# Bio-electrochemistry

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## Lecture – 09
## Standard Potentials – III

Welcome back to the lecture series in Bio-electrochemistry. So, we are into the 9th lecture or the 4th lecture of the second week.

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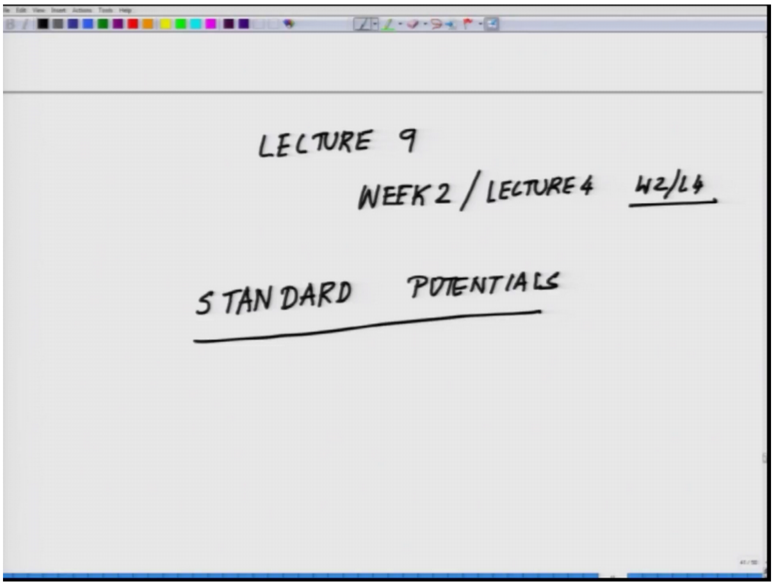

So, we are into lecture 9 which is basically week 2 slash lecture 4 of week 2 W 2 L 4 . So, today we will resume on standard potentials where we have discussed previous 2 classes standard potentials.

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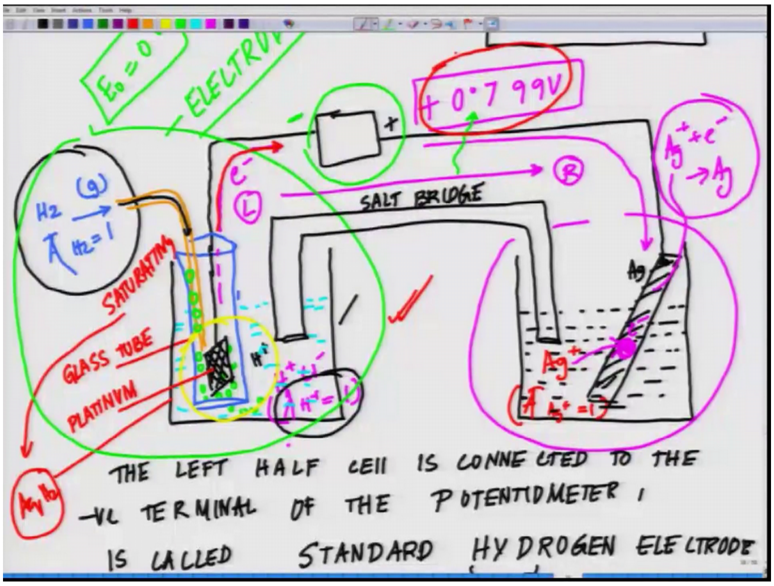

THE LEFT HALF CEll IS CONNECTED TO THE -VE TERMINAL OF THE POTENTIOMETER, IS CALLED STANDARD HYDROGEN ELECTRODE

So, in the last class if I go back if you remember what we talked about was. So, we talked about the hydrogen electrode standard hydrogen electrode and I told you that this is the first kind of electrode, while the next section while we will move on to after the post Nernst equation we will move on to potentiometry and electrode you will realize.

So, this is the first kind of electrode what we have dealt which is standard hydrogen electrode consisting of a platinum metal, where it is being continuously infused with hydrogen gas whose activity is of course, one as we mentioned if you remember it this is hydrogen gas and this is kept in a HCL solution hydrogen chloride solution, where H plus ions activity is one and there is a equilibrium which happens across this electrode across and on this electrode what is happening is that there is an equilibration like this.

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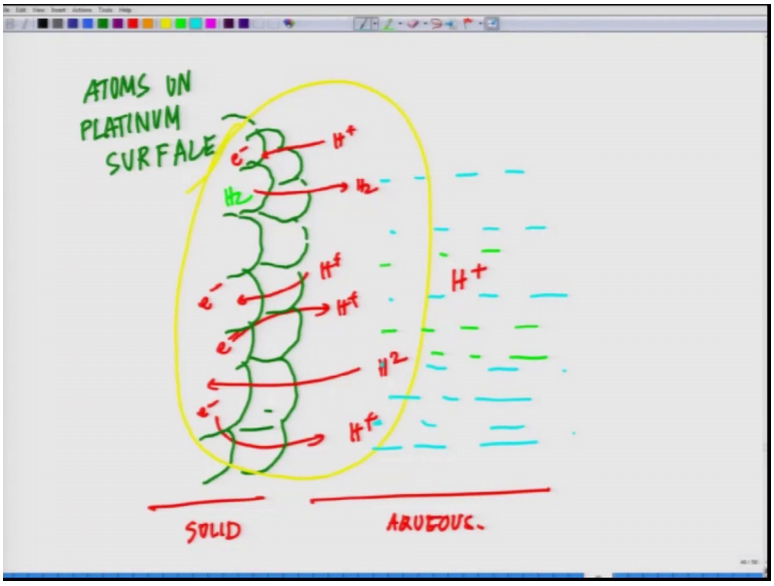

Where this is the platinum surface shown in green and this is the aqueous medium, where H plus ions are present 1 second 1 second let me and the equilibria which is being developed out here is something like as I shown you in the reaction H 2.

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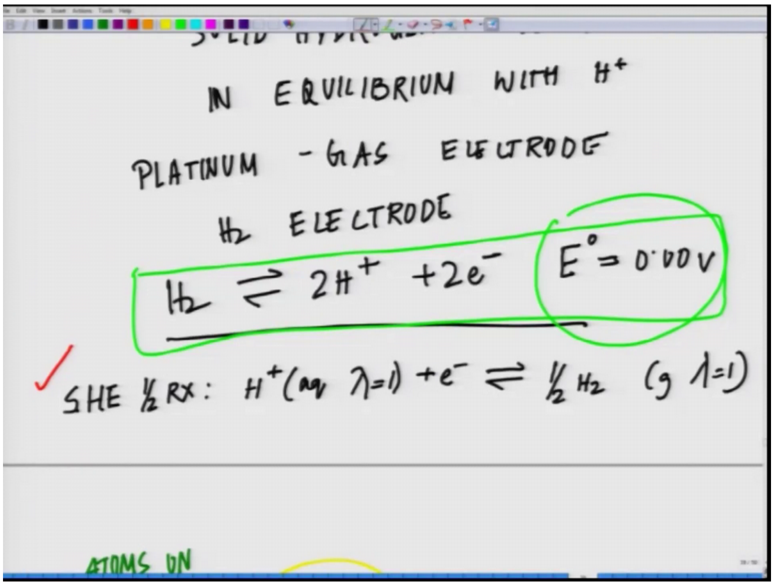

IN EQUILIBRIUM WITH $H^+$

PLATINUM - GAS ELECTRODE

$H_2$ ELECTRODE

$H_2 \rightleftharpoons 2H^+ + 2e^-$ $E^\circ = 0.00\,V$

✓ SHE ½ RX: $H^+(aq\ \lambda=1) + e^- \rightleftharpoons \frac{1}{2} H_2\ (g\ \lambda=1)$

And you can again rewrite it there are different books which will put it something like this standard hydrogen electrode reaction standard hydrogen electrode half reaction will be basically H plus, in aqueous with an activity of 1 plus electron it is a reversible reaction what you are getting half H 2 hydrogen gas which is gaseous phase with activity of 1.

Which is essentially the same reaction.

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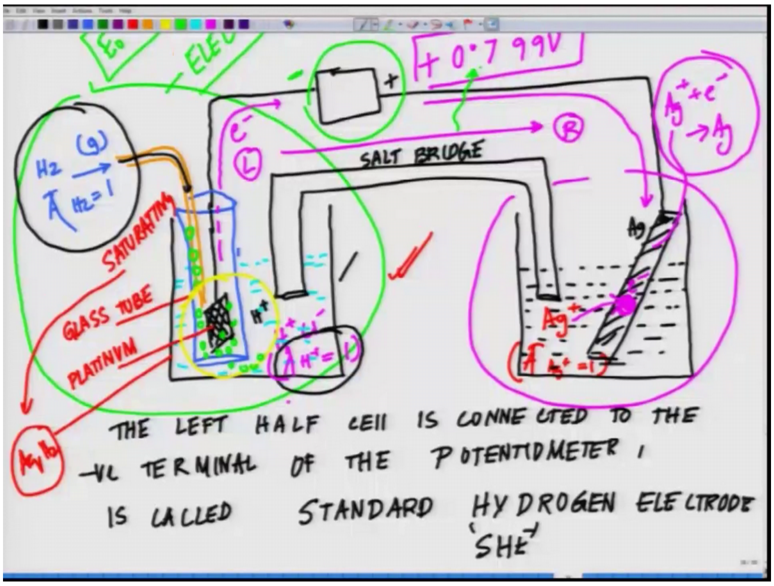

THE LEFT HALF CEll IS CONNECTED TO THE -VE TERMINAL OF THE POTENTIOMETER, IS CALLED STANDARD HYDROGEN ELECTRODE 'SHE'

What is important here to know the stream of hydrogen which is bubbled through the electrode saturates the solution. So, what you are seeing here is this is out here essentially, what is happening is that this hydrogen, which is being bubbled through this this hydrogen bubbling, which is coming this is essentially the stream of hydrogen bubble through the electrode saturates the solution with aqueous hydrogen.

So, in other words you are having out here aqueous hydrogen this is getting saturated saturating with aqueous hydrogen and the activity of aqua the gas hydrogen is unity, if the pressure of hydrogen is 1 bar and the reaction that comes to the equilibrium at the surface of platinum electrode is being shown here.

So, this is essentially is the standard hydrogen electrode reaction of the half reaction and what is being done to it is. So, arbitrarily assign a potential of 0 that is what we have discussed.

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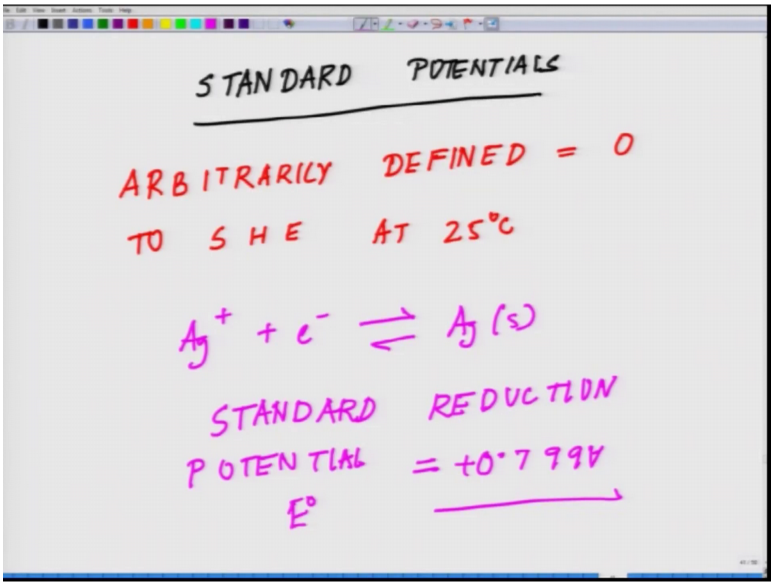

STANDARD POTENTIALS

ARBITRARILY DEFINED = 0

TO SHE AT 25°C

$$Ag^+ + e^- \rightleftharpoons Ag(s)$$

STANDARD REDUCTION POTENTIAL = +0.799V

$E^\circ$

Is then and totally arbitrarily defined, lay defined number which is a 0. So, arbitrarily define potential 0 to standard hydrogen electrode at so 25 degree centigrade. So, keep this in mind. So, the voltage measured by the meter in figure 13 points figure out here in this particular figure where we saw the hydrogen electrode going through out here .

So, the voltage what you are observing is very interesting when you attack this half-cell to the another half-cell. So, essentially now what is happening try to understand the reaction what is happening, silver is there which is a surface which are which is getting reduced. So, from the solution Ag plus goes and deposits here and looks for an electron in this situation, what is happening the electron from here are flowing. So, silver and what you are observing out in the meter is a positive.

So, now you remember the axiom what I used trying to tell you positive 0.7 9 9 volt why this is important. So, if you remember that I told you something earlier. So, I will go back to that one of the previous classes I told you about the potentiometer, where the potentiometer will stand. So, if you recollect this indicates the positive voltage out here indicates when electron flows into the negative terminal. So, you are observing a positive voltage out here it means electrons are moving on to the negative terminal.

So, electron flow is like this. So, from the standard hydrogen electrode the electrons are flowing in this direction and they are eventually reaching here where Ag. So, what was the reaction we started with a reaction was this 1, where silver ions from the aqueous medium. So, silver ions are traveling from the aqueous medium on the surface of the Ag Ag metal and out here this silver is obtaining an electron and becoming Ag this is a reduction reaction, which is happening and your potentiometer is showing a volt of positive 0.7 9 9 volt and this is very important value because this is the value which is essentially your, the standard reduction potential.

So, for the reaction A g plus plus electron making Ag solid so, the standard reduction potential is which is 0 point positive 0 point t 7 9 9 volt and the positive tells us that electron flows from left to right through the meter. So, the electron is flowing from left this is your left and this is your right and electron flow is happening like this that is what gives you a positive value out here.

Now, this part is exceptionally important for you to understand and in future this will come very handy and that is why I am taking. So, much time on all these things.

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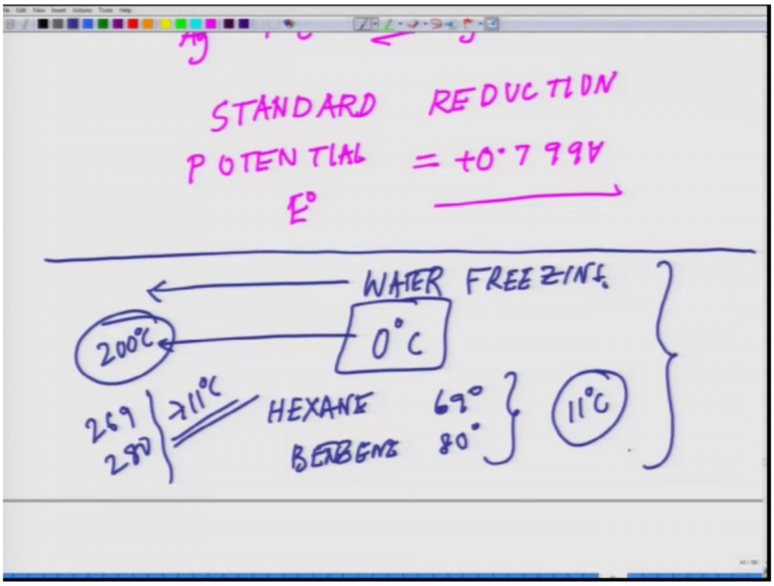

So, we have arbitrarily assigned a potential of 0 to the standard hydrogen electrode at 25 degree centigrade and the voltage measured by the meter is being shown as plus 0.7 9 9.

Now, this is another thing what I wanted to highlight because this will come handy because from standard hydrogen electrode we have moved to different other kind of reference electrode as we will talk more about the reference electrode. So, it is something like this say for example, I say the water freezes at say water freezes at 0 degree centigrade now if water freezes at 0 degree centigrade then and then we say that hexane boils at says 69.

So, let me take 2 example hexane hexane boils at say you know 69 and benzene boils at 80. So, the difference between the 2 what we essentially did when we have cadmium and silver electrode. So, the difference between the 2 will be 11 degree centigrade right now say for example, if this is the we are talking about water freezing freezing happening at that point.

Now suppose I change the reference from 0 to say you know 200 degree centigrade I change the reference arbitrarily, I change the reference then what will happen these 2 values will be shifting to say 269 and 280 a still the difference will remain 11 degree centigrade.

So, in other word what I wanted to highlight through this analogy is you can always develop other kind of simple references as long as you and calibrate your reference electrode with a standard hydrogen electrode. And as we will move through you will realize there Ag, Ag cl silver, silver chloride electrodes, which are used as a reference electrode, because you have to realize one thing you cannot carry a standard hydrogen like you cannot carry a hydrogen cylinder all the time to have the standard being set practically it is not I would not say not feasible, but practically it is something like a very cumber something.

So, but why we are studying it because this is where it all the tables all the charts all the basics are there, but then from there we shift it is something like say for example, I say 0 degree. So, I said the, it is a freezing at say 200 degree or something you know it does not matter. So, I can change the reference with respect to one standard reference and as long as those reference and the deviations from the reference are the same I do not have to worry.

So, as will move forward you will realize that there are different kind of electrodes, where people have used different references, but those references were calibrated or are calibrated with standard hydrogen electrode, but the first one where all these assumptions came was started with arbitrarily defined standard hydrogen electrode as at 25 degree centigrade as 0.

So, it has a potential 0 with respect to it. So, for this reaction the reduction potential in other word if I have to understand physically what does that mean physically; that means, what is the power with which it can pull an electron towards it, what is it is reduction power it is reduction power is expressed in volt in terms of potential, what is your potential could you clear this example could you get this to you could you pull this bucket could you pull the electron what is your power your power lies in plus 0.7 9 9 volt and that is your power.

Now, anything higher than that will have more power in other word anything say for example, I say point 0.7 I say 0.8 . So, 0.8 means I have more power to pull the electron I will be pulling electron faster than you and anything lesser than that if I say a negative value say imagine. So, that will give us a different kind of situation it means that has lesser power than one we have defined in terms of pulling electron.

So, again you can define in 2 ways as I am repeatedly telling you try to the market you can delete that what is the power to give away the electron which is your against getting oxidized. So, in that case you will it will be defined as instead of a standard reduction potential, it will be called as a standard oxidation potential, but generally we do not define it like that the general thumb rule which most of the books will follow and I am going to follow is a standard reduction potential. In other word what is the potential with which it can pull an electron towards it instead of giving have electron. So, we are not dealing with this, but theoretically yes you can always talk like that.

Standard reduction potential. So, if you know the power that this is the power with which you can pull an electron then you can calculate the work done, how you can do if you know the amount of charge you remember the Eq work done voltage multiplied by the charge. So, that way you can say on this electrode this much work is being done by the electron.

So, realizing how we will correlate all these things with those very first class if you remember very earlier classes, in the first week I told you about all the different formula if I just have to go back if you remember, where we have talked about all these work done and all those basic parameters we talked about here it is work done remember.

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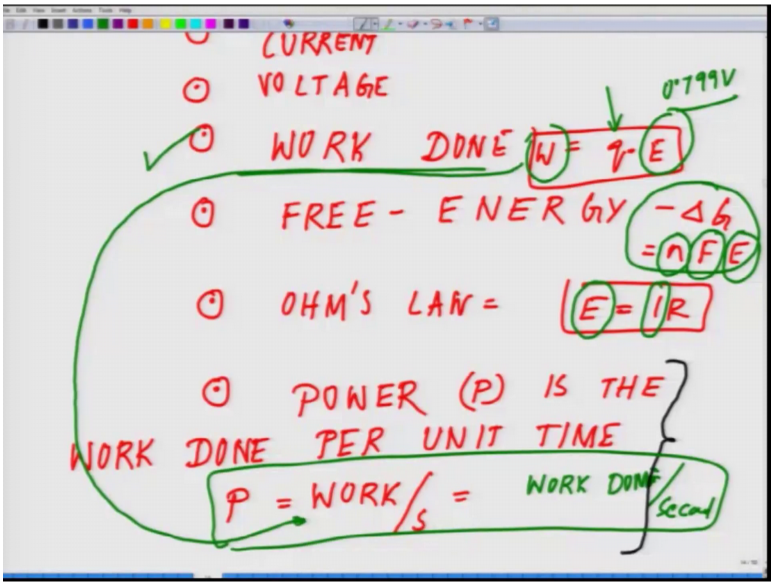

- CURRENT
- VOLTAGE
- WORK DONE $W = q \cdot E$ 0.799V
- FREE-ENERGY $-\Delta G = nFE$
- OHM'S LAW = $E = IR$
- POWER (P) IS THE WORK DONE PER UNIT TIME

$P = \text{WORK}/s = \text{WORK DONE}/\text{Second}$

So, now, if you know the E, which is, your in volts. So, say for example, I say 0.7 9 9 volt and if you know the charge on the electron then you can and how many electrons are moving then you can calculate what will be the work done.

So, see all this basic formula is formulae are coming back into the place. Now if you know the work done then from the work done what you can do you can calculate the power. So, work done per second work done per second so, that will give you the power of the cell. So, that brings us to those very words you heard this battery has this much power this cell has that much power where all these things are getting derived these are getting derived from this very simple equation. So, and that is why I am taking. So, much time on the basics if you understand this basics that everything will make sense to you.

Similarly, from there you can calculate the delta G, which is n out here which is in the mould faradays constant and E you know. So, if you know this then you can calculate the free energy. So, with one small value you can really open up the whole gamut of things what all you can do. So, you need couple of parameters. So, essentially the 2 parameters where everything works is either you have the voltage or you have the current if you know either 1 of these 2 you can really play around very neatly with the system.

So, that is why I wanted to go back and let me come back where I am. So, this was a very early on and I want you to want you people to revise through those basic things that from these values we can do the work done what is the work is being done and how much work is being carried out in the whole process. So, from here we will move on to I will now show you a practical table I will put a table in front of you that will give you an idea. Say for example, this is just a small part of the table you will find most of these tables or maybe I will add 1 into fluorine which is F 2, gaseous state plus 2 electron making it 2 F minus I am just putting all the different O 3 which is ozone gaseous state plus 2 H plus plus 2 electron making it o 2 gas plus H 2.

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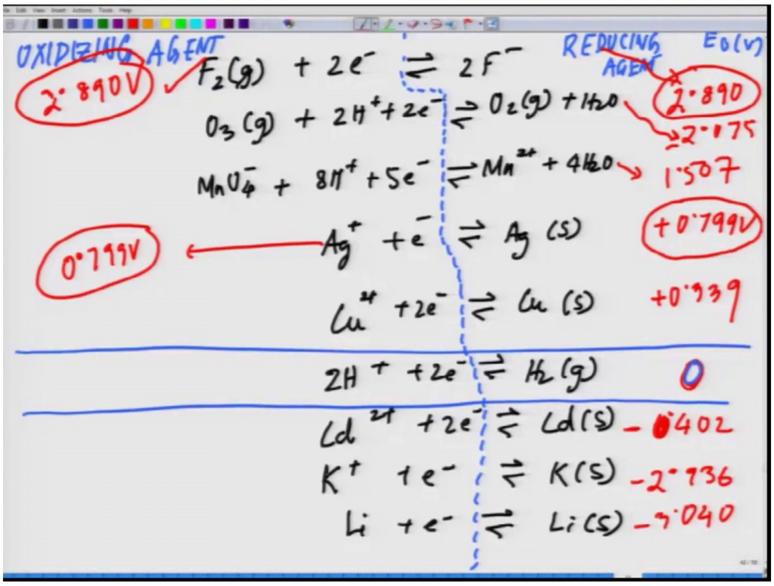

OXIDIZING AGENT — REDUCING AGENT — E0(V)

2·890V — $F_2(g) + 2e^- \rightleftharpoons 2F^-$ — 2·890

$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$ — 2·075

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ — 1·507

0·799V ← $Ag^+ + e^- \rightleftharpoons Ag(s)$ — +0·799V

$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ — +0·339

$2H^+ + 2e^- \rightleftharpoons H_2(g)$ — 0

$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$ — -0·402

$K^+ + e^- \rightleftharpoons K(s)$ — -2·936

$Li + e^- \rightleftharpoons Li(s)$ — -3·040

Similarly, M n O 4 plus 8 proton plus 5 electron these are the different compounds I am just giving an kind of example of M n 2 plus plus 4 H 2 O. Similarly Ag we have already talked about it Ag plus electron Ag solid copper 2 plus plus 2 electron making it Cu solid similarly 2 H now this is the reaction what we have already talked about H 2 gas.

Now, cadmium 2 plus plus 2 electron making it cadmium solid, similarly potassium plus plus electron making it potassium solid, similarly lithium plus electron making it lithium solid, now you remember one of the values right this value all of you remember. Now what I am giving you is E 0 values on this column E 0 in volt E naught standard reduction potential and these agents. So, if I had to really you know split it up and then put all of them in line between this on this side what you are having are the oxidizing agents.

So, you remember oxidizing agents are the ones which get reduced in the process and reducing agent which gets oxidized in the process. So, if you remember this value this is

0 this is what we have assigned it now you remember for silver silver it was positive 0.7 9 9 volt now copper which is plus 0.3 3 9.

Similarly, for fluorine it is 2.8 9 0 and these are all experimentally determined values. Similarly for oxygen once again this was for fluorine and oxygen is out here which is 2.0 7 5 for manganese it is M n O 4 it is 1.5 0 7. Now if you go below hydrogen this is where you are falling cadmium minus 4 0 2 0.4 0 2 potassium minus 2.9 3 6 minus 3.0 4 0.

Now, I told you something I wanted to show you that picture what I drew earlier out here this is that reference you remember, I told you that there is a reference with reference to it we have certain things which are on the negative side which are on the positive sides. now coming back here is your situation, what does this physically means physically if you look at this picture say fluorine has a value of 2.8 9 0 as compared to silver which is 0.7 9 9.

So, let us write down the value 2.8 9 0 volt and have silver 0.7 9 9 volt. Now in this situation say for example, I make a cell of silver and fluorine just imagine for the imaginary sake and I ask you the question, who is going to pull the electron faster maybe someone has to pull the electron faster.

So, in this case that 2.8 9 0 volt of the fluorine will tell you can immediately lou to the this has much more positive value it means it has more power to pull the electrons. So, if these 2 are starting and there is electrons sitting out here say for example, this is the electron somewhere out here this is the electron and these 2 my 2 hands say for example, I place it like this somewhere something like this, I place it and these are the 2 1 is fluorine and 1 the other 1 is silver who is going to pull the electrons faster this floor this is going to capture the electron faster.

So, it means if I make a cell with fluorine and silver the electron will flow away from fluorine sorry from silver to fluorine, because fluorine has a much more power to pull the electron towards it in other word work done for the electron to move will be much more higher in case of fluorine has compared to much more spontaneous as compared to silver. Now think of a situation we had this cell when we talked about a cadmium and a silver electrode.

Now cadmium and silver when we made that cell what we showed now if we go back. So, we showed that in that case the electron. So, cadmium is getting oxidized and the electron is moving from left to right to the silver electrode to reduce the silver electrode. Then we had this standard hydrogen electrode out here we showed the electrons from standard hydrogen electrode moves and reduces the silver. Now how we could figure that out because our voltage was showing on the negative terminal electrode is reaching.

Now, I give you a situation where again we have the same situation on this side.

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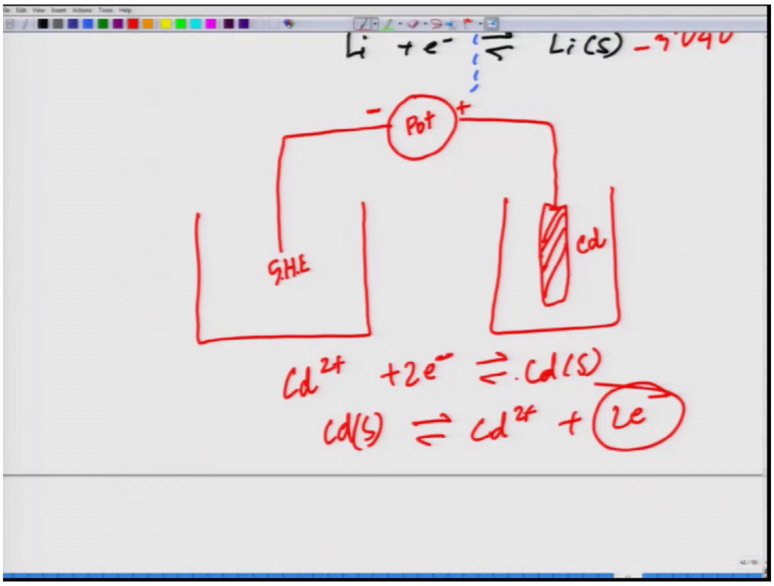

We have the standard hydrogen electrode she and on this side this is half-cell we have the cadmium electrode. Now we wanted to measure the cadmium the standard hydrogen electrode is attached to the negative terminal of the potentiometer what and this is the positive side.

So, now what will happen now in this situation by the convention the left hand side is a platinum electrode attached to the negative reference terminal of the potentiometer and the right hand electrode is attached to the positive terminal. Now in this situation in order to measure the standard potential of the half reaction of cadmium 2 plus plus 2 electron making cadmium or in this situation it is basically cadmium cell C d 2 plus plus 2 electron where it is giving away these 2 electrons.

So, this is a situation now what we are observing in this situation is. So, you have on one side the cell is like this.

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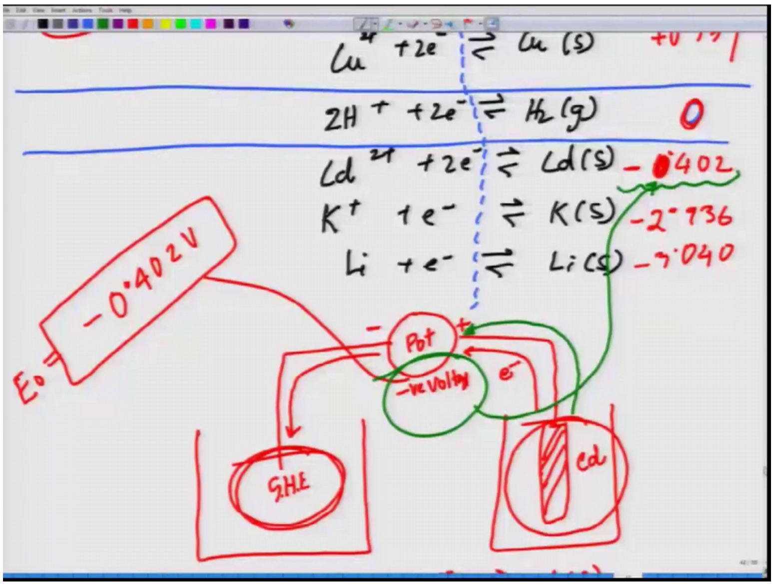

Standard hydrogen electrode she C d 2 plus in aqueous the activity is equal to 1 and C d solid and what we are observing is it is showing you a out here if you follow the chart it is showing you negative voltage and the negative voltage is minus 0.4 0 to volt. Which is; that means, in this situation this electrode standard hydrogen electrode has more power to polar electron as compared to cadmium, because the electron flow is now happening in the reverse direction like this and if you remember the axiom I told you when the electron is reaching the negative terminal of the potentiometer, you will see a positive shift, if the electron is reaching the negative terminal sorry the positive terminal of the potentiometer, if the electron is traveling follow the diagram, if the electron is travelling to the positive terminal of the potentiometer.

Then you will observe a negative voltage and that is precisely is why you see. So, in other word what is the physical meaning of it is that if there is a competition between standard hydrogen electrode versus cadmium electrode then standard hydrogen electrode has more power to snatch the electron towards it as compared to the cadmium electrode. And that is why you see the electron will be drifting in a reverse direction from right to left unlike left to right what you still happen in cadmium on the left silver on the right left right electron drifting.

Standard hydrogen electrode on the left silver electrode on the right electron is drifting. Now cadmium electrode on the right on the left you have the standard hydrogen electrode electron is drifting from right to left and your meter showing a negative voltage which is 0.4 0 2.

So, I believe with this background of understanding standard potential standard reduction potential you will be able to draw your own story. So, the negative sign means that the electron flows from cadmium to platinum a direction opposite to that of this other cells.

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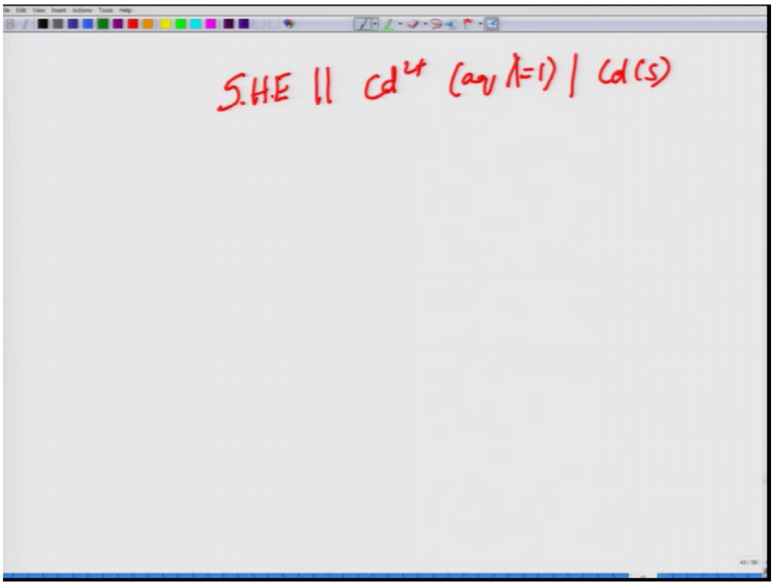

$$S.H.E \parallel Cd^{2+} (aq, \lambda=1) \mid Cd(s)$$

So, with this background I want you to kind of revise through because I took 3 classes purposefully on standard potentials, because this is one concept which will come very handy as will move through.

So, what we will do we are in the second week though and we have talked about only one kind of electrode which is standard hydrogen electrode. In the next class after this we will talk about the Nernst equation followed by the series of electrodes what will be dealing with.

So, I again advise you please concentrate on the basics it is all about the basics and I am only you know churning out the most important aspects what you needed to know as a biologist to do by electrochemistry please get your basics right please.

So, that is why I am going very slowly I am not really worried about the bulk what you know what is important you know the basics very well from one set of value you should be able to back calculate what is happening how much work is done how these things are happening. So, please please please it is my kind request, please concentrates on the basics I am going slow for you people. So, that you understand the basics once and for all. So, I will close in here in the next class will talk about the Nernst equation and will follow up from there.

Thank you.