.

At the cathode reduction, takes place and electrons are transferred from electrode to the oxidized species. External circuit carries the electrons from anode to cathode. The electrical circuit is completed by ionic conduction through the solution.

Welcome to our second class on electro chemistry. I want to remind you that a cell reaction whenever a direct current passes through an electrolytic cell. Oxidation and reduction take place at anode and cathode respectively, and at the anode oxidation takes place with the transfer of electrons from the reduced species to the electrode.

At the cathode cathode reduction takes place and the electrons are transferred from the electrode to the oxidizing species. We have covered all these in the last class, now when the electric circuit is completed ionic conduction occurs through the solution.

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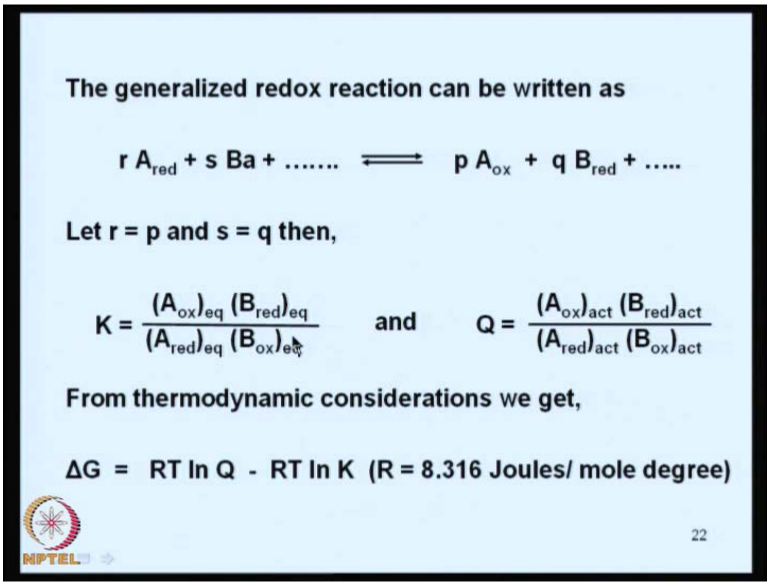

The generalized redox reaction can be written as

$$r\,A_{red} + s\,Ba + \ldots\ldots \rightleftharpoons p\,A_{ox} + q\,B_{red} + \ldots..$$

Let r = p and s = q then,

$$K = \frac{(A_{ox})_{eq}\,(B_{red})_{eq}}{(A_{red})_{eq}\,(B_{ox})_{eq}} \quad \text{and} \quad Q = \frac{(A_{ox})_{act}\,(B_{red})_{act}}{(A_{red})_{act}\,(B_{ox})_{act}}$$

From thermodynamic considerations we get,

ΔG = RT ln Q - RT ln K (R = 8.316 Joules/ mole degree)

So, this equation we have seen that they generalized their redox equation in the last class. That a moles of r moles of A species, A and s moles of species B get oxidized to p moles of oxidant A and q moles of reductant B then we have written an equilibrium constant. And then we have written a thermo dynamic constant that is q which which is essentially same as equilibrium constant except, the equilibrium terms are replaced by activity and this activity is nothing but, concentration into multiplied by its activity coefficient. Since both these are thermodynamic considerations, we get the free energy delta G it should be corresponding to their difference between RT ln Q minus RT ln K that your r is 8.316 joules per one mole per degree.

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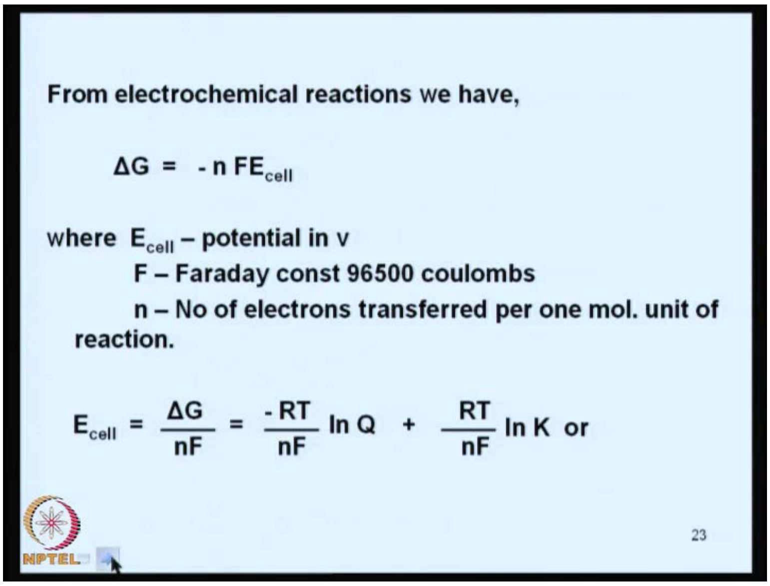

From electrochemical reactions we have,

$$\Delta G = -nFE_{cell}$$

where E_{cell} – potential in v

F – Faraday const 96500 coulombs

n – No of electrons transferred per one mol. unit of reaction.

$$E_{cell} = \frac{\Delta G}{nF} = \frac{-RT}{nF} \ln Q + \frac{RT}{nF} \ln K \text{ or}$$

And then we have also shown that the free energy is also equivalent to number of electrons transferred and number of faradays and the E M F of the cell that is potential of the cell in volts. Then we can write comparing these two equation; this is delta G with respect to electro chemistry and the previous slide delta G the thermo dynamic quantities then we have combined these two and equate it then we have written E cell is equal to RT, minus RT by nf ln Q, plus RT by nf ln K then we have separated the equilibrium and activity coefficients with respect to put species A and species B.

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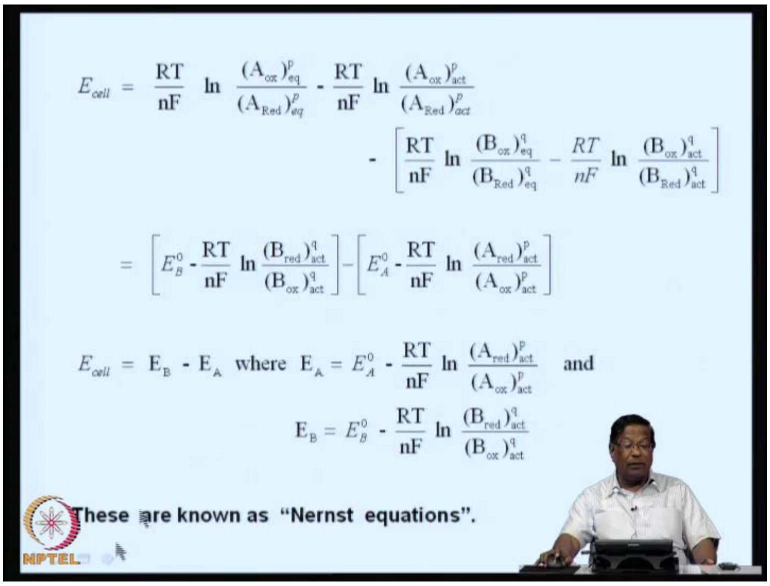

$$E_{cell} = \frac{RT}{nF} \ln \frac{(A_{ox})^p_{eq}}{(A_{Red})^p_{eq}} - \frac{RT}{nF} \ln \frac{(A_{ox})^p_{act}}{(A_{Red})^p_{act}} - \left[\frac{RT}{nF} \ln \frac{(B_{ox})^q_{eq}}{(B_{Red})^q_{eq}} - \frac{RT}{nF} \ln \frac{(B_{ox})^q_{act}}{(B_{Red})^q_{act}} \right]$$

$$= \left[E^0_B - \frac{RT}{nF} \ln \frac{(B_{red})^q_{act}}{(B_{ox})^q_{act}} \right] - \left[E^0_A - \frac{RT}{nF} \ln \frac{(A_{red})^p_{act}}{(A_{ox})^p_{act}} \right]$$

$$E_{cell} = E_B - E_A \text{ where } E_A = E^0_A - \frac{RT}{nF} \ln \frac{(A_{red})^p_{act}}{(A_{ox})^p_{act}} \text{ and}$$

$$E_B = E^0_B - \frac{RT}{nF} \ln \frac{(B_{red})^q_{act}}{(B_{ox})^q_{act}}$$

These are known as "Nernst equations".

So, the E cell is actually given by the difference between the two; that is potential of the first cell B, minus potential of the cell A. where, the actual potential is given by E A is equal to E naught A minus RT by nf A reductant multiplied by number of moles and that is the activity; that is, if this concentration term actually refers to activity.

Similarly, we have written for B, now this equations where E A is equal to E naught a minus RT by nf ln A reductant by A oxidant moles of p at activity coefficients. Similarly, for these these are known as Nernst equations this we have covered in the last class.

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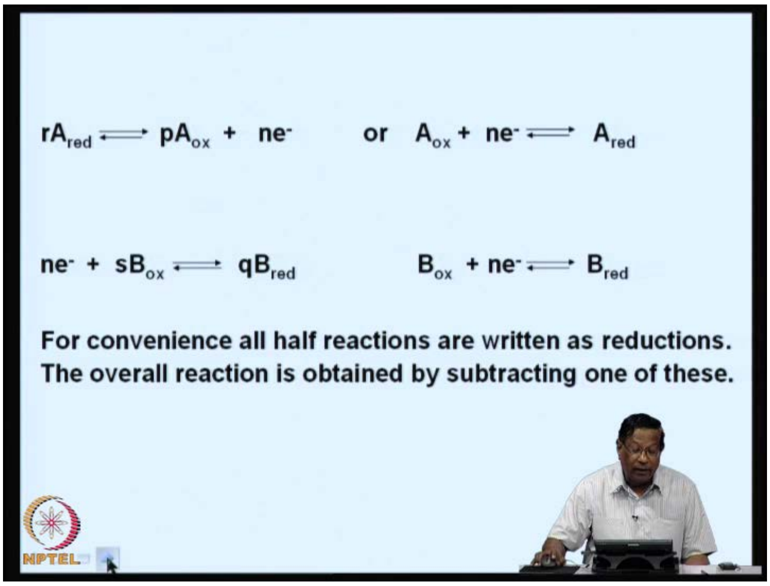

$rA_{red} \rightleftharpoons pA_{ox} + ne^-$ or $A_{ox} + ne^- \rightleftharpoons A_{red}$

$ne^- + sB_{ox} \rightleftharpoons qB_{red}$ $B_{ox} + ne^- \rightleftharpoons B_{red}$

For convenience all half reactions are written as reductions.
The overall reaction is obtained by subtracting one of these.

Now, for convenience; that means, what actually we have done is, we have written half cells; the half cells actually represent only one species reaction occurring at one species only one cells are connected together they represent a complete cell.

So, we have written A oxidant is plus n number of electrons is equal to A reductant similarly half cell reaction, the other half cell even though it is the electrons are accepted here. In the other cell it should be released here, but even though, if the electrons are released we still write B ox plus ne is equal to B reductant; that means, we have algebraically changed this this equation to right oxidant at the left electrons at the left and the reductant on the right side of the equation.

This we can do for any of the half cell reactions. So far, convenience all the half cells are written as reductions; that means, in this format, the overall reaction is obtained by the subtracting the bigger one smaller one from the bigger one.

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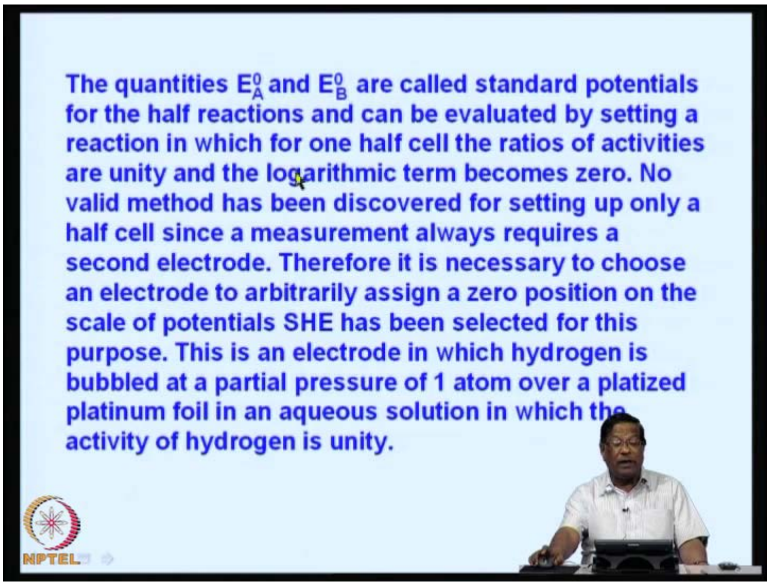

The quantities E^0_A and E^0_B are called standard potentials for the half reactions and can be evaluated by setting a reaction in which for one half cell the ratios of activities are unity and the logarithmic term becomes zero. No valid method has been discovered for setting up only a half cell since a measurement always requires a second electrode. Therefore it is necessary to choose an electrode to arbitrarily assign a zero position on the scale of potentials SHE has been selected for this purpose. This is an electrode in which hydrogen is bubbled at a partial pressure of 1 atom over a platized platinum foil in an aqueous solution in which the activity of hydrogen is unity.

So, the quantities E naught A and E naught B are called as standard electrode potentials, for the half cell reactions and they can be evaluated by setting a reaction in which one half cell, the ratios are reality and the logarithmic term become zero. So, no valid method has been discovered for setting up only a half cell of any reaction, it has to be coupled with another half cell where reduction or oxidation takes place.

Therefore it is necessary to choose an electrode to arbitrarily assign a zero in a position on the scale of potentials, for this we are using standard hydrogen electrode as a standard one by convention, it is not by, it is not a scientific chosen system, but for our convenience we have chosen standard hydrogen electrode as representing zero voltage.

So, what are your standard hydrogen electrode, it is an electrode in which a hydrogen is dipped in a solution, there platinum wire is dipped in a solution, containing hydrogen ions and hydrogen is being bubbled through the solution at a partial pressure of one atmosphere, over a platinised, aluminum, platinum foil in an aqueous solution in which the activity of hydrogen is unity; that means, concentration multiplied by activity coefficient.

So, the when the activity coefficient is one then concentration into one is activity basically.

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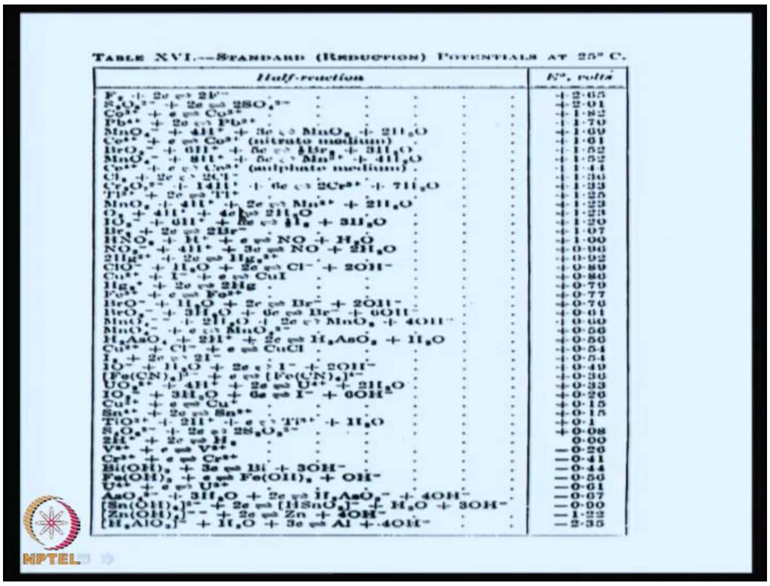

TABLE XVI.—STANDARD (REDUCTION) POTENTIALS AT 25° C.

Half-reaction	*E°, volts*
$F_2 + 2e \rightleftharpoons 2F^-$	+2·65
$S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$	+2·01
$Co^{3+} + e \rightleftharpoons Co^{2+}$	+1·82
$Pb^{4+} + 2e \rightleftharpoons Pb^{2+}$	+1·70
$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$	+1·69
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ (nitrate medium)	+1·61
$BrO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}Br_2 + 3H_2O$	+1·52
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	+1·52
$Ce^{4+} + e \rightleftharpoons Ce^{3+}$ (sulphate medium)	+1·44
$Cl_2 + 2e \rightleftharpoons 2Cl^-$	+1·36
$Cr_2O_7^{2-} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1·33
$Tl^{3+} + 2e \rightleftharpoons Tl^+$	+1·25
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$	+1·23
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$	+1·23
$IO_3^- + 6H^+ + 5e \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+1·20
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1·07
$HNO_2 + H^+ + e \rightleftharpoons NO + H_2O$	+1·00
$NO_3^- + 4H^+ + 3e \rightleftharpoons NO + 2H_2O$	+0·96
$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+}$	+0·92
$ClO^- + H_2O + 2e \rightleftharpoons Cl^- + 2OH^-$	+0·89
$Cu^{2+} + I^- + e \rightleftharpoons CuI$	+0·86
$Hg_2^{2+} + 2e \rightleftharpoons 2Hg$	+0·79
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0·77
$BrO^- + H_2O + 2e \rightleftharpoons Br^- + 2OH^-$	+0·76
$BrO_3^- + 3H_2O + 6e \rightleftharpoons Br^- + 6OH^-$	+0·61
$MnO_4^{2-} + 2H_2O + 2e \rightleftharpoons MnO_2 + 4OH^-$	+0·60
$MnO_4^- + e \rightleftharpoons MnO_4^{2-}$	+0·56
$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons H_3AsO_3 + H_2O$	+0·56
$Cu^{2+} + Cl^- + e \rightleftharpoons CuCl$	+0·54
$I_2 + 2e \rightleftharpoons 2I^-$	+0·54
$IO^- + H_2O + 2e \rightleftharpoons I^- + 2OH^-$	+0·49
$[Fe(CN)_6]^{3-} + e \rightleftharpoons [Fe(CN)_6]^{4-}$	+0·36
$UO_2^{2+} + 4H^+ + 2e \rightleftharpoons U^{4+} + 2H_2O$	+0·33
$IO_3^- + 3H_2O + 6e \rightleftharpoons I^- + 6OH^-$	+0·26
$Cu^{2+} + e \rightleftharpoons Cu^+$	+0·15
$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$	+0·15
$TiO^{2+} + 2H^+ + e \rightleftharpoons Ti^{3+} + H_2O$	+0·1
$S_4O_6^{2-} + 2e \rightleftharpoons 2S_2O_3^{2-}$	+0·08
$2H^+ + 2e \rightleftharpoons H_2$	0·00
$V^{3+} + e \rightleftharpoons V^{2+}$	−0·26
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	−0·41
$Bi(OH)_3 + 3e \rightleftharpoons Bi + 3OH^-$	−0·44
$Fe(OH)_3 + e \rightleftharpoons Fe(OH)_2 + OH^-$	−0·56
$U^{4+} + e \rightleftharpoons U^{3+}$	−0·61
$AsO_4^{3-} + 3H_2O + 2e \rightleftharpoons H_2AsO_3^- + 4OH^-$	−0·67
$[Sn(OH)_6]^{2-} + 2e \rightleftharpoons [HSnO_2]^- + H_2O + 3OH^-$	−0·90
$[Zn(OH)_4]^{2-} + 2e \rightleftharpoons Zn + 4OH^-$	−1·22
$[H_2AlO_3]^- + H_2O + 3e \rightleftharpoons Al + 4OH^-$	−2·35

So, the activity should be one; that means, the reference should be zero that arbitrary value we have chosen. So, if the hydrogen ion standard hydrogen electrode is showing zero volts, others may be showing positive value compare to zero and some may be showing a negative value.

For example, if you take a look at this figure, I have written here, the figures are not very clear, but it is a standard reproduction from any of the text books, all what is, what the title says is? Standard reduction potential at 25 degrees centigrade. So, here you can see like somewhere in the middle you will see 0.00 here. So, 2 H plus, plus 2 e going to H 2 and that shows zero, above this all the reactions are showing positive values.

For example, here it is iron plus 2 electron going to Fe 3 it shows plus 2.65 volts it means when an iron electrode is connected with the standard hydrogen electrode it shows 2.56 volts. So, similarly we have sulphate S 2, O 8 plus, 2 E going to SO 4 that shows 2.01 then I am choosing an arbitrary random value that is iodine here, plus 2 electrons going to 2 I minus that is iodide electrode and that shows plus 0.51.

So, tin here is another one, SN 4 plus, plus 2 electrons going to stannous that is shows 0.1 phi. So, if you connected two hydrogen electrodes, what you would see is 0.00; that is the standard hydrogen electrode, after that we have the values which are lower than that. That is chromium 3, plus electron going to chromium two plus and that value is minus 0.41. So, H 2 Al O 3 last one, plus waters with 3 electrons, it going to aluminum it shows minus 2.35.

One conclusion you can draw from this is. So, all the electrode chemical, electrochemical reactions show either positive value with respect to standard hydrogen electrodes or negative values with with respect to standard hydrogen electrode. Now, the things which are showing positive values, they are all called as oxidizing agents and the one compared with the negative values are called reducing agents.

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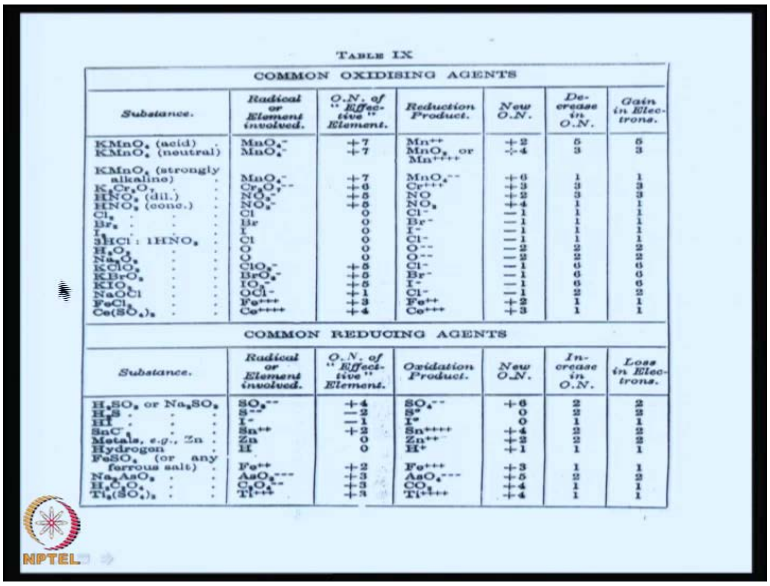

TABLE IX

COMMON OXIDISING AGENTS

Substance.	*Radical or Element involved.*	*O.N. of "Effective" Element.*	*Reduction Product.*	*New O.N.*	*Decrease in O.N.*	*Gain in Electrons.*
$KMnO_4$ (acid)	MnO_4^-	+7	Mn^{++}	+2	5	5
$KMnO_4$ (neutral)	MnO_4^-	+7	MnO_2 or Mn^{++++}	+4	3	3
$KMnO_4$ (strongly alkaline)	MnO_4^-	+7	MnO_4^{--}	+6	1	1
$K_2Cr_2O_7$	$Cr_2O_7^{--}$	+6	Cr^{+++}	+3	3	3
HNO_3 (dil.)	NO_3^-	+5	NO	+2	3	3
HNO_3 (conc.)	NO_3^-	+5	NO_2	+4	1	1
Cl_2	Cl	0	Cl^-	−1	1	1
Br_2	Br	0	Br^-	−1	1	1
I_2	I	0	I^-	−1	1	1
3HCl : 1HNO_3	Cl	0	Cl^-	−1	1	1
H_2O_2	O	0	O^{--}	−2	2	2
Na_2O_2	O	0	O^{--}	−2	2	2
$KClO_3$	ClO_3^-	+5	Cl^-	−1	6	6
$KBrO_3$	BrO_3^-	+5	Br^-	−1	6	6
KIO_3	IO_3^-	+5	I^-	−1	6	6
NaOCl	OCl^-	+1	Cl^-	−1	2	2
$FeCl_3$	Fe^{+++}	+3	Fe^{++}	+2	1	1
$Ce(SO_4)_2$	Ce^{++++}	+4	Ce^{+++}	+3	1	1

COMMON REDUCING AGENTS

Substance.	*Radical or Element involved.*	*O.N. of "Effective" Element.*	*Oxidation Product.*	*New O.N.*	*Increase in O.N.*	*Loss in Electrons.*
H_2SO_3 or Na_2SO_3	SO_3^{--}	+4	SO_4^{--}	+6	2	2
H_2S	S^{--}	−2	S^0	0	2	2
HI	I^-	−1	I^0	0	1	1
$SnCl_2$	Sn^{++}	+2	Sn^{++++}	+4	2	2
Metals, *e.g.*, Zn	Zn	0	Zn^{++}	+2	2	2
Hydrogen	H	0	H^+	+1	1	1
$FeSO_4$ (or any ferrous salt)	Fe^{++}	+2	Fe^{+++}	+3	1	1
Na_3AsO_3	AsO_3^{---}	+3	AsO_4^{---}	+5	2	2
$H_2C_2O_4$	$C_2O_4^{--}$	+3	CO_2	+4	1	1
$Ti_2(SO_4)_3$	Ti^{+++}	+3	Ti^{++++}	+4	1	1

So, we can make further choice something like this, we can have a choice of common oxidizing agents and here, if I use potassium permanganate its radical is Mn O 4 minus oxidation state is plus 7. And when it is when it oxidizes other systems manganese reduces from Mn O 4, minus 2 Mn 2 plus; that means, new oxidation state is plus 2 compared to plus 7. That means the change in the decrease in the oxidation number is 5; that means, gain in electrons is 5; that means, it requires 5 electrons and for this reaction to proceed.

So, this is a very strong oxidizing agent in our experience. Similarly, I can go for nitric acid. So, here it is plus 5 oxidation state and then it is minus 1. So, plus 5, plus 4 and 1 oxidize one electron. So, it cannot be as strong an oxidizing agent as potassium permanganate, like this if you look at the oxidation potentials of the oxidants you can make a list of which are the strong oxidizing agents.

Similarly, we can compare the E M F, with respect to hydrogen electrode and decide whether H 2 S O 3 is a better reducing agent, stronger reducing agent or oxalic acid; obviously, you can have a choice of different chemical reactions which can be graded with respect to the oxidizing and reduction properties as compared to hydrogen.

So, we have different kinds of electrodes now. Earlier, I had described the standard hydrogen electrode is basically a solution of H C L of 1 of 1 unit activity where hydrogen is being bubbled with a platinum wire fixed into the solution. Now, I can have different kind of electrodes not necessarily the gas and metal etcetera, they are described as three types belonging to three types electrodes; of the first kind electrodes, of the second kind and then electrodes of the third kind, let us look at what is first kind electrodes of the first kind.

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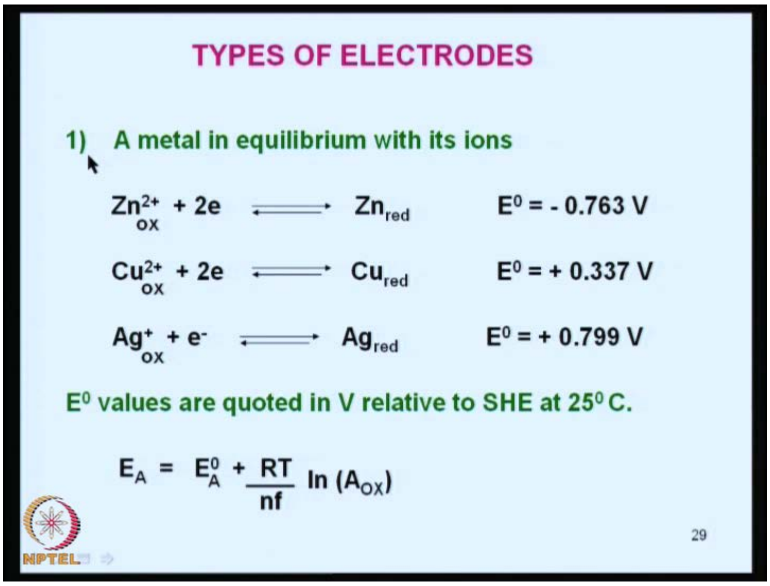

TYPES OF ELECTRODES

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, it actually it means a metal rod in equilibrium with its ions that is the electrode of the first kind. I have given you three examples here zinc metal, zinc solution with two oxidation state it gains two electrons to give you zinc metal; that means, a zinc metal is dipped in a solution of zinc zinc solution Zn 2 plus solutions and that when it is when it is connected with a standard hydrogen electrode you would see an E M F of minus 0.763 volts and their example is, copper electrode dissolving copper electrode dipped in a copper solution and the reaction would be Cu 2 plus, plus 2 electrons going to copper metal; that is reductant remember that most of the all the metals are in the reduced state their solutions are in the oxidized state.

So, compare to if you put connect this with hydrogen you will get 0.337 volts. So, which is a better ah oxidizing agent, among these two this is minus ,this is plus and this would be a zinc this would be a better reducing agent, because it is minus value compared to standard hydrogen electrode this way we can get comparison.

So, similarly I can have a silver wire dipped in a solution of silver nitrate; that is Ag plus in the oxidized state, I am writing here at the bottom as a subscript there reaction would be Ag plus, plus e minus going to silver reductant and the standard reduction potential is 0.0799 volts.

So, like this we can have the reactions written and the E M F of the potential is given by this expression E A is equal to E naught A; that is standard electro potential with respect to hydrogen electrode plus RT by nf ln A oxidant and that is the actual E M F is standard electrode potential plus that modified by the oxidant and reductant ratio actually there should be A reductant at bottom here, in this equation ln A oxidant divided by ln A reductant. But reductant value is metal and for metal activity is one. So, we we write a reductant instead of writing a reductant we are writing one.

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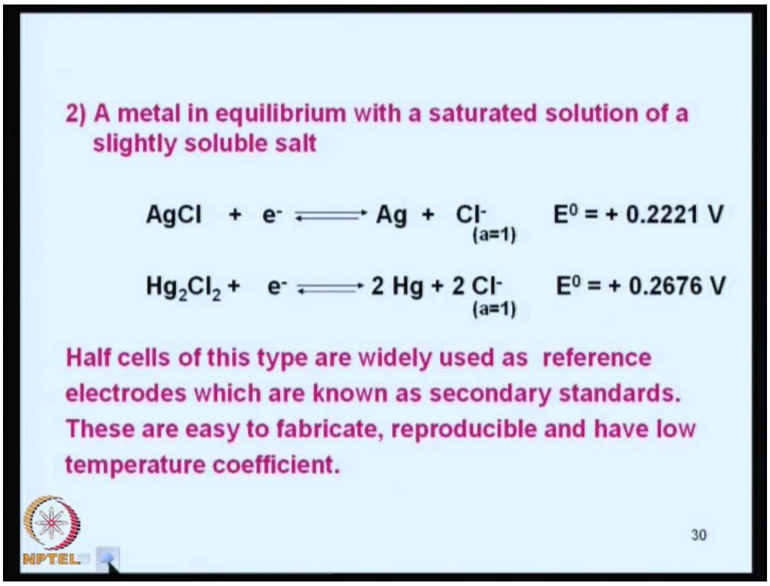

2) A metal in equilibrium with a saturated solution of a slightly soluble salt

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

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

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, similarly, I can have a metal in equilibrium with a saturated solution; that means, I take a metal rod dip it in a saturated solution of a slightly soluble salt for example, I can take silver chloride.

Silver chloride is very sparingly soluble. So, you make a solution in a beaker, take some water add some amount of silver chloride part of it will dissolve and remaining part will remain as the powder at the bottom of the electrode; that is a salt solution in equilibrium with it is a solution. In that if, I put a silver electrode I will have , I have a half cell known as silver silver chloride plus electron, the reaction is represented by it will pick up an electron and goes to go to silver metal and release a chloride ion and the standard electrode potential is 0.2221 volts.

Similarly, I can choose rather sparingly soluble salts like mercurous chloride Hg 2 Cl 2, plus e minus going to 2 H g plus 2 Cl minus. Here, also a single electron is involved and the E naught for this half cell reaction is given by 0.2676 with respect to standard hydrogen electrode.

So, half cells of this type are widely used as reference electrodes, see it is very difficult to have a platinum electrode with a solution of hydrogen chloride, gas bubbling such a complicated reaction and even to maintain or measure routinely we do not need them.

It is a very difficult to maintain such electrodes systems therefore, what we do is since the silver electrode just what I described silver silver chloride in equilibrium with its own solution, does give reproducible results with respect to standard hydrogen electrode and it gives you a value of 0.2221 volts. Now, that itself we can use it as a reference electrode, instead of standard hydrogen electrode. So, I can use tools silver silver chloride electrode as a reference electrode and half therefore, mercury chloride also we can use it as half cell and reference cell.

Half cells of these types are widely used as reference electrodes which are also known as secondary standards. So, instead of setting a primary standard all the time with all its complications it is better to use secondary standard these are easy to fabricate. And they are reproducible and they have very low temperature coefficients; that means, if the temperature varies you still, you will not see much of the much change in the E M F, because they have a very low temperature coefficient; that means, temperature does not have a significant effect on the E M F.

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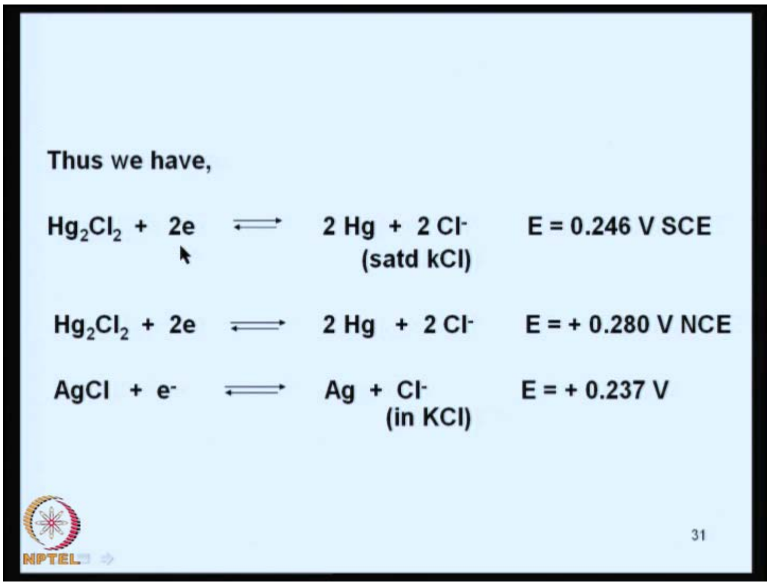

Thus we have,

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

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

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

Now, we can look at the reactions of the silver silver chloride electrodes that is Ag 2 Cl 2, it can pick up two electrons and then it forms mercury metal and then plus 2 Cl minus. I can use saturated potassium chloride solution and when you measure the E M F of this it shows you 0.246 volts versus standard calomel electrodes.

So, if you this is known as standard calomel electrodes. Mercury, mercuric chloride solution, mercurous chloride solution in presence of standard KCl solution that is saturated that one. So, Hg 2 Cl 2 if it is a same reaction can be represented, but it shows 0.280 versus standard hydrogen electrodes. So, Ag Ag C l will show you 0.237 volts.

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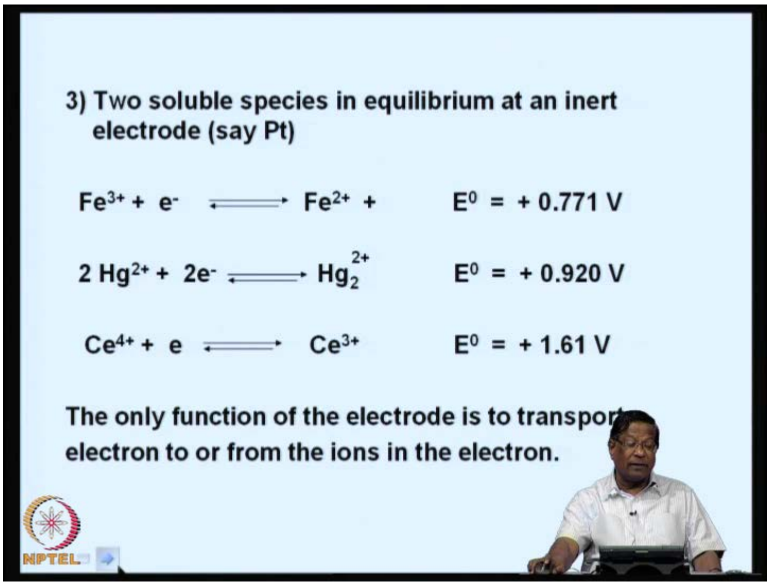

3) Two soluble species in equilibrium at an inert electrode (say Pt)

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

So, all these reactions can be used as reference electrodes. Now, let us look at the third look at the third kind of electrode electrodes, we normally come across this is nothing but two soluble species are there; that means, the oxidized state is also a solution and reduced state is also a solution earlier. We had zinc as the reduced state and Zn 2 plus that is the bivalent zinc ions were in the oxidized state.

Similarly, silver Ag plus, plus Cl minus going to Ag Cl in silver is the reduced species that is a metal and Ag plus is a solution. So, we have oxidized are reduced species in solution our oxidized species as solution and reduced species as the…

Now, I am looking at systems in which the oxidized species also a solution and reduced species is also a solution, examples include ferric and ferrous; ferric solution contains Fe 3 plus and ferrous solutions contains Fe 2 plus. So, Fe 3 plus, plus electron goes to Fe 2 plus look at this reaction please and you will see that ferric ion, will pick up one electron to give you Fe 2 plus; that means, when it picks up a negative charge positive charge should go down by one unit and it gives you a Fe 2 plus.

And E naught for this reaction when compare to a standard hydrogen electrode is 0.77 volts. Similarly, I can have two mercurous ions and two electrons going to Hg mercuric ion 2 Hg 2 plus and this reaction is briefly referred as mercurous to mercuric this is ferric to ferrous, then I can have ceric to cerous mercuric to mercurous and ferric to ferrous ceric to cerous.

On the left side, I have the oxidized species on the right side, I have the reduced species in the same convention and, but the only difference is this Fe 2 plus is in solution, Hg 2 plus is in solutions Ce 3 plus is in solution; that means, we do not have a metal electrode corresponding to either Fe 3 plus or Fe 2 plus, mercurous and mercuric, ceric and cerous. So, what are the electrodes the electrodes are basically inert electrodes something like platinum they do not take part in the reaction.

The only function of the electrode is to transport the electron to or from the ions in the solutions this is known as electrodes of the third kind. Now, I would like to summarize again, a metal ion in solution and equilibrium with a metal electrode same metal, same ion that is electrode of the first kind. Electrode of the second kind is a metal ion in equilibrium with its own solution, but the solution is saturated with respect to a salt; that is a second kind, third kind is oxidized species also in solution, reduced species is also in solution. I have two platinum electrodes dipping in ferric and ferrous solutions, ceric and cerous solution, and mercuric mercurous solution etcetera.

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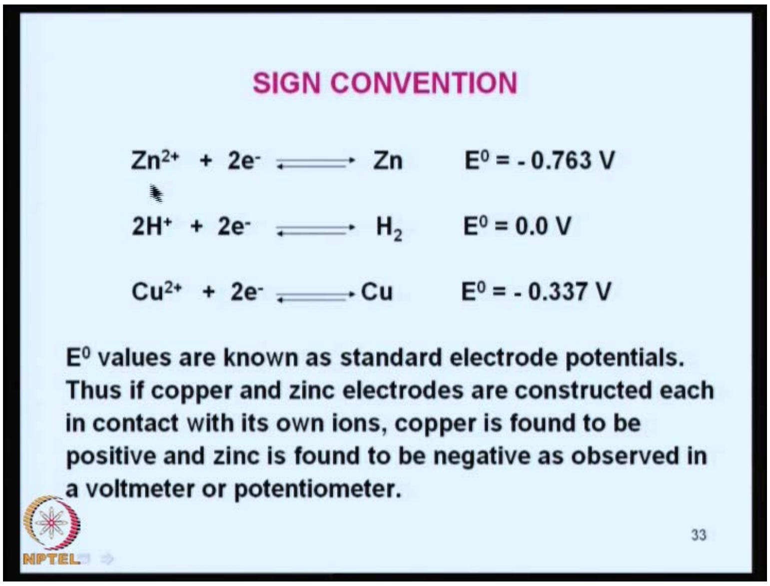

SIGN CONVENTION

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

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

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

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.

And the sign convention says that zinc 2 plus, plus two e minus, this is how we are writing? It shows0.763 volts and hydrogen electrode, I am writing in the same way H plus on the left side, electrons on the left side and reduced species on the right side, it shows 0.00 and Cu 2 that is E naught and Cu 2 plus, plus 2 e minus going to Cu; that is minus 0.337 volts.

So, one is a reducing agent, one is an oxidizing agent and this is a neutral agent that is 00. So, the E naught 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 a potentiometer. So, this is what? The convention says that your right the oxidized species on the left and reduced species on the right.

Now, let us define a little some more terms with respect to electrochemistry which you come across very regularly, one is one is reversibility, what is reversibility? A half cell what we have written, so far, is said to be reversible, if a change in the direction of the current flow reversibly half reaction; that means, most of the half cells act reversibly in normal solutions, normal circumstances consider this zinc zinc chloride system itself.

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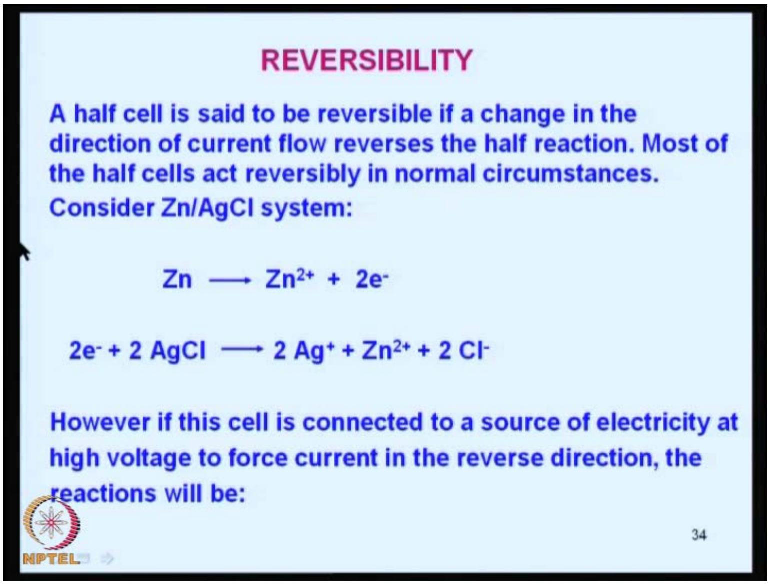

REVERSIBILITY

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:

The half cell it says zinc goes to zinc 2 plus, plus 2 electrons and on the other side 2 electrons released from zinc this zinc system will react it 2 Ag Cl to produce silver plus ions and zinc ions. So, if this cell is connected to a source at high source of electricity to force the current to move in the reverse direction, the reaction will be the other way; that is the instead of current coming from zinc to silver. So, it will flow from say zinc to silver to zinc.

So, the all these reactions are reversible; that means, you change the polarity current will go from positive to negative and you change the polarity again, it will come back to this negative to positive all you got to do it is a question of choosing the right way. So, if you want to coat zinc, coat silver on zinc then what you should be doing is silver should be dissolving and then depositing on zinc. So, if you reverse the reaction you can collect the zinc from the collect silver from the zinc electrode. So, the electroplating reactions are mostly based on this type of considerations.

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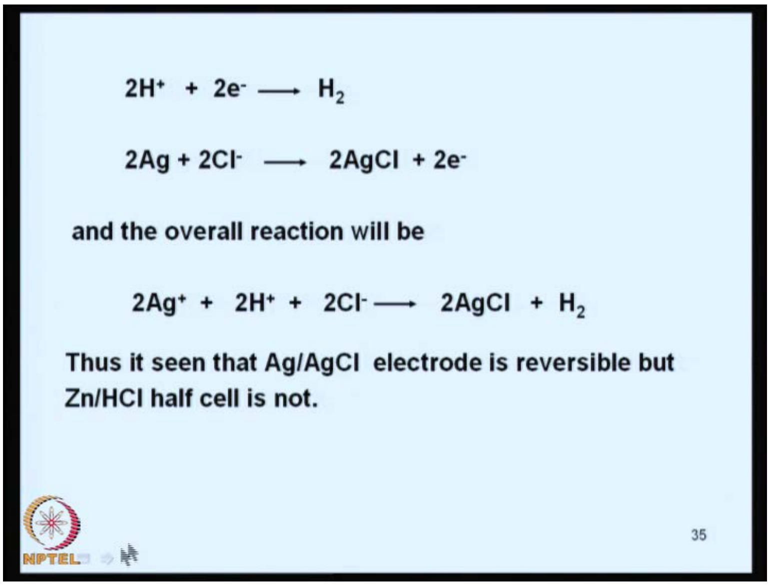

$$2H^+ + 2e^- \longrightarrow H_2$$

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

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.

So, now look at this reaction 2 H plus, plus 2 e minus goes to H 2 2 Ag plus 2 Cl minus goes to 2 Ag Cl, plus 2 electrons, this is what happens in the silver silver chloride system. Because, there is some acid also H plus goes to H 2. So, the overall reaction of this reaction would be we I just add this two and two electron and two electrons will cancel. So, we write 2 Ag plus this reaction plus 2 Cl minus and 2 H plus goes to 2 Ag Cl and H 2. Thus, it is seen that silver silver chloride electrode is reversible, but zinc half cell is not reversible. So, we can carry out this reaction only in one direction. So, not all reactions are reversible, but some reactions are reversible, some reactions are not reversible depending upon the thermo dynamic properties.

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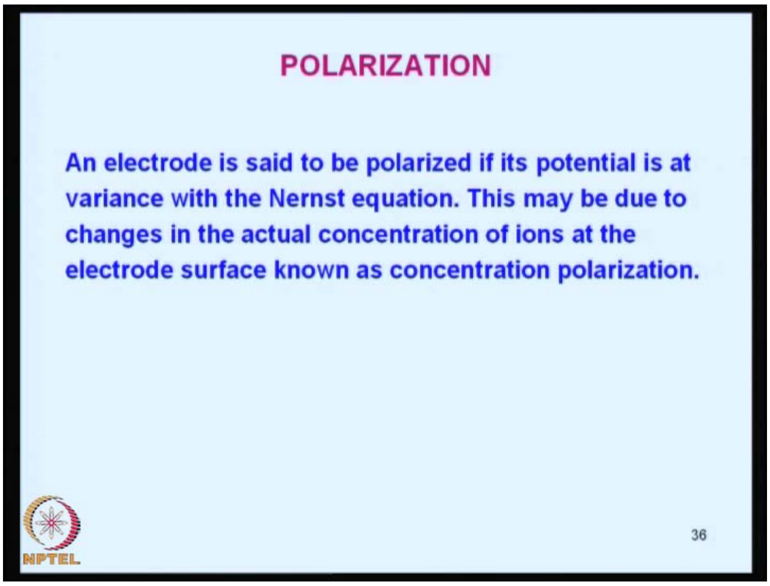

POLARIZATION

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.

Now, another term I want to describe to you is 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 the ions at the electrodes surface known as concentration polarization. This is a very important concept, I wish you spend more time to understand this concept and also I refer you to some standard text books to understand the this polarization reaction; that means,

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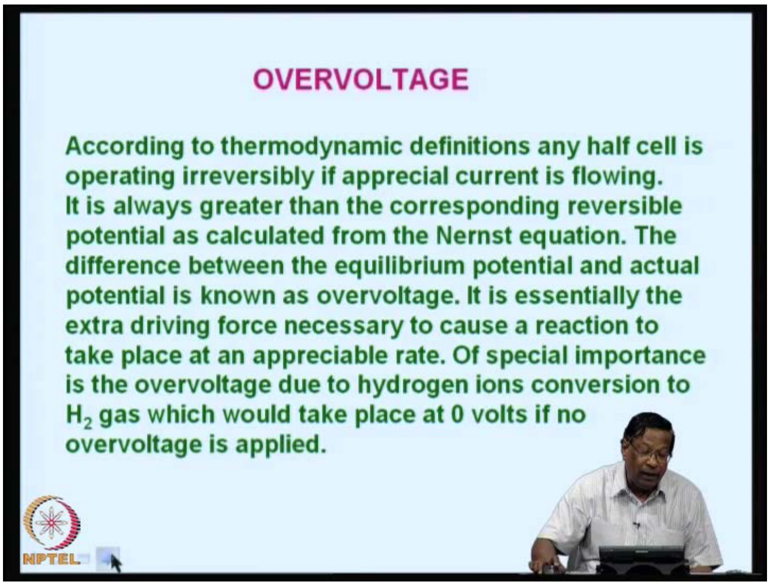

OVERVOLTAGE

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.

If you see any variation from the applied voltage, what you are expecting? If, it is not there it means there is some moment of polarization here I give additional potential, but the reaction does not occur. So, what happens to the charge only when the charge is passing through then the reaction will proceed, but you apply the potential it does not precede in the reaction, proceed in the correct way? So, it will show you the higher applied potential, but no reaction. So, that is polarization.

We will come back to polarization again, but that is a term I wanted to introduce on you tube and another concept is over voltage. According to thermo dynamic definitions any half cell is operating irreversibly, if appreciable current is flowing if the current is flowing the reaction is going in one direction; that means, it is operating irreversibly it is always greater than the corresponding reversible potential as calculated from the Nernst equation. Otherwise it cannot go in the reversible direction, the Nernst equation, what you calculate? If, the potential is greater than that the reaction will be preceding continuously; that means, you are giving energy more than the Nernst equation demands.

So, the difference between actual equilibrium potential and the actual potential is known as over voltation; that means, you are giving extra voltage to the system. And the what it means; it is essentially extra driving force we are giving to the system energy you can call it force necessary to cause a reaction to take place at a appreciable rate at an appreciable rate, of special importance is the over voltage due to hydrogen ions conversion to hydrogen gas which would take place at zero volts if no over voltage is applied.

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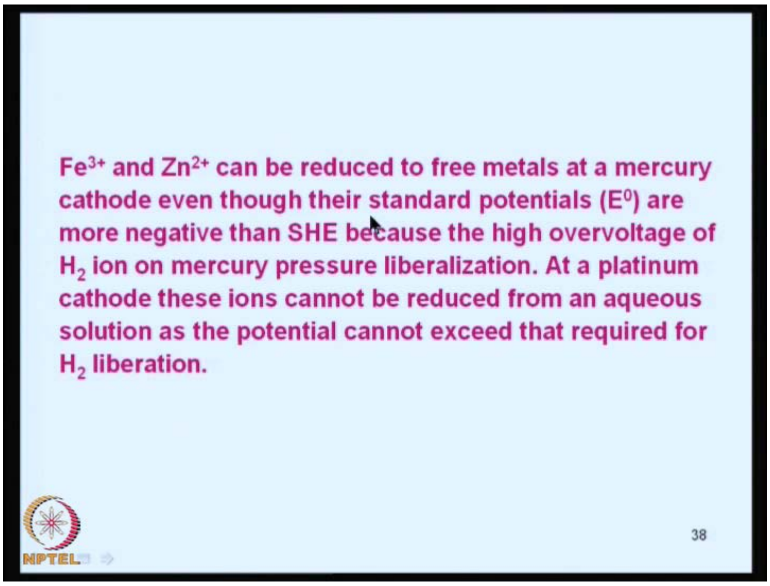

Fe^{3+} and Zn^{2+} can be reduced to free metals at a mercury cathode even though their standard potentials (E^0) are more negative than SHE because the high overvoltage of H_2 ion on mercury pressure liberalization. At a platinum cathode these ions cannot be reduced from an aqueous solution as the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

So, this over voltage is another concept very important in your day to day operations. For example, ion 3 plus and zinc 2 plus can be reduced to free metals at a mercuric cathode even though their standard potentials are more negative than standard hydrogen electrode. Because, we are applying high over voltage of hydrogen ion on mercury and there is libration of hydrogen.

At a platinum cathode these ions cannot be reduced from an aqua solution, as the potential cannot exceed the required rate for hydrogen liberation. So, the based on the chemical reactions what we have described. So far, is a number of analytical techniques have been developed either by the measurement of measurement of the voltage, current and resistance etcetera.

And I would like to explain to you, what are these basic analytical techniques? That we have been employing one is potentiometer; that is direct application of the Nernst equation through the measurement of potentials of non polarizable electrodes under conditions of zero current.

You apply an additional voltage, the reaction will proceed, how long it will proceed? Until the applied applied voltage becomes extra voltage becomes zero; that means, until the reaction attains equilibrium. So, potentiometer is the direct application of the Nernst equation through the measurement of the potentials of non polarized electrode and none equalized under non equilibrium conditions.

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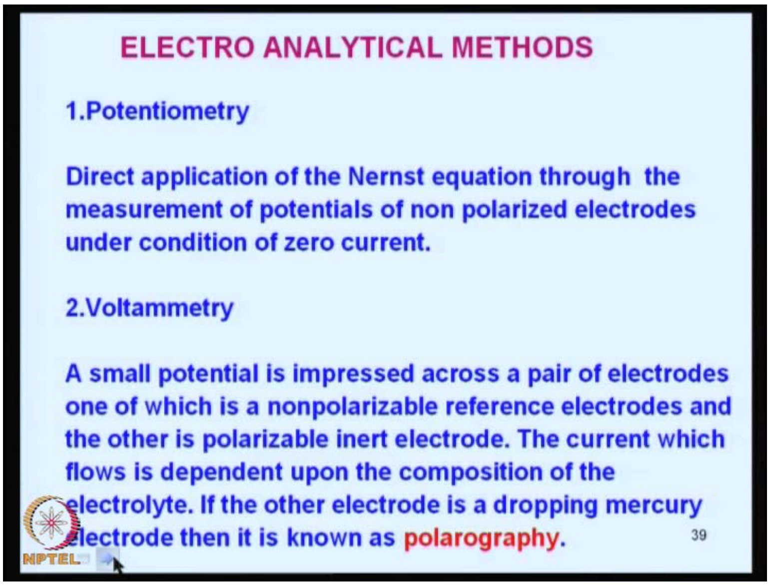

ELECTRO ANALYTICAL METHODS

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, another technique is voltametry here, what we do is? A small applied current is impressed across a pair of electrodes; one of which is a non polarizable reference electrode; that means, you apply any amount of voltage it would not take the it would not show you a chemical reaction. So, the electrode is said to be non polarizable

Now, in voltametry we are using a non polarizable reference electrode and the other is polarizable and that is an inert electrode, the current which flows is dependent upon the composition of the electrolyte. So, if the other electrode with a dropping mercury electrode then it is known as polarography. So, in polarography is another technique in which the voltage our current is measured in which the electro one electrode is non polarizable and another electrode is polarizable.

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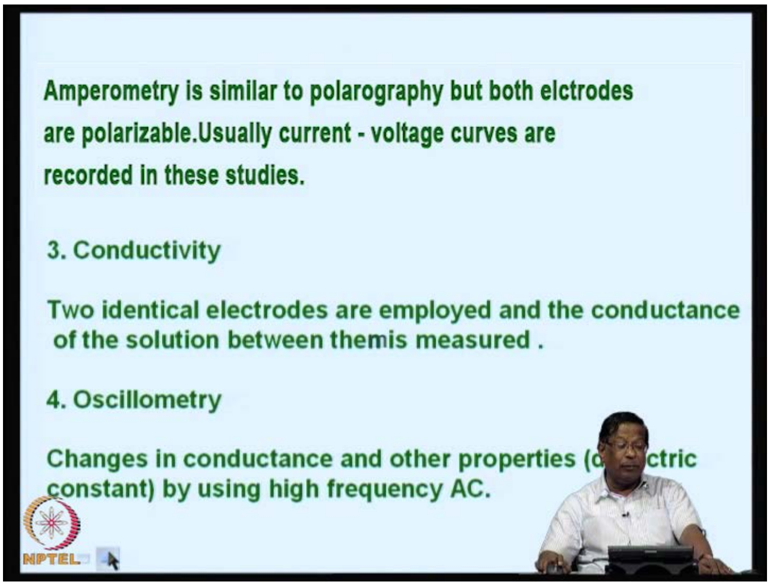

Amperometry is similar to polarography but both elctrodes are polarizable.Usually current - voltage curves are recorded in these studies.

3. Conductivity

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

4. Oscillometry

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

Amperometry is similar to polarography, but both electrodes are now polarizable usually current voltage curves are recorded in these studies. Now, there is a small error here it is actually it is not H capital, it is not polarography and usually current voltage curves are recorded in these studies. So, third is conductivity we can take two identical electrodes and conductance of the solutions between them is measured. Oscillometry changes in the conductance and other related properties such as dielectric constants are measured by using high frequency alternating current.

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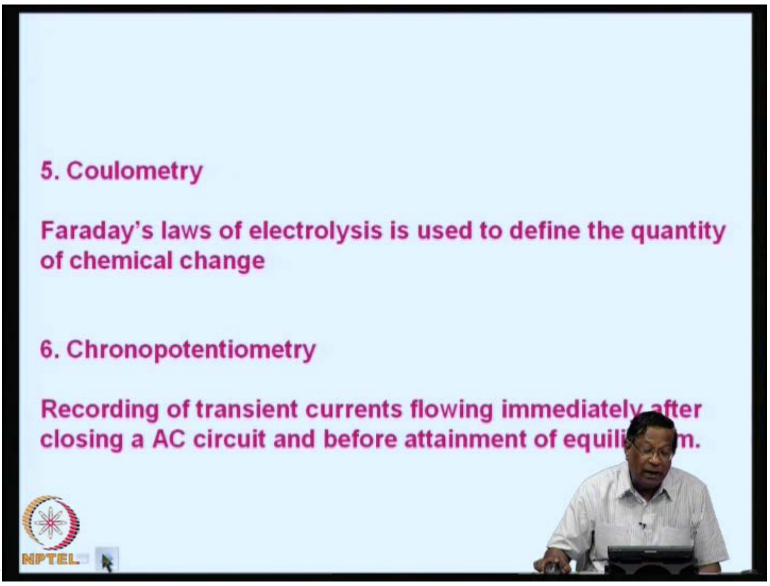

5. Coulometry

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 equili m.

The another technique is coulometry; that is use of faraday's laws of electrolysis to define the quantity of chemical change depending upon the amount of electricity, we pass through the solutions; that means, you pass one faraday one colon and then the equivalent quantity of the substance should be deposited. So, electro deposition techniques are based on coulometry and chronopotentiometry is recording of transient currents flowing immediately after closing an AC circuit, but before attainment of the equilibrium that is transient changes as and when they occur before they attain the equilibrium is, what I measure in chronopotentiometry? We do not have to really worry about these techniques, because I am not going to teach you all of it, I am going to teach you only polrography and potentiomeetry.

So, other things you can look them up in standard text books, but if you understand potentiometry and polarography you will understand most of the other concepts in other analytical techniques. I have described earlier with respect to potentiometry, voltametry amperometry, coulometry, conductimetry and then chronopotential all these things will become very simple, if you understand the potentiometry and polrography.

Now, the requirement is most of the concepts of electro chemistry are defined in this two techniques. Therefore, if you understand these two techniques we would we would not have any difficulty in understanding other techniques, whenever there is a need for you to go for those techniques or you want to study for you can study on your own.

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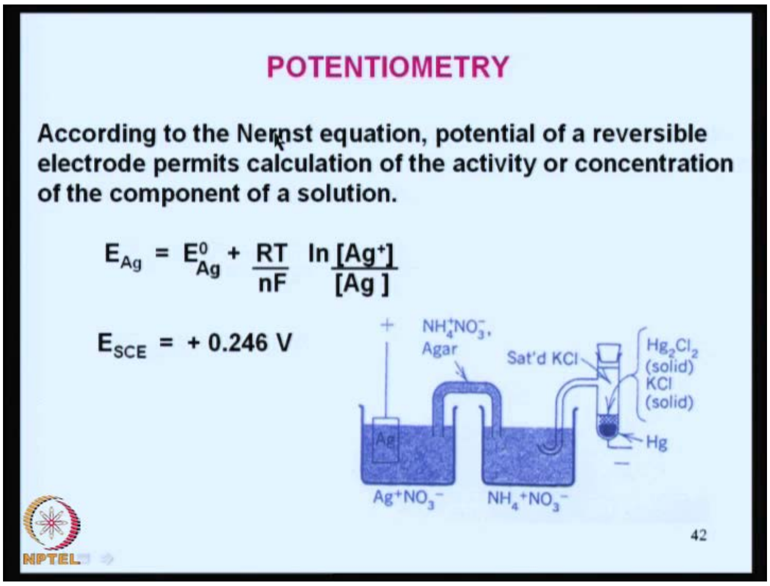

POTENTIOMETRY

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

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

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

Now, I want to take you to potentiometry, the potentiometry is a separate science by itself and according to the Nernst equation potentials of a reversible electrode permits the calculation of the activity or concentration of the components of a solution. For example, here I am showing you a silver nitrate solution and with a cataion here and another beaker contains ammonium nitrate solution and then it is connected to calomel electrode; that is Ag 2 Cl 2 that is electrode of the second kind. Mercurous chloride in KCl and then inert electrode and you take a wire from the bottom containing mercury that is Ag 2 Cl 2 plus chloride plus mercury.

So, this is a reference electrode, calomel electrode is one which we use very regularly for most of the reference works and silver silver chloride electrode is has got its own other uses and it is much still simpler to use silver silver chloride electrode compared to calomel electrode, but commercial versions of calomel electrodes are available you can easily buy them in the market. And use them for your studies this is one of the reasons why electro chemistry has become so popular, because most of the chemical components cost almost nothing we can just with the modest investment you can set up an electro chemical laboratory and do high quality of work.

So, coming back to this potentiometry we can write the equation here in the in this slide. Basically, what is happening I have my silver solution and then there is a salt bridge containing ammonium nitrate and agar and the one end is dipped in silver nitrate and other end is dipped in ammonium nitrate solution and which is connected electrically to the calomel electrode and this silver electrode is here and both this and minus are connected to a potential source a like a battery or other systems. So, this is the system.

Now, I can write an equation like this E Ag that is potential of silver ion is nothing but standard electro potential of the silver ion E naught Ag plus RT by nf ln oxidize the state by reduced state. For example, in this standard form of expression and silver without charge is metal that is at the bottom of this equation as the denominator and silver plus is this thing and since most of the metals have got activity as one, we can write E naught E Ag is equal to E naught Ag plus RT by ln Ag plus, because ln Ag is 1. So, against this we have E SCE is saturated calomel electrode is connected and that has got a standard voltage of 0.246 volts.

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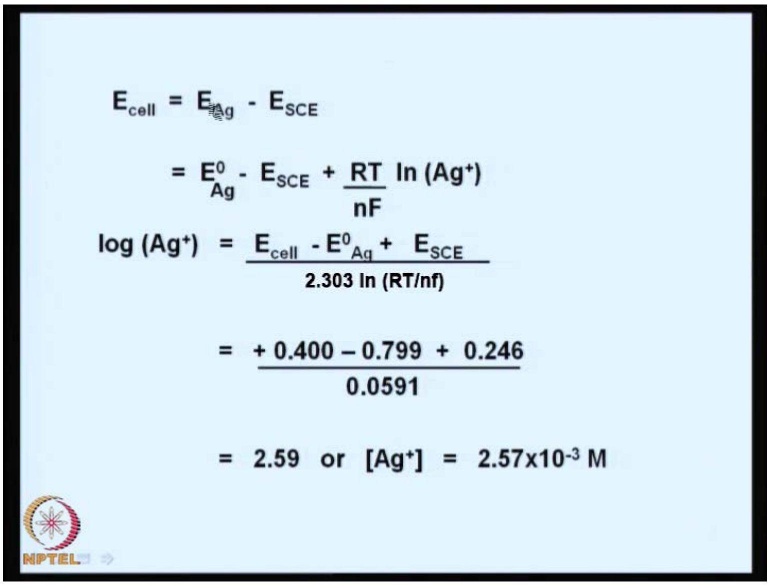

$$E_{cell} = E_{Ag} - E_{SCE}$$

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

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

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

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

Now, look at it when we connect both these two we get some amount of current electric potential. So, the potential of the cell potential of the cell is given by E Ag minus E SCE; that is we can write E Ag as E naught Ag plus RT by nf ln Ag plus E SCE remains the same. Now, E cell I can rearrange this equation as log Ag plus is equal to E cell minus E naught Ag, plus E SCE and transferring this on the other side and divided by 2.303 RT by nf. So, that is converted to logarithmic scales. So, by putting the numerals each cell is 0. 400 E naught Ag is 0.799 and this is 0.246 that is calomel electrode and divided by 2.303 RT by nf; that is that is a standard value is 0.0591 this multiply or when you put all the constant in this.

It is a good number to remember, because RT by nf to multiplied by 2.303 is 0.591. So, when you solve this you get ln log Ag plus is equal to 2.59 or convert it into silver concentration Ag plus is equal to if you had to take the antilog of this, that would give you 2.57 into 10 raise to minus 3 molar; that means, when you have this cell when you have this cell and if it shows you the 0.400 volts at the concentration of silver should be E 2.57 into 10 raise to minus 3 just by measuring the potential just by measuring the potential.

Now, putting all the thermo dynamic equations was able to calculate, how much of silver is there in the solution? Just by measuring the potential that is the beauty of potentiometry, you measure the potential you can straight away calculate the concentrations of silver chloride silver silver chloride both of them you can, but it is the actually the what you are measuring the activity for our for our convenience we are not taking activities into consideration. Because, most of the solutions what we are dealing with are suppose to be dilute solutions especially in potentiometry and voltametry and activity coefficient is almost taken to be same as one that is concentration and activity are almost replaceable in each of this.

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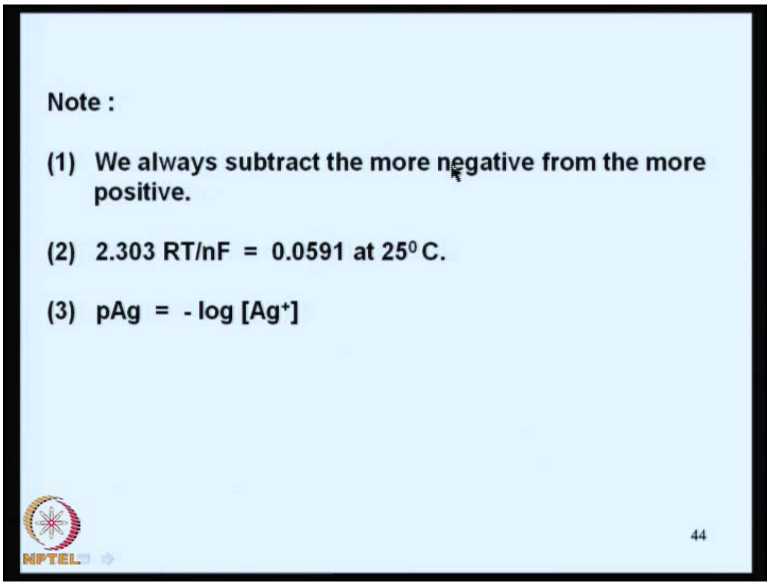

Note :

(1) We always subtract the more negative from the more positive.

(2) 2.303 RT/nF = 0.0591 at 25^0 C.

(3) pAg = - log [Ag^+]

We will also further note that the we always subtract the more negative value from the more positive value; that means, the natural reaction it should be, but the output should be positive more negative should be subtracted from the more positive and then 2.303 RT by nf is 0.0591 and P Ag is nothing but negative log of Ag. So, if you remember this is a form of notation actually third one negative or instead of writing negative log of Ag plus, we are simply writing p Ag the significance will become very clear to you very shortly, because when we write H plus we get p H plus p H.

So, as an another example consider a cell of platinum electrode dipping in 0.1 normal ferrous sulphate with standard calomel electrode, saturated calomel electrode is as another unit; one is an electrode, platinum electrode dipping in a concentration of in a solution of ferric.

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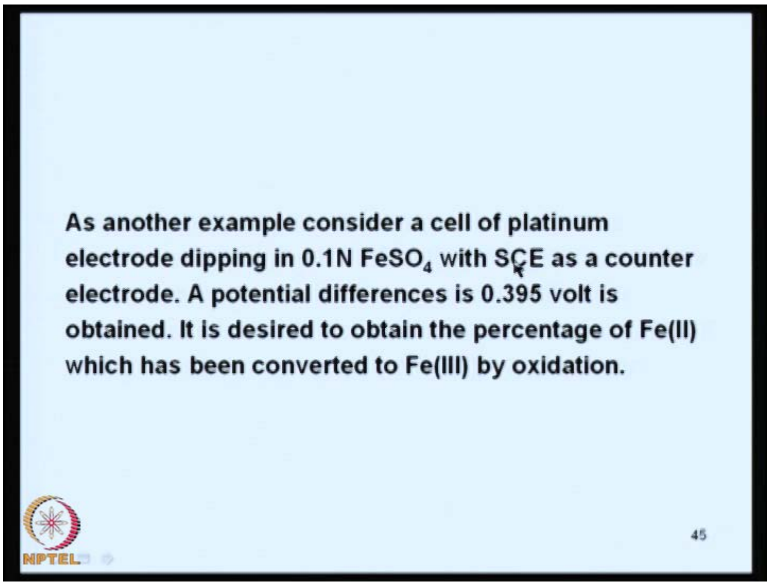

As another example consider a cell of platinum electrode dipping in 0.1N $FeSO_4$ with SCE as a counter electrode. A potential differences is 0.395 volt is obtained. It is desired to obtain the percentage of Fe(II) which has been converted to Fe(III) by oxidation.

And connected to a salt bridge in another system, the salt bridge is connected to saturated calomel electrode. Just like, what I had shown you in the previous one, here this is solution of ion solution with a platinum electrode the remaining part remains the same, the rest of it remains the same.

So, if you consider such a cell potential difference of about 0.395 volts is obtained you just connected to SHE and standard electro battery and what you will be observing is 0.395 volts let us it is only an example. It is desired to obtain the you can calculate actually the ferrous which has been converted into ferric; it is a very simple reaction basically what we write is like this E M F of ferric to ferrous electrode that is actually platinum electrode the species are ferric to ferrous in contact with each other is nothing but, the standard electrode potential of ferric ferrous with respect to hydrogen electrode that is available from the table, which I had shown you earlier plus RT by nf ln Fe 3 plus by Fe 2 plus; that is ferric ferrous oxidized species divided by the negative species concentrations actually.

So, if you measure the E cell actual difference and connected we can write as E Fe 3 plus by Fe 2 plus plus RT by nf ln Fe 3 plus by Fe 2 plus this is actually E cell, you can rearrange these equations this equation actually at log of Fe 3 plus by Fe 2 plus and retaining on the left hand side, E cell on the right hand side actually E cell minus, this I am transferring this side that is minus E naught Fe 3 plus etcetera. And then E SCE standard electrode, calomel electrode should come there and then divided by RT by nf that is 0.0591 volts.

So, the voltage what you are getting is minus 2.20 that is not the voltage actually it is minus 2. Minus 2.20 is the number what you are getting by reorganizing this this tells you that the ferric taking antilog of this ferric to ferrous would be nothing but 6.3 into 10 raise to minus 3 take the antilog of this; that means, 0.63 percent; that means, 0.63 percent of the ferric ferrous solution has been converted in a given solution. If you connect 0.1 molar ferrous sulphates with standard calomel electrode and you are getting 0.395 volts just by knowing the value of 0.395 volts we are able to calculate, what is the ferric concentration and what is the ferrous concentration? Whether it is pure ferric or not, so pure ferric.

So, it is a very useful entity which can, which tells you that whether a given system is, in what condition that is, if the subject if the more of ferric and less of ferrous is there you would get ratios nearer to one and if more of ferrous and less of ferric is there; that means, if the chemical is impure you would get higher ratio. So, just by knowing the E M F, you can calculate the actual concentrations.

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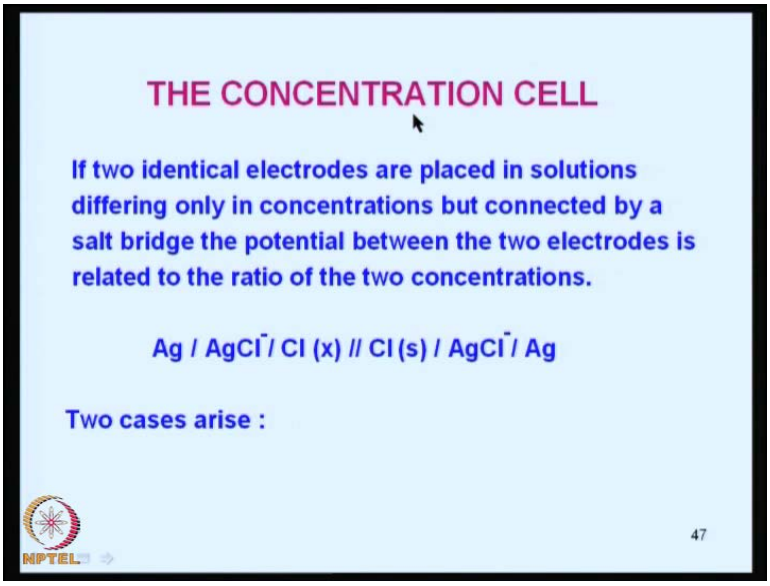

THE CONCENTRATION CELL

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.

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

Two cases arise :

Similarly, consider another system in which I have two similar electrodes, but dipped in solutions of different concentrations we can take a look at this. If two identical electrodes are placed in solution 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. Consider for example, this this cell here, I have put silver electrode in a solution of silver chloride and connected with a chloride solution of having concentration x and that is one half cell the other half cell is chloride solution of a standard standard chloride solution having same silver chloride and silver electrode Ag Ag Cl electrode we call this.

So, actually this is known as junction potential. Junction I have silver silver chloride electrode dipped in a solution of chloride solution of unknown x, but it is connected with a salt bridge to another solution containing a none amount of chloride that is standard, but silver another silver silver chloride electrode has been dipped in that.

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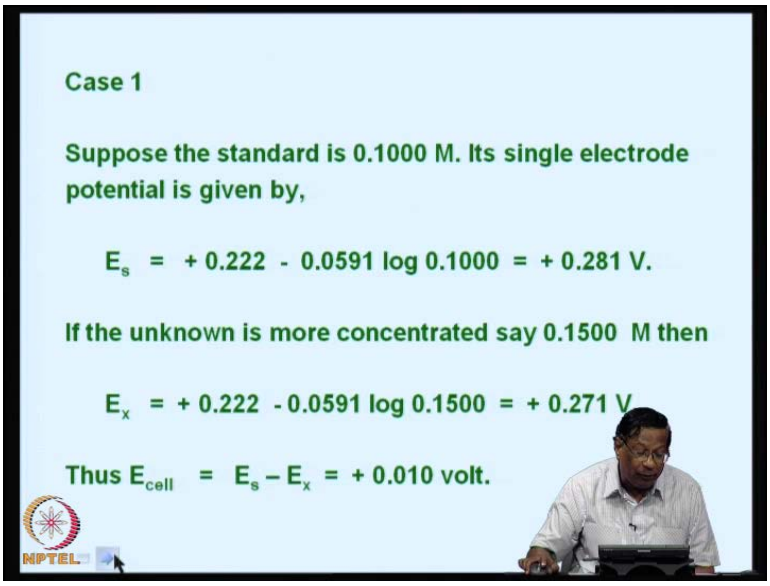

Case 1

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

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

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

So, we can look at the system like this suppose the standard is 0.1000 M molar it is a single electrode potential is given by Nernst equation; that is E standard is equal to0.222 volts, minus 0.0591 volts log of the oxidized species that is concentration log of the concentration of the oxidized species that is 0.1000 M here reduced species is one, because it is metal and that value is 0.281 volts. If, the unknown is more concentrated let us say 0.1500 molar, here it is 0.1000, here it is 0.1500 then E x unknown, I can write like this 0.222 volts, minus 0.059 volt, 0.591 same equation. I am rewriting as on the top and log of point instead of 0.100 I am going to write 0.1500, since the electrodes are same since the silver silver chloride and silver on the left and right are same they cannot contribute to any difference in the voltage what you observe, but the only difference should come from the concentration of the standard and the unknown. So, we can calculate, actually E cell you can measure by connecting the electrode connecting the solutions to a source of electricity, what you would see? Is 0.1 volt flowing through and that is nothing but, E standard minus E x standard, E x unknown.

Now, imagine I have a solution of 0.68 molar then I can write a similar equation and E cell is equal to 0.010 volt just go back for 0.1 and 0.15 you are getting 0.01volt.

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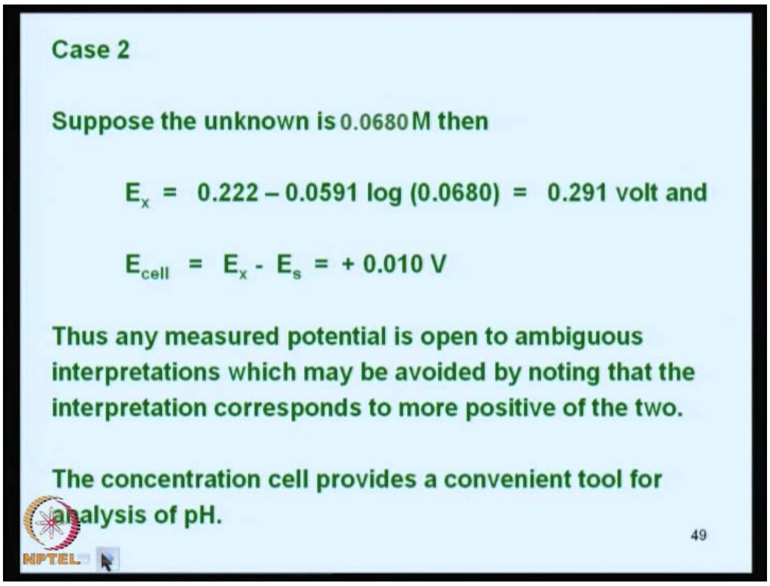

Case 2

Suppose the unknown is 0.0680 M then

$$E_x = 0.222 - 0.0591 \log (0.0680) = 0.291 \text{ volt and}$$

$$E_{cell} = E_x - E_s = +0.010 \text{ V}$$

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.

And even when the unknown is changed to 0.680 you are still getting 0.010 volt. So, any measure potential is open to ambiguous interpretations which may be avoided by noting that the interpretation corresponds to more positive of the 2. So, the concentration cell; this is a concentration cell it provides us a convenient tool for the measurement of p H. How we will see later. Thank you. .