Bio-electrochemistry

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Lecture – 10
Nernst Equation

Welcome back to the lecture series in Bio-electrochemistry. So, today we are into the 10th lecture or the last lecture of the second week the 5th lecture of the second week.

So, as of now we have talked about the standard potentials and today we will be concluding this week with the Nernst equation. As I told you that we are running slightly off because we are supposed to do the different kind of electrodes and potentiometry, but I purposefully devoted this week on the basic fundamentals. And today is todays class is kind of this is one of the most important and critical aspects what we are going to deal that is Nernst equation. Nernst equation as a genesis it was formulated by water Nernst back in the last decade of 18th century around 1890 yes series of papers, which talked about he worked on several areas, but one of the areas what will be talking today is about EMF electro motive force.

So, as of now just even before I give you the basic concept and the write up of the Nernst equation let us recollect during our standard 8th or 9th or 10th we read about le Chatelier’s principles those who have forgotten just recollect say for example, there is a reaction taking place say a plus b is equal to c plus d or a plus b reversible like you know will make 2 products c plus d.

So, now we always remember that if the concentration of a plus b is higher than the product or the reactant if the reactant which is on the left hand side a plus b giving rise to c plus d. So, if a plus b concentration of a plus b is higher then automatically the reaction will proceed towards right direction or towards making more product, but say for example, it is a reversible reaction if a c plus d or the product concentration is higher than the reaction will move on the reverse direction it will make a and b of course, within the framework of thermodynamics if it is being allowed and what sort of energy to be needing, but this is what we have learned and based on that le Chatelier’s principle we had the activity coefficients and we have developed k is equal to if you remember absolute c multiplied by d divided by a multiplied by b and all these things you all have studied at some point or other.

So, the key question what Nernst equation or Nernst himself tried to answer in terms of the EMF and as well as taking the analogy of le Chatelier's principle is what will be the driving force could we calculate the driving force on a reaction like this a plus b the reversible arrows to c plus d, what is the total driving force. In other word having said this let me give you a philosophical situation or much more I would say a practical situation and then the philosophical scientific philosophical thinking behind it.

So, say for example, we have we have talked about the silver and cadmium electrode you remember and we remember that in the cadmium we are having the oxidation and in this silver we are having the reduction right. So, the electrons who are leaving the cadmium electrode in the outer circuit and they were being drawn by the silver electrode on the right hand side like on the left hand side, we had cadmium on the right hand side we have the silver if you recollect if I just go back of where we have drawn that kind of electrodes.

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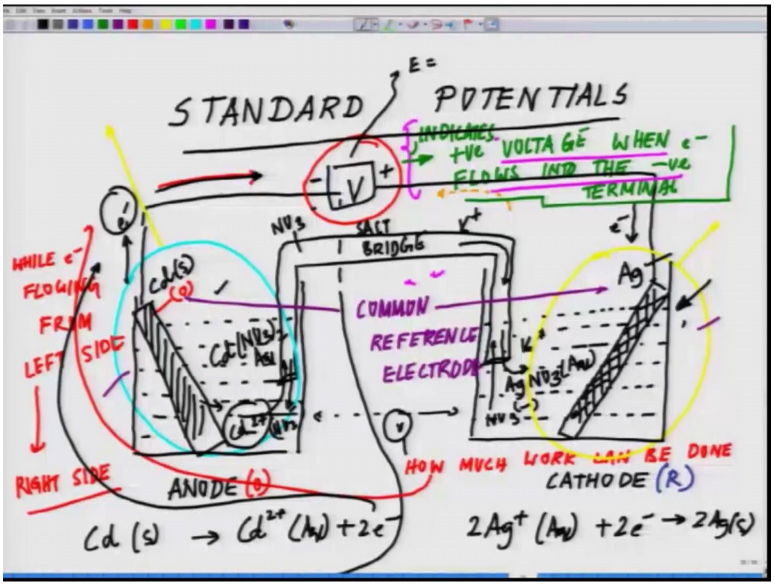

STANDARD POTENTIALS

$Cd(s) \rightarrow Cd^{2+}(Aq) + 2e^-$

$2Ag^+(Aq) + 2e^- \rightarrow 2Ag(s)$

So, here you see the cadmium electrode here you see the silver electrode and the electron is traveling like this. Now say for example, in this in this situation where we actually calculated the standard potentials of cadmium as well as silver what will be the driving force could we calculate the total driving force in this situation, that is because if you remember we never given any value of the e here ok.

So, what is the driving force which you will drive the electrons which will make it to do the work from moving from cadmium to the silver electrode solid silver electrode? So, this is what Nernst equation has addressed and that is what we are going to talk about today. So, let us resume the lecture.

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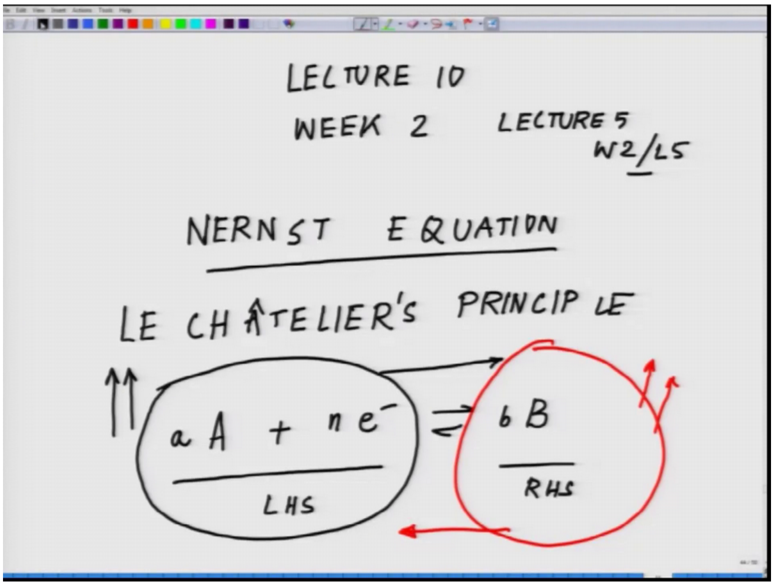

LECTURE 10

WEEK 2 LECTURE 5

W2/L5

NERNST EQUATION

LE CHÂTELIER's PRINCIPLE

$$aA + ne^- \rightleftharpoons bB$$

LHS

RHS

So, this is our lecture 10 Week 2 lecture 5 of week 2 W 2 l 5 and the topic what we are dealing today is Nernst equation.

So, as I told you le Chatelier’s principle tells us that increasing the reactant concentration drives a reaction to the right and increasing the product concentration drives the reaction to the left this is what le Chatelier’s principle tells us. So, in other word if we write a reaction like this plus n e make it B.

Now, if the concentration so this is on the left hand side lhs and this is on the right hand side RHS. So, now if the concentration on this side is more so the reaction will proceed if the concentration is more reaction will proceed towards right. Similarly let us use another color if the concentration here is more than the reaction will proceed towards the left and what Nernst equation tries the net driving force for a reaction is expressed by Nernst equation.

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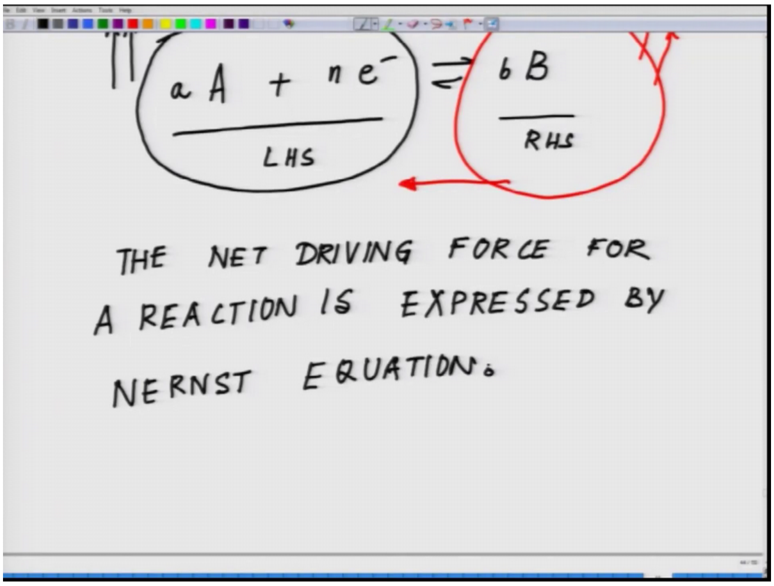

$$aA + ne^- \rightleftharpoons bB$$

THE NET DRIVING FORCE FOR A REACTION IS EXPRESSED BY NERNST EQUATION.

The net driving force for a reaction is expressed by Nernst equation and whose 2 terms include. So, if I put the Nernst equation in place. So, it has 2 basically 2 terms.

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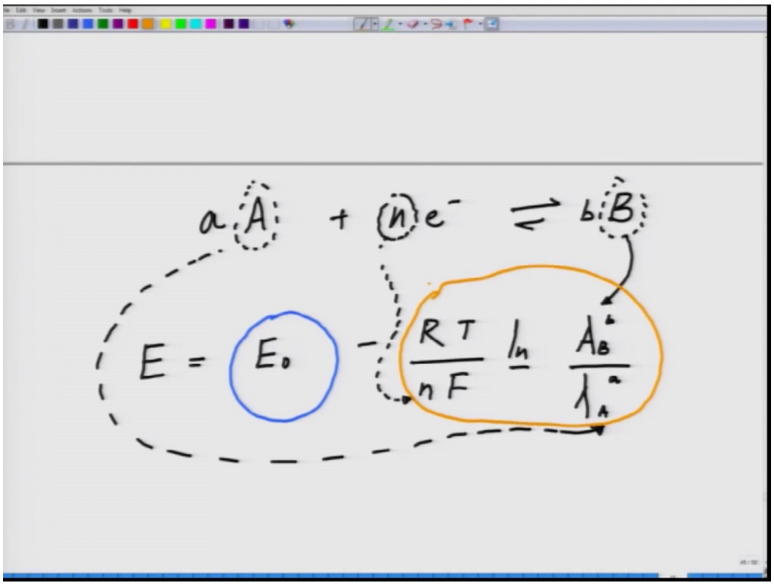

$$aA + ne^- \rightleftharpoons bB$$

$$E = E_0 - \frac{RT}{nF} \ln \frac{A_B^b}{\lambda_A^a}$$

So, the Nernst equation for reaction what just now I showed say for example, if this is the reaction and if I had to put the Nernst equation in place? So, it will be e which is in volt standard potential E 0 minus gas constant absolute temperature number of electron faradays constant natural log this is the natural log and concentration of B concentration of a.

So, essentially what I am talking about is reactant is to the product A and this is your number of electrons what is being shown here. Now if you look at this equation there are 2 terms 1 is the standard potential and there is another term this is your standard potential term and this is the second term, which is what are these 2 terms signifying the net driving force for a reaction as we have said is governed by the Nernst equation and whose 2 terms include driving force under standard conditions.

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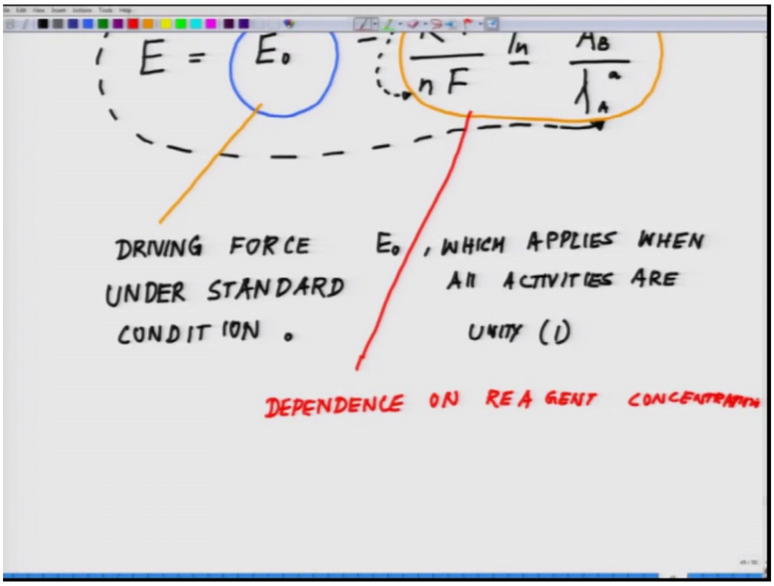

DRIVING FORCE UNDER STANDARD CONDITION.

E0, WHICH APPLIES WHEN All ACTIVITIES ARE UNITY (1)

DEPENDENCE ON REAGENT CONCENTRATION

So, this is essentially the driving force under standard condition this is one the first term which is where basically E 0, which applies when all activities are unity we have already talked about it when all activities are unity or in other 1 and the second one the, second term which is this term pull it out this second term is showing the dependence on reagent concentration and if you see the second term reagent concentration. Now what does that physically means is a physical meaning to this 2 things and for that I will be again going back taking help of the diagram here to make you understand.

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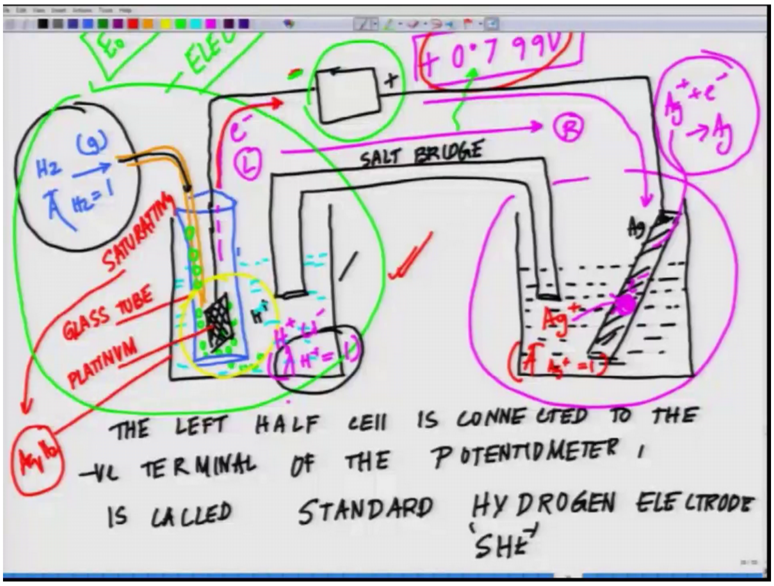

THE LEFT HALF CEll IS CONNECTED TO THE -ve TERMINAL OF THE POTENTIOMETER, IS CALLED STANDARD HYDROGEN ELECTRODE 'SHE'

So, say for example, when we were talking about the standard potential out here standard potential out here, whether it was cadmium whether it is silver when we were measuring the standard potential we assume everything is unity all concentration everything is unity and we calculate the standard potential. Which is not a not an issue, but the problem is in real life there may be situation, where it is not essential that everything will be unity I may vary the concentration on say silver side, I may vary the concentration on the cadmium side for 1 unit I know this is it with that I have to add for that main unit how much it will be something like that analogy.

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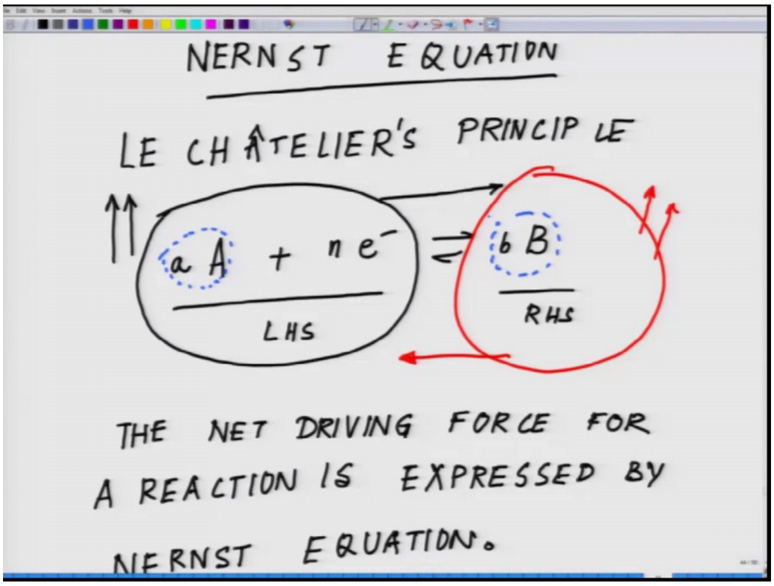

NERNST EQUATION

LE CHÂTELIER's PRINCIPLE

$$a A + n e^- \rightleftharpoons b B$$

THE NET DRIVING FORCE FOR A REACTION IS EXPRESSED BY NERNST EQUATION.

So, if they are not unity if the concentration, if this value what we talk about now coming back having shown you this if out here. If these values are not unity, if this is not unity or if this is not unity, then this second term what you see which is coming here will come into play.

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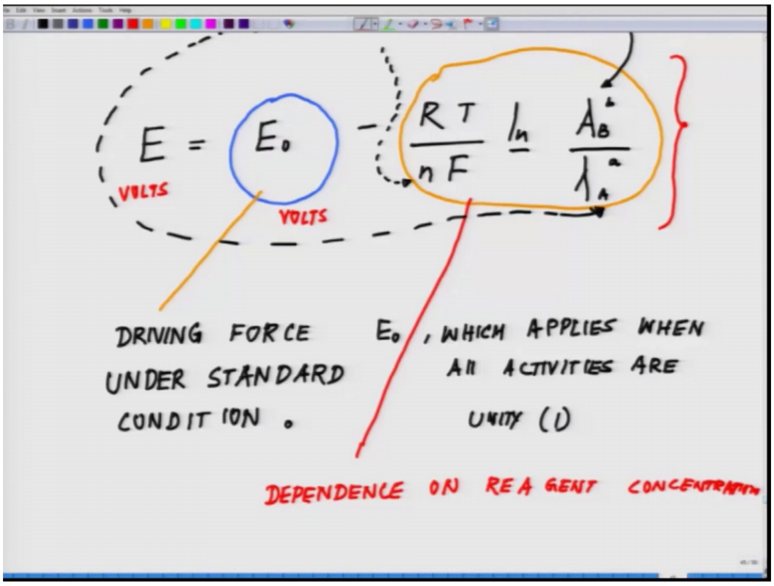

$$E = E_0 - \frac{RT}{nF} \ln \frac{A_B^b}{A_A^a}$$

VOLTS

VOLTS

DRIVING FORCE UNDER STANDARD CONDITION.

E_0, WHICH APPLIES WHEN All ACTIVITIES ARE UNITY (1)

DEPENDENCE ON REAGENT CONCENTRATION

Now if you look at this term what does this term stands and actually. So, this is in volts this is in volts now what about this term how this term is in volt or anything so will talk about it now.

Now, remember this term now we are going to you know do a unit analysis of this particular term this particular term, if I look at it R T n F natural log this term could be further dealt, now before we get into this term let us put the values of let us put what is stands for what your E 0 is standard reduction potential.

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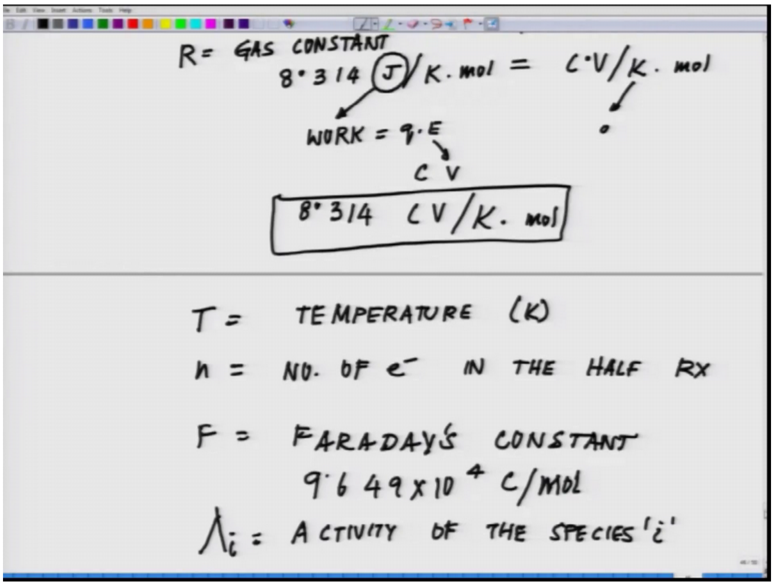

R= GAS CONSTANT

$8.314\ J/K \cdot mol = C \cdot V/K \cdot mol$

$WORK = q \cdot E$

C V

$\boxed{8.314\ CV/K \cdot mol}$

T = TEMPERATURE (K)

n = NO. OF e^- IN THE HALF RX

F = FARADAY'S CONSTANT

$9.649 \times 10^4\ C/MOL$

A_i = ACTIVITY OF THE SPECIES 'i'

Since we are only dealing with reduction potential; standard reduction potential where A A A B is equal to 1 which is the unity I mentioned that, then you have R which is the gas constant there is gas constant term is 8.3 1 4 Joules per Kelvin mol and which could also be written if it is in joules. So, if you remember in the very first class I told you joules is the expression for work and work is q charge into the potential. So, potential could be expressed in V and charge could be expressed as coulomb as C right.

So, I can actually write this as a unit analysis and you realize where this will come pretty handy C into V per this is degree this is temperature kelvin. So, I actually can write 8.314 C V unit of temperature per mol and this will help us in doing the analysis of the unit analysis. Then T is temperature in kelvin temperature in kelvin and then we have n which is equal to number of electrons in half reactions, number of electrons in the half reaction.

So, remember whenever we are doing Nernst equation you have to ensure that we do the comparison with same number of electrons, then F is equal to faradays constant which is 9.6 4 9 into 10 to the power 4 coulombs per mol and then you have the activity of the species activity of the species in question, which is the i-th species it could be anything a b what isoever.

So, now what you can do the logarithmic term in the Nernst equation the reaction quotient which is your.

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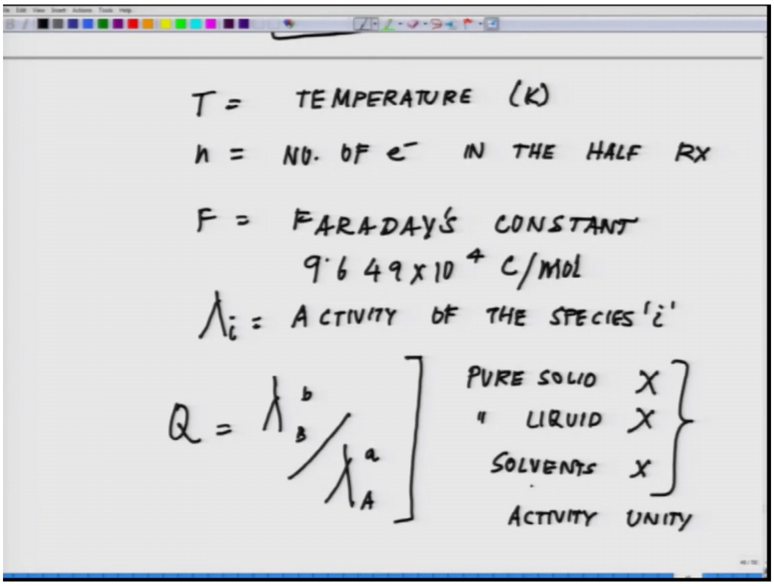

$T =$ TEMPERATURE (K)

$n =$ NO. OF e^- IN THE HALF RX

$F =$ FARADAY'S CONSTANT

9.649×10^4 C/MOL

$\lambda_i =$ ACTIVITY OF THE SPECIES 'i'

$$Q = \lambda_B^b / \lambda_A^a$$

PURE SOLID X

" LIQUID X

SOLVENTS X

ACTIVITY UNITY

Q which is in this case it is b upon a by A, Q has the same form as the equilibrium constant, but the activities need not have their equilibrium values this is a important part to realize. So, the activities need not have their equilibrium values and pure solid pure liquids and solvents are omit it from Q because their activities at unity or close to unity.

So, remember for the Q you cannot use pure solid you have to omit it pure liquids again you have to omit it and solvents you have to omit it, because their activity are unity and if the activity becomes unity then this whole equation will become 0.

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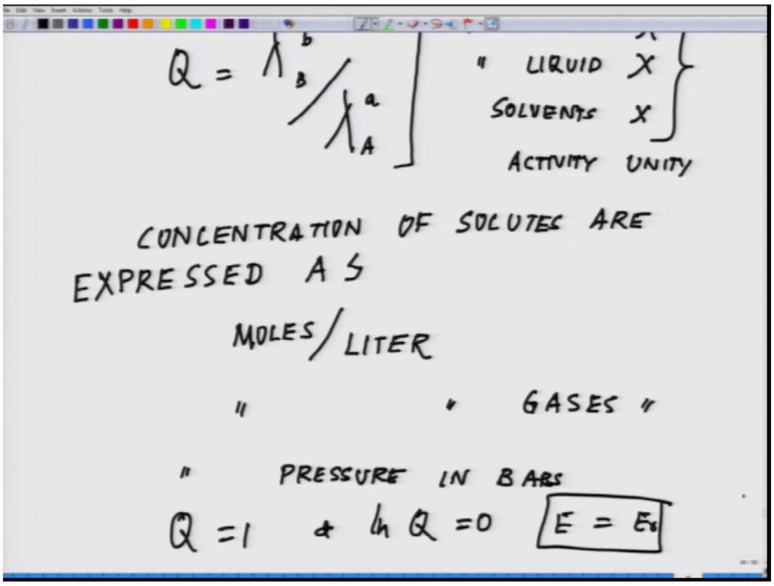

$$Q = \lambda_B^b / \lambda_A^a$$

" LIQUID X

SOLVENTS X

ACTIVITY UNITY

CONCENTRATION OF SOLUTES ARE EXPRESSED AS

MOLES/LITER

" " GASES "

" PRESSURE IN BARS

$Q = 1$ & $\ln Q = 0$ $\boxed{E = E_0}$

Now or close to unity concentrations of solutes are expressed as this is the important part concentration of solutes are expressed as concentration of the solutes are expressed as moles per liter, this is 1 part and concentration of gases are expressed as pressure in bars concentration of gases are expressed are expressed as pressure in bars.

So, keep this in mind and when all activities are unity Q is equal to one if Q is equal to 1 as I was telling you and then natural log of Q is equal to 0 and that will give you e is equal to E 0.

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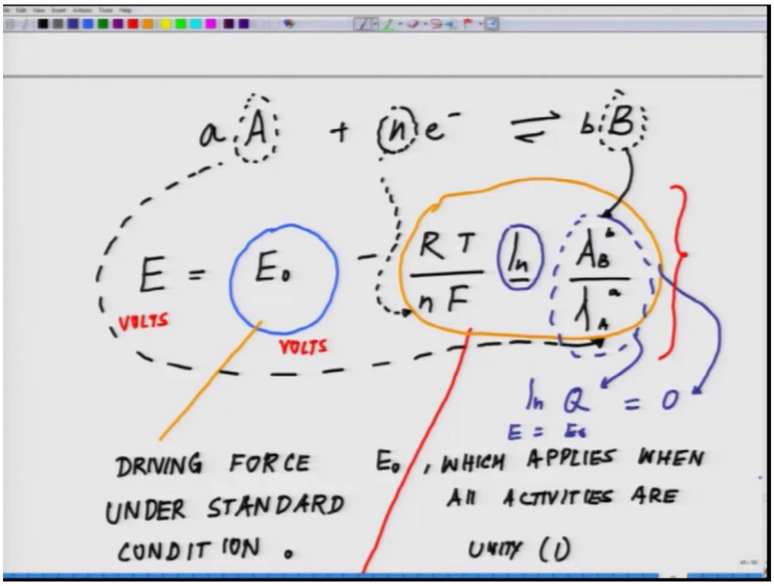

So, now, if you look at this equation if out here so this is the term we are talking about if this whole thing becomes unity, then the natural log ln of if I denote this by Q that becomes 0 and in that situation your E is equal to E 0, because this whole term will become than 0. So, keep that in mind.

So, now another important conversion what is being done is changing this natural log into the base 10 which is much more easy to work with. So, now the next thing is converting the natural logarithm into the base 10 logarithm and inserting the value of T.

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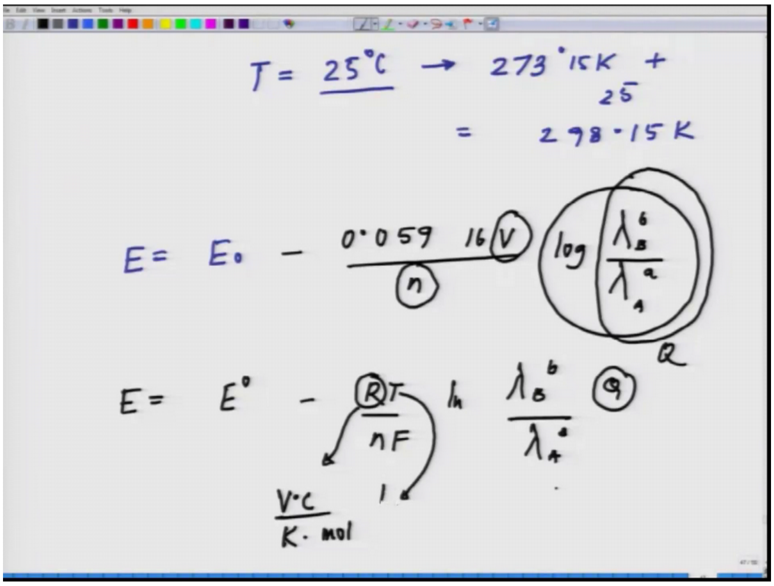

$T = 25^\circ C \rightarrow 273.15 K + 25$

$= 298.15 K$

$$E = E_0 - \frac{0.05916\,V}{n} \log \underbrace{\frac{\lambda_B^b}{\lambda_A^a}}_{Q}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\lambda_B^b}{\lambda_A^a}$$

$\frac{V \cdot C}{K \cdot mol}$ 1

So, this equation works at the value of T of 25 degree centigrade which is essentially 273 degree kelvin 2 7 3 1 5 kelvin plus 25. So, that makes it 2 9 8.1 5 Kelvin.

So, now Nernst equation at 25 degree centigrade is E is equal to E 0 now last term I am dealing with minus 0.0 5 9 you are multiplying everything 0 5 9 1 6 volt divided by n log of by the potential change by 59.16 part. So, this is the electron millivolt for each factor of 10 change in Q and this is that Q term for every unit change or for each factor of 10 change in Q this is the amount which is changing out here.

Now, what is important here is to realize how this v is being reached. So, this V could be reached in a very simple way. So, if you look at the original formula the original formula was like this E is equal to E 0 minus RT nF natural log A B b minus A A a which is your Q. Now what you can do is you can. So, this one you can expressed as I showed you V C per mol and Q 1 second. So, this is the unit of the R then you have the key which is coming from temperature and underneath you have n, which is it has no unit it is just coming as it is not just a number and then you have faradays constant and the unit of faradays constant is your coulombs per mol c upon mol.

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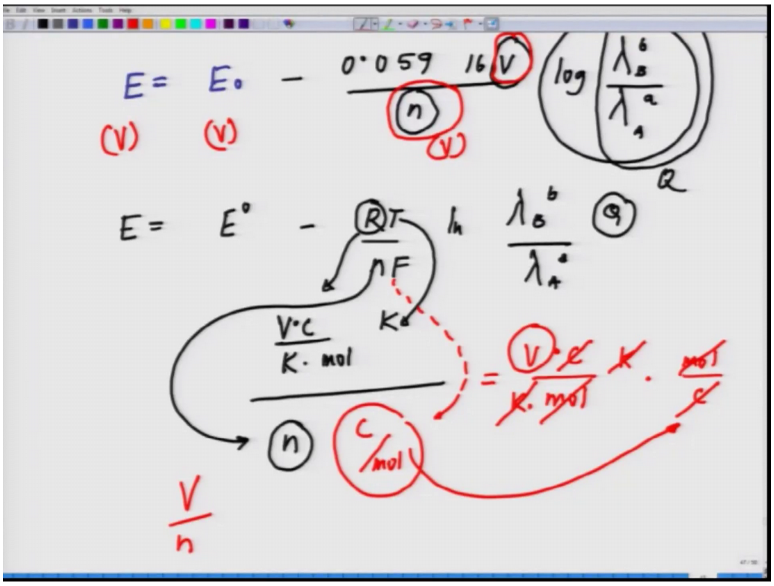

So, this is what you are essentially getting. So, if you now place it becomes unit analysis becomes V C upon mol of course, you have the key here you have another K here. So, this K this K cancels. So, you have V C upon mol multiplied by mol upon C, which is this one C C cancel mol mol cancel your left with V. So, what you have V upon n and this is precisely what you see here V, which is in voltage and n it is just a number. So, this is in voltage this is in voltage this is the third voltage.

So, you are dealing with 3 different voltages out here and remember it multiplying a half reaction does not change the E 0 you can multiply a half reaction anyway a Nernst equation for a complete reaction is something like this, if you have to see the Nernst equation for a complete reaction it is E is equal to E plus minus E minus.

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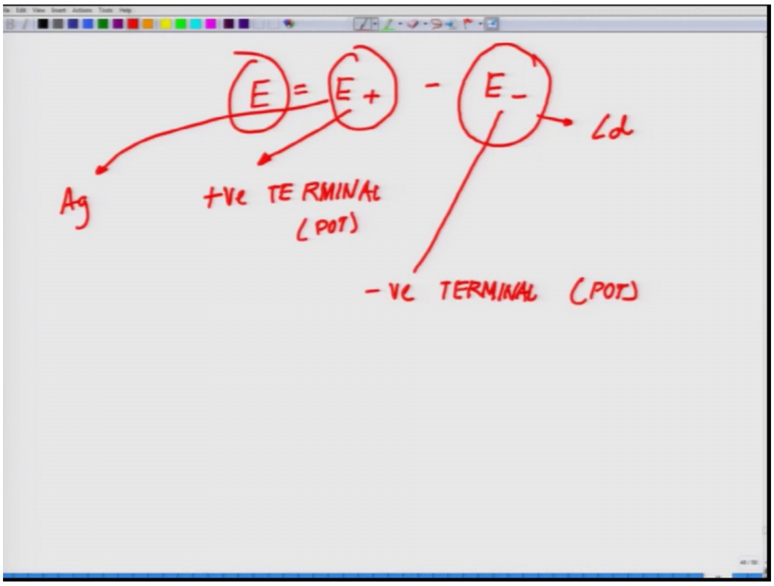

Where E plus is the potential electrode attached to the positive terminal potential of the electrode attached to the positive terminal and potential of the electrode attached to the negative terminal of the potentiometer negative terminal of the potentiometer.

So, that way if you look at it this is the potential what you have on the cadmium in our case when we talked about and this will be the potential, what you will be observed in the case of silver, because this is attached to the positive terminal of the potentiometer. So, keep that in mind. So, essentially once you add these things you will be able to get the final value of the Nernst equation.

So, what I will do I will close in here and in the next class we will be starting with the different kind of electrodes and I will take a small example from here, how really to put the Nernst equation in place I will devote some 10 minutes, where I will give you a little bit more clues on it and we will talk much more about next 2 3 classes about electrode and the potentiometry with this background. So, what I will request you know you are almost halfway through the course please go through the basics these are the very very fundamental basics what needed to be imbibe into your understanding so, that you can really develop a very good conceptual framework to understand the basics of Bio-electrochemistry.

Thank you.