Bio-electrochemistry

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Lecture – 11

Relationship Between Standard Electrode Potential and Equilibrium Constant

Welcome back to the lecture series in Bio-electrochemistry. So, we have finished 10 lectures as of now and the last lecture were concentrated on last couple of lectures are concentrated on Nernst equation. So, though in the last week we were supposed to switch over to the different form different kinds of electrode, but we rather is moving towards that topic much more slowly.

So, the reason being I am again reiterating the point that, I wish your fundamentals should be very clear. Now coming back to the Nernst equation and the reaction when we described. So, if you realize if you have 2 different electrodes say a and b cadmium and silver. So, there are 2 different level of equilibrium which are getting established.

So, a galvanic cell produces electricity because the cell reaction is not at equilibrium, but once it reaches equilibrium automatically the voltage will become 0 and nothing will flow and that is what precisely happens in a battery, when the when we say this common word the battery drains out battery is no more doing the performing the reaction. So, here there are batteries, which are rechargeable essentially think of what is happening just put your logic in place.

So, you have say current flowing from a to b or b to a whatsoever, because the reaction is not at equilibrium. So, once it reaches equilibrium the voltage across them becomes 0. So, there would not be any further flow of because there it there it has reached equilibrium.

Now, if you reverse the polarity. So, what you essentially did so, there are chemical reactions which led to the electricity production. Now if you put electricity then you can recharge it back by allowing the chemicals to maintain another new set of potentials. So, essentially you can reverse and that is where it comes the whole concept of rechargeable batteries.

So, this is just a deviation from our normally, but course of a study, but what is important for you to understand that there are 2 sets of equilibrium which are being said. So, say for example, you have electrode a you have electrode b. Now electrode a is in equilibrium with it is own surrounding whenever, we if you remember that when we measured that if you put a hydrogen probe there in sync with that.

Similarly, electrode b is in equilibrium with it is own reference electrode and then a and b has a different set of equilibrium among each other. So, individual cells so here we call each one of these as individual cells. So, just to put it something like this we are into Week 3 this is lecture 11, week 3 this is first lecture of week 3 lecture 1 W 3 L 1.

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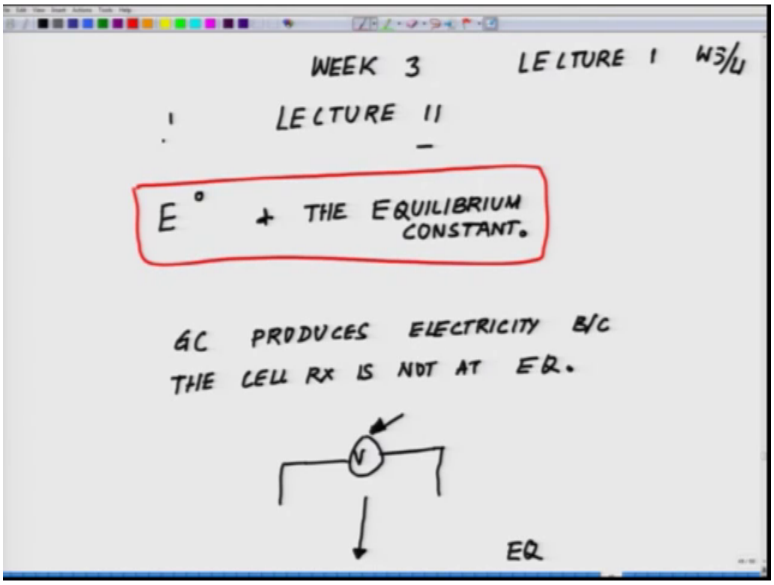

WEEK 3 LECTURE 1 W3/L1

LECTURE 11

E° + THE EQUILIBRIUM CONSTANT.

GC PRODUCES ELECTRICITY B/C THE CELL RX IS NOT AT EQ.

And what I am trying to tell you is so by essentially what we are doing today is we will be touching upon, the relation between E 0 and the equilibrium constant. So, what I highlighted just now is that a galvanic cell produces electricity, because the cell reaction is not at equilibrium.

Galvanic cell produces electricity because the cell reaction is not at equilibrium reaction is not at equilibrium. So, this is one of the fundamental thing the potentiometer allows negligible current. So, the concentration of the cells remain unchanged if we replace the potentiometer say for example, you have this potentiometer, which is connecting to say cell. So, when you are connecting it with a potentiometer there is a negligible current which is flowing through allow negligible current. So, the concentration in the cell remain unchanged.

If we replace the potentiometer with the wire say for example, you are removing the potentiometer and allowing the electrons to flow through, if we replace the potentiometer with a wire there will be much more current and the concentration would change until the cell reach the equilibrium, at that point nothing would drive the reaction and E would become E will become 0.

So, when a battery which is a galvanic cell runs down to 0 volt the chemicals inside have reached equilibrium and the battery is dead. So, this is one concept which I wish you should understand. The second thing what is important here is let us relate the E for a whole cell to the reaction quotient Q.

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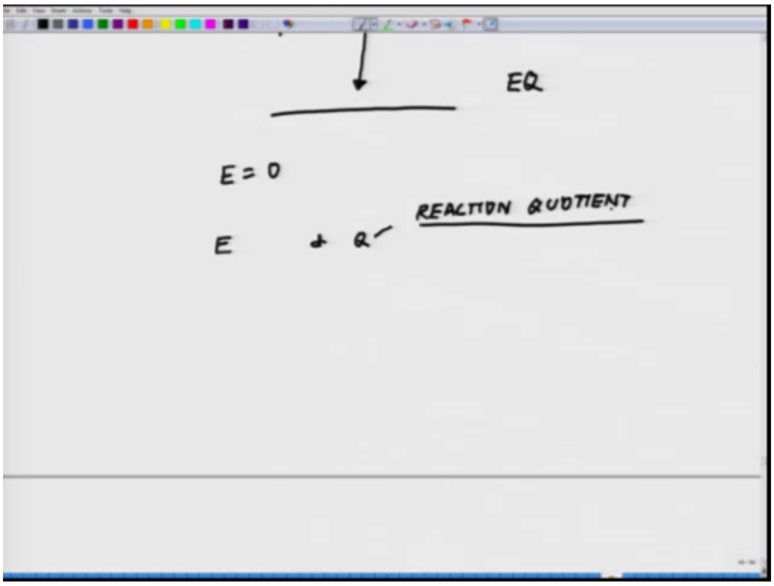

So, we are trying to relate E and Q, which is the reaction quotient reaction Q U O T I E N T reaction quotient.

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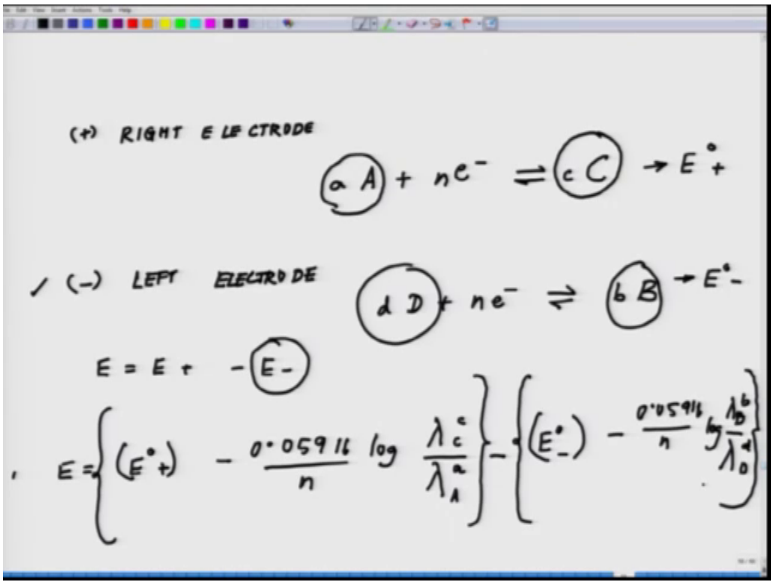

(+) RIGHT ELECTRODE $aA + ne^- \rightleftharpoons cC \rightarrow E^\circ_+$

(−) LEFT ELECTRODE $dD + ne^- \rightleftharpoons bB \rightarrow E^\circ_-$

$$E = E_+ - E_-$$

$$E = \left\{(E^\circ_+) - \frac{0.05916}{n}\log\frac{\lambda_C^c}{\lambda_A^a}\right\} - \left\{(E^\circ_-) - \frac{0.05916}{n}\log\frac{\lambda_B^b}{\lambda_D^d}\right\}$$

So, now, say for example, on your right hand electrode. So, let us write down both the reaction so on your right electrode you have the reaction like a A plus n e and c C whereas, on your left electrode you have a second set of reaction going d D plus n e b B. Now, if you write down the Nernst equation for us so, this is the right electrode. So, this is your 0 plus this we have already talked 0 minus.

Now, at equilibrium we have already talked about E equal to 0. Now the Nernst equation for this will looks like something like this, we know that E is equal to E plus minus. So, this is your E minus term and this is your plus term.

Now, if you write this equation it will become something like this. E is equal to 0 plus minus. So, this is minus 0 point I am not deriving it further because you have you already know this divided by number of electrons log the base 10 c.

So, essentially I am writing in this part this term and this term is coming there A a minus put the big brackets there minus, you have the second term which is the left electrode now coming into play which is E minus electrode, which is E 0 minus.

Now, here is the minus term so, this is the whole term by the way minus 0.05916 divided by n log. So, you have the other reaction as this is b B and this is d D. So, you have d D and you are closing upon the bracket. So, this is what the Nernst equation will look like.

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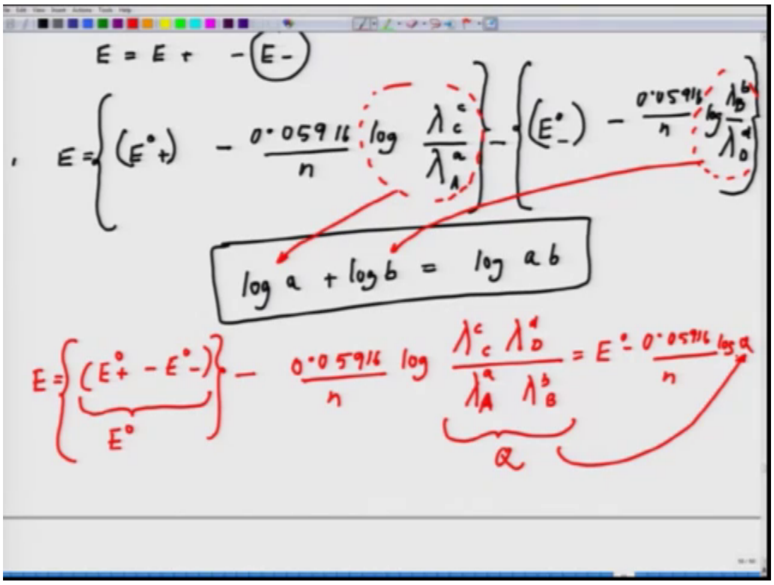

$$E = E_{+} - \boxed{E_{-}}$$

$$E = \left\{ (E^{\circ}_{+}) - \frac{0.05916}{n} \log \frac{\lambda_C^c}{\lambda_A^a} \right\} - \left\{ (E^{\circ}_{-}) - \frac{0.05916}{n} \log \frac{\lambda_B^b}{\lambda_D^d} \right\}$$

$$\boxed{\log a + \log b = \log ab}$$

$$E = \left\{ \underbrace{(E^{\circ}_{+} - E^{\circ}_{-})}_{E^{\circ}} \right\} - \frac{0.05916}{n} \log \underbrace{\frac{\lambda_C^c \lambda_D^d}{\lambda_A^a \lambda_B^b}}_{Q} = E^{\circ} - \frac{0.05916}{n} \log Q$$

Now, we know that log a plus log b is equal to log a b, this relation we are aware of if we know this relation. So, essentially your this term and your this term are basically very similar to this. So, we can really multiply these 2 terms so, if you rearrange this whole thing. So, then the equation becomes E is equal to E 0 plus minus E 0 minus which whole terms is essentially is your E 0 minus, I am putting additional brackets.

So, that you do not get confused 0.05916 divided by number of electrons log c d D divided by sorry A a b B this whole term is your Q.

So, now if you write this term this becomes your E 0, which is standard potential minus 0.059 16 divided by n log Q.

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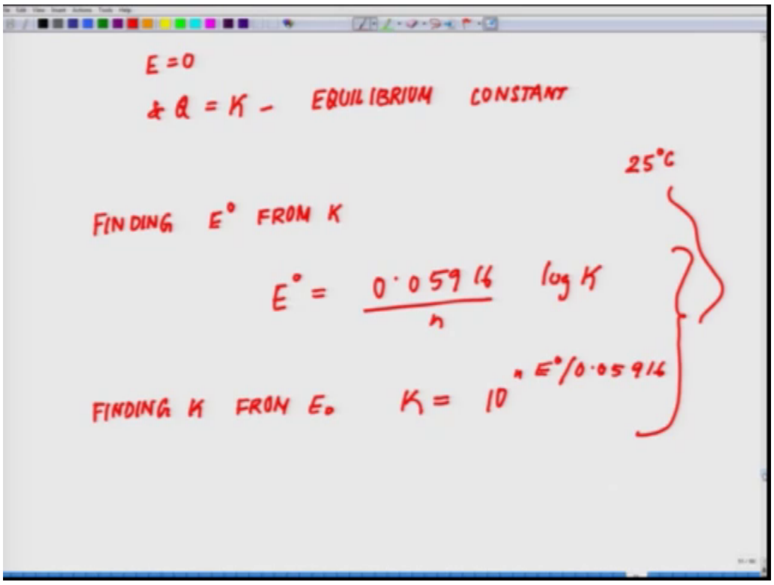

$E = 0$

$\& \; Q = K$ - EQUILIBRIUM CONSTANT

25°C

FINDING E° FROM K

$$E^\circ = \frac{0.05916}{n} \log K$$

FINDING K FROM E_0 $\quad K = 10^{nE^\circ/0.05916}$

Now, simplifying the equation so in a special case when E equals to 0 and Q is equal to K that is where you are fine trying to find the equilibrium constant, because mind it these are different kind of reactants which are involved in this whole process. So, what you are getting in that situation you are finding E 0 from K, that makes it E 0 equals to 0.05916 divided by n is equal to log K.

Similarly, finding K from E 0 is equal to is K is equal to 10 n E 0 0.05916 and all these reactions are happening at 25 degree centigrade.

So, this is where we are establishing a relationship between E 0 and the equilibrium constant, this is the relation which I wanted to establish with you people. The next thing what I wish to established is tell as chemical probes.

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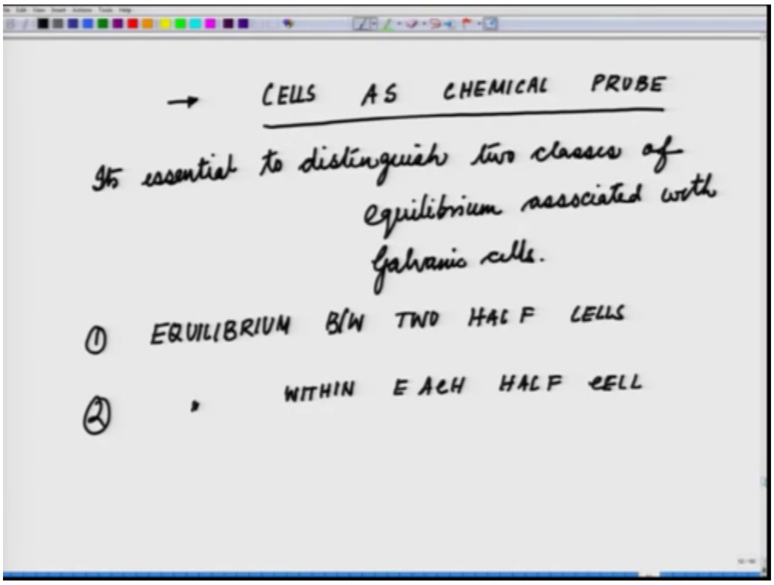

→ CELLS AS CHEMICAL PROBE

Its essential to distinguish two classes of equilibrium associated with galvanic cells.

① EQUILIBRIUM B/W TWO HALF CELLS

② " WITHIN EACH HALF CELL

So, here when we talk about the cell we essentially mean the half cells, cells as chemical probes what does that mean I am coming to that. So, I told you that equilibrium has to be established at 2 different level a equilibrium has to be established on the half cells and equilibrium has to be established between the half cells.

So, we can understand that any of these parameters, if it is unknown and if you know the other 3 parameters we can figure out what is the fourth parameter just keep it in mind. So, let us enumerate what all I am trying to highlight here. So, the 0.1 it is essential to distinguish 2 classes of equilibrium associated with galvanic cells.

It is essential to distinguish 2 classes of equilibrium associated with galvanic cells. So, what are those? So, the first one is equilibrium between 2 half cells, equilibrium between 2 half cells 0.1 and second one is equilibrium within each half cell.

So, now what I will do use this opportunity to explore how this could be used to find out hydrogen ion concentration H plus ion concentration? So, let me draw a cell and keep another thing in mind if a galvanic cell has a non-zero voltage then the net cell reaction is not at equilibrium. We said that the equilibrium between the 2 half cells has not been established and if we allow the half cells to stand long enough to come to chemical equilibrium within each half cell.

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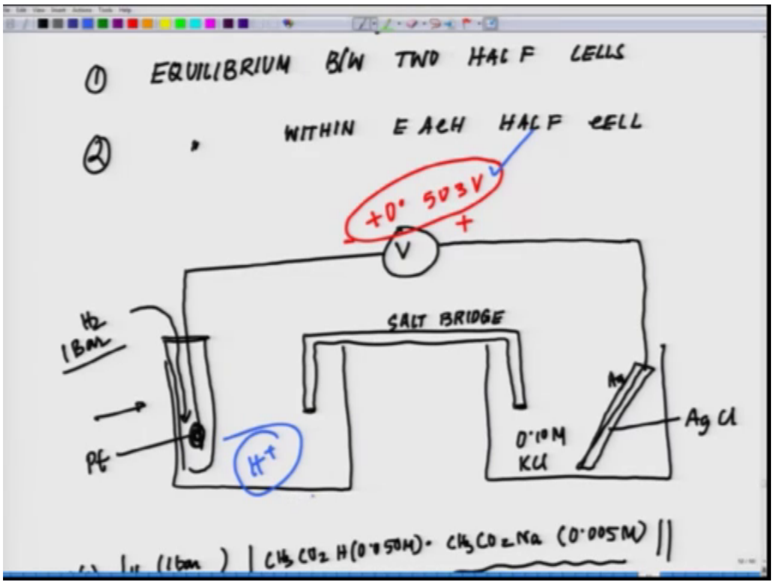

So, keeping that in mind let us draw the cell so, here is one cell here is the next cell. So, these 2 cells are connected with a salt bridge, your salt bridge connecting them and you have a voltmeter connected there and on your right hand side you have silver electrode which is A g g cell electrode and this is an 0.10 molar K C L.

This is A g and this is your salt bridge here you have a the typical hydrogen electrode with a platinum and you have hydrogen at 1 bar right and in this side what you have. So, if I put the cell reaction this is platinum solid hydrogen at 1 bar and this is balancing with C H 3 C O 2 H 0.050 mol multiplied by C H 3 C O 2 N a with 0.005 mole.

So, which is essentially a buffer this is what is buffering it you knew the double line showing the other side the right hand side of the reaction, which is chloride minus 0.10 mole with A g C l solid A g solid. So, this is what the reaction looks like.

So, now we allow the half-cell to stand long enough to come in chemical equilibrium within each half cell. For example, on the right hand side what you are having is A g C l solid it is coming in equilibrium with A g plus aqueous plus C l minus aqueous is that equilibrium.

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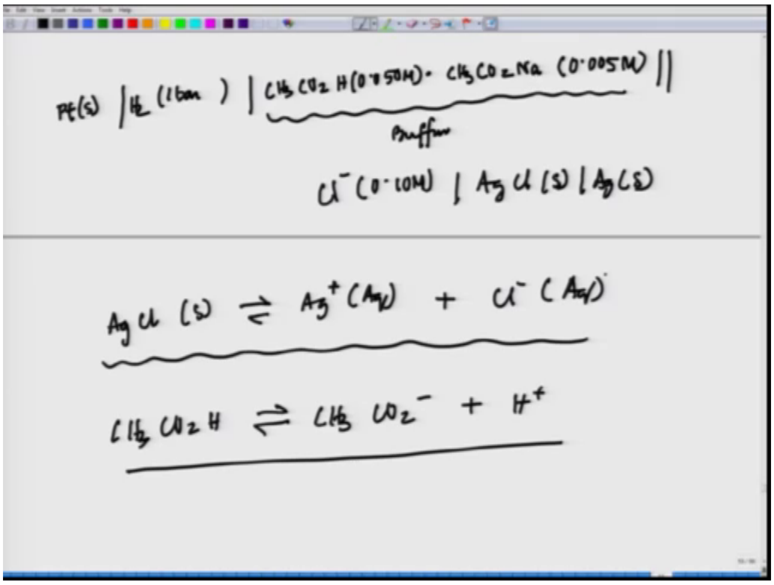

$$Pt(s) \mid H_2 (1 bar) \mid \underbrace{CH_3CO_2H (0.050M) \cdot CH_3CO_2Na (0.005M)}_{Buffer} \parallel$$

$$Cl^- (0.10M) \mid AgCl(s) \mid Ag(s)$$

$$\underline{AgCl(s) \rightleftharpoons Ag^+(Aq) + Cl^-(Aq)}$$

$$\underline{CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+}$$

So, this is where it is reaching an equilibrium on the other hand other side, it is simply on the other side, what you are having is C H 3 C O 2 H is coming in equilibrium with C H 3 C O 2 minus plus H plus this other left hand side is also at equilibrium. So, both the reactions at the individual at within each half cell is at equilibrium.

The redox reaction for the right half of the cell, which is if you see on this half of the cell the redox reaction is something like this if I write the redox reaction, on the right hand side it will be A g C l solid plus electron making it A g solid chloride minus 0.1 molar and E 0 plus is 0 .222 volt.

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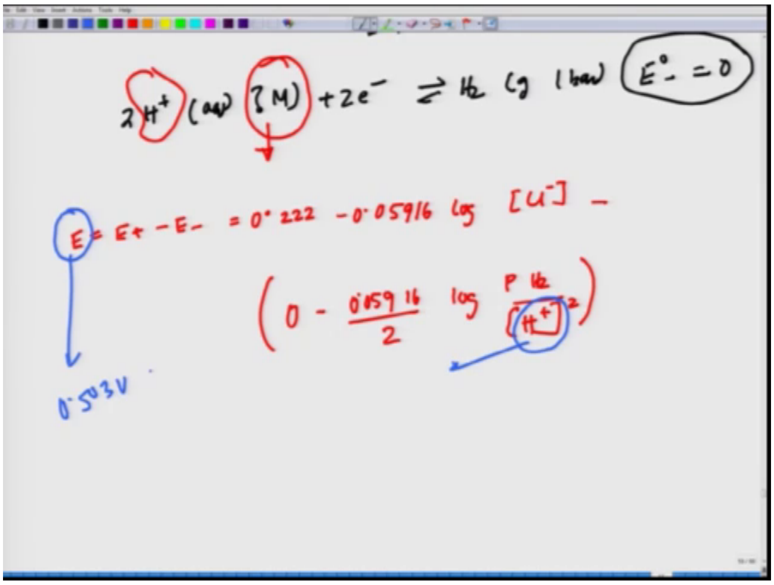

$2H^+ (aq)\ (?\,M) + 2e^- \rightleftharpoons H_2\ (g\ 1\ bar)$ $\boxed{E^\circ_- = 0}$

$E = E_+ - E_- = 0.222 - 0.05916 \log [Cl^-] - \left(0 - \frac{0.05916}{2} \log \frac{P_{H_2}}{[H^+]^2}\right)$

$0.503V$

But what is the reaction in the left cell the only element we find in 2 oxidation state is hydrogen. So, we see that hydrogen bubbles into the cell, if you look at it carefully. So, what you are observing. So, there is an hydrogen bubbling which is happening and only element we find in the 2 oxidation state is hydrogen.

And we also realize that every aqueous solution contains H plus therefore, hydrogen is present in 2 oxidation state and the half reaction can be written as so now, I am writing the half reaction of the left hand side which could be written as 2 H plus aqueous, we do not know how much is the molarity plus 2 electron giving rise to hydrogen, which is gas 1 bar and E 0 negative is equal to 0 this is what we are assuming.

So, what we do not know is what is the concentration of this H plus ions? So, the next reaction is not at equilibrium, because the major voltage is 0.503 and so the measured. So, this is what is a so the net measured what we are measuring is out here if you look at it this value if you look at it carefully.

So, then this value is plus 0.503 volt so, it means whenever this is showing this value which is this side is negative this side it is positive, it means the cell is not at equilibrium. So, and that cell reaction is not at equilibrium because the measured value is 0.503 volt not 0 volt.

So, the Nernst equation for the cell reaction will be now if you write the Nernst equation for it will be something like this, E is equal to E plus minus E minus. This is the case then 0.222 which is on the silver chloride side 0.05916 log of C l minus, minus here it is 0 minus 0.05916 divided by 2 log.

Now, what we do not know here is this term this term is unknown to us after inserting the known quantities, we discovered that the only unknown is the H plus. So, the measured voltage therefore, allows us to find H plus. So, now, what you do out here you know this is known to us right, which is your 0.503 volt this is experimentally you are measuring it, because this is not at equilibrium.

So, if you insert this value this is what I am trying to tell you insert this value there and then you pull down this whole thing 0.222 minus 0.05916

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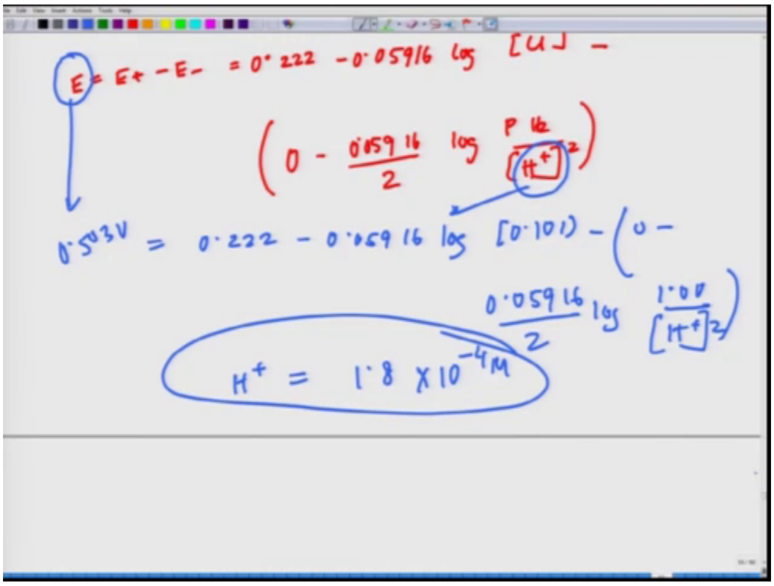

$$E = E_+ - E_- = 0.222 - 0.05916 \log [Cl] - \left(0 - \frac{0.05916}{2} \log \frac{P_{H_2}}{[H^+]^2}\right)$$

$$0.503V = 0.222 - 0.05916 \log [0.101] - \left(0 - \frac{0.05916}{2} \log \frac{1.00}{[H^+]^2}\right)$$

$$H^+ = 1.8 \times 10^{-4} M$$

Then you have log of 0.101 minus 0 minus 0.05916 divided by 2 log of 1, then you will calculate that h plus concentration is equal to 1.8 10 to the power minus 4 mole.

So, you realize this in turn allows us to evaluate the equilibrium constant for acid base reaction that comes to equilibrium in the left hand side. So, you are realizing that based on this you can really take it to the next level where you can calculate it is equal to C H 3 C 0 2.

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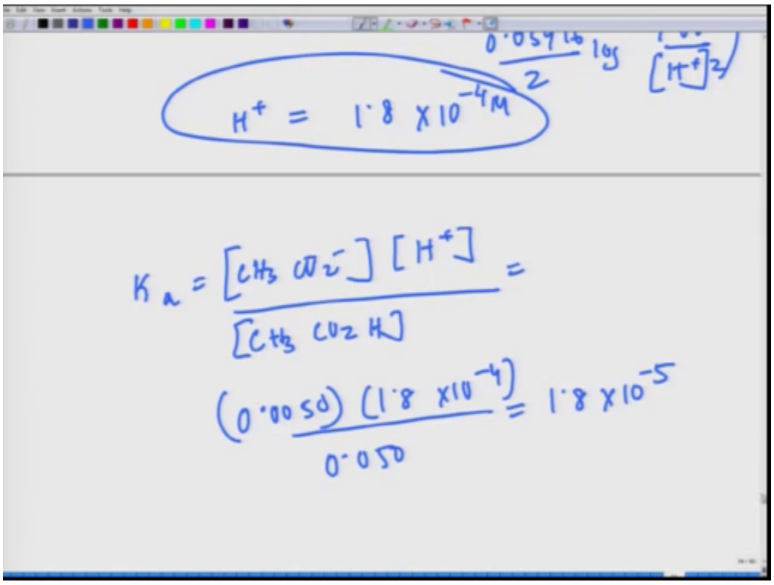

$\frac{0.05916}{2} \log \frac{}{[H^+]^2})$

$H^+ = 1.8 \times 10^{-4} M$

$$K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} =$$

$$\frac{(0.0050)(1.8 \times 10^{-4})}{0.050} = 1.8 \times 10^{-5}$$

So, if you remember on the left hand side how the concentrations of these were shown C H 3 C O 2 H and if you insert the values, now this is what you are going to get, and that brings us to 5. So, if you realize that we now have a probe to measure the H plus ion concentration proton concentration using this type of cell we could determine the equilibrium constant of acid dissociation and base hydrolysis on the left cell.

So, you realize that these kind of cells could come very handy when you have to translate between a chemical reaction and the electrical output and vice versa electrical output and a chemical reaction. So, here see it is a very simple thing where if you know the redox reaction, if you can build up the redox reaction out here what you did you really can figure out how to measure the concentration. So, what we essentially did we measured this value which was unknown to us.

So, this is how it is a very simplest example I wish you to go through it very carefully this is how you measure in a simplest term in a very simple term the different kind of analytes, which are present especially here is H plus ion concentration, which will tell you essentially this is in a way you are telling what is the P H, which is H plus ion concentration is it acidic P H or is it a basic P H.

So, I will close in here and the next class we will be introducing some of the bio molecules as of now we have talked about most of it is most of it is the inorganic part. So, we will talk about the significance of E 0 in for the biochemistry.

Thank you.