

**Bio-electrochemistry**  
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**Lecture – 12**  
**Cell as Chemical Probe and Biochemists Formal Potential**

Welcome back to the lecture series in Bio-electrochemistry. So, in the last class I gave you a taste of what all the power a electrochemical cell can offer for you. So, looking at the voltage and the concentration of the reactants on the different half cells, if there is one component which is unknown you can figure that out. And in the last class we talked about how we were analyzing H plus ion concentration.

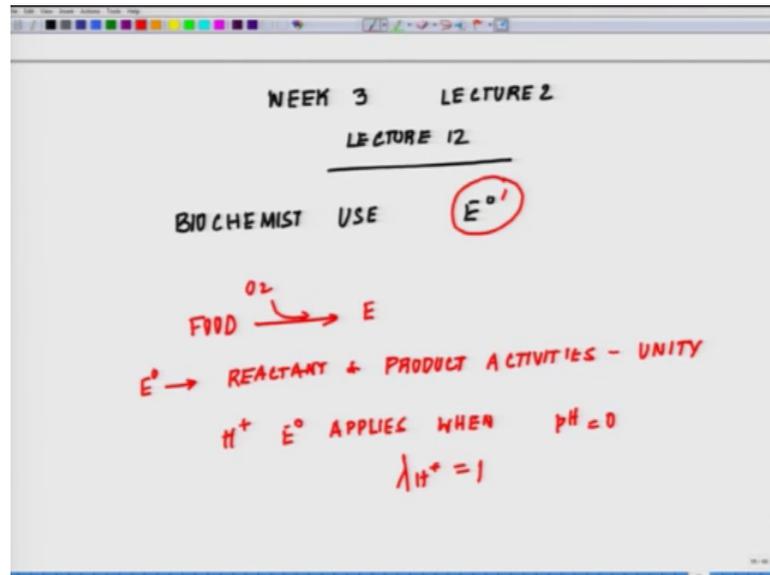
So, one thing what I wish to highlight now is how it differs when we translate these systems in biological systems what does that mean? So, that essentially means that most of the biological systems are nothing, but redox chemistry. There is electron transfer happening all over the place the whole biology whether it is starting from photosynthesis to respiration.

Whatever you talked about these are nothing, but transfer of electrons of course, not at the inorganic level huge amount of electrons are getting transferred, but end of the day it is oxidation and reduction, which is happening, which is the fuel or the machinery, which is driving the whole energetics?

So, could we directly translate the value of  $E^0$  what we have as of now derived electrode reduction potential, standard reduction potential to the biological systems. Actually that is not possible, why that is not possible? We will discuss it today very briefly and from there we will move on to different forms of electrodes. And that was the reason why I kind of delayed this far almost took 4 5 plus additional classes as of now, to come to this point because there are certain aspects, which we needed to understand.

So, let us start the class which is our week 3 lecture 2 and this is overall this is lecture 12.

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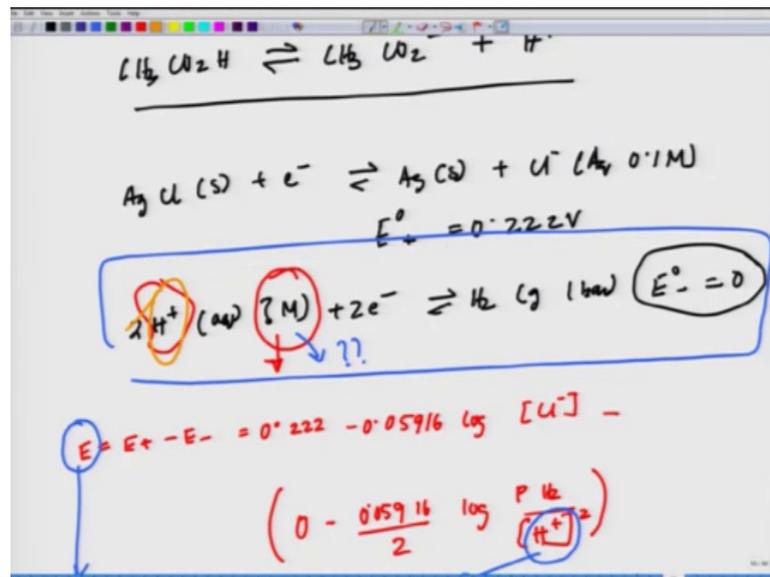
And Lecture 12 we will be talking about biochemists use of  $E^{\circ'}$  and now I am adding one more term to that  $E^{\circ}$  prime, which is different from  $E^{\circ}$ . In respiration molecules from food are oxidized by oxygen. So, this is a common thing you know these are getting oxidized; this is what happened in respiration to yield energy or metabolic intermediate.

The standard reduction potential that, we have been using so far applies to systems in which all activities of the reactants and product are unity. Whenever we calculate  $E^{\circ}$ , we assume reactant and product, activities are unity this is our assumption. And if  $H^+$  is involved in the reaction  $E^{\circ}$  applies, when an  $H^+$  is involved in the reaction  $E^{\circ}$  applies when  $pH$  is equal to 0 or in other word a  $H^+$  equals to 1.

So, whenever  $H^+$  appears in a redox reaction or whenever reactant or product or acid or basis reduction potentials are  $pH$  dependent. So, this is one catch which I wanted to bring to your notice. In the last example if you see when we talked about  $H^+$  concentration. So, to realize that standard potentials, standard reduction potential calculation are based on the fact that  $pH$  is 0 and all the activities are unity, which is perfectly fine as long as we are dealing with such system.

But think of a situation think of the last class when he talked about a situation like this.

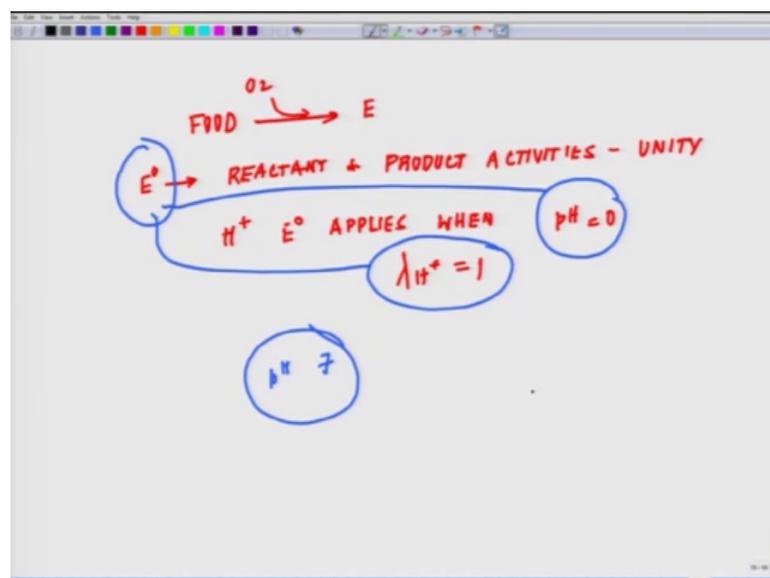
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Where one of the key contestant is this, now as soon as you have H plus ions coming into the play the game changes. Because it shifts a p H and as soon as it shifts the p H then the dissociation, association all the activities everything go for a toss.

Having said this let us realize another fact that biological system does not works at p H 0 except probably in your stomach or in the gu the gut, where you are digesting the food which is extremely acidic p H, but the whole biology works at p H 7.

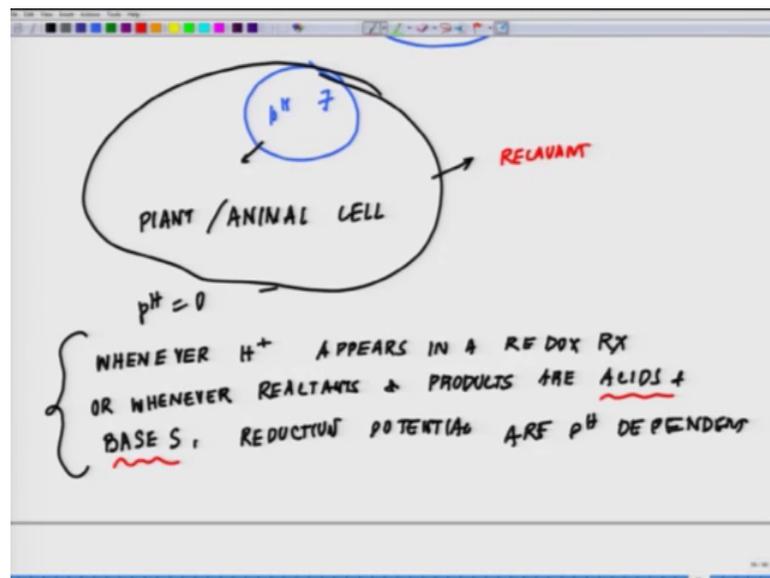
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So, now our basic premise of using  $E^0$  was at  $pH\ 0$ , which is perfectly fine and where everything was unity, but we cannot directly transfer it in the biological systems, because we are dealing with  $pH\ 7$  situation.

So, that is where we will be now proceeding further. So, because the  $pH$  inside a plant or animal cells. So, for example, 1 second inside a plant or animal cell the  $pH$  is 7.

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So, the reduction potential that apply at  $pH\ 0$  are not appropriate for example, at  $pH\ 0$  say for example, we take an example at  $pH\ 0$  the ascorbic acid or vitamin c is a reducing strength, is a powerful reducing agent than Succinic acid. However, at  $pH\ 7$  this order is reverse it is the reducing strength at  $pH\ 7$  not  $pH\ 0$  that is relevant to a living cell.

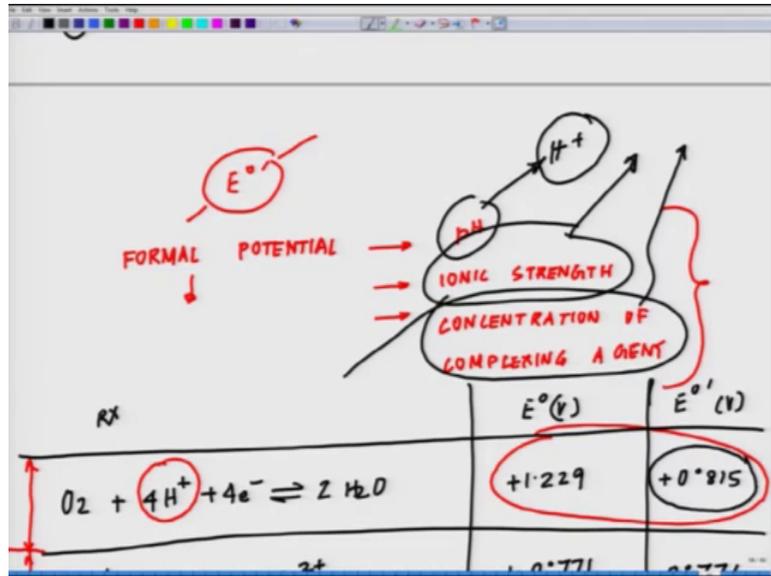
And always remember whenever H plus. So, this I want you to realize, whenever H plus appears in a redox or reaction, or whenever reactant and products are acid or basis, whenever reactants and products are acids and bases, the reduction potential are  $pH$  dependent. So, keep this aspect very clear in your mind.

So, it is the reducing strength at  $pH\ 7$  not at  $pH\ 0$  that is relevant to living cell, this is our critical point to remember. And always realize that we have all such situation, where you have acid bases which are involved in the biological modules.

So, now what is the way to get around it the standard potential for a redox reaction is defined for a galvanic cell in which all activities are unity. Now the formal potential this

is this part is very important that what we are going to talk about, which is represent by E 0 prime sorry this is essentially E 0 prime like this.

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So, is the reduction potential that applies under a specified set of conditions this is our, which is used by the biochemist formal potential.

So, this is we are getting into the domain of bio electrochemistry. Now is a reduction potential that applies under a specific set of conditions, which includes p H ionic strength concentration of complexing agent.

At this point you people have to remember these 3 aspects biochemist called the formal potential at p H 7 as E 0 prime this is that E 0 prime. Now I will put some of the values for you to realize how E 0 prime looks like say.

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Rx	$E^{\circ}$ (V)	$E^{\circ}$ ' (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.815
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	0.771
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.535	+0.535
CYTOCHROME $a$ ( $Fe^{3+}$ ) + $e^-$ $\rightleftharpoons$ CYTOCHROME $a$ ( $Fe^{2+}$ )	+0.290	+0.290

For example, let us draw a small table of some of these values.

So, the reaction out here  $E^{\circ}$  v, which is standard potential and here you have  $E^{\circ}$  prime in volt. Now let us take the first reaction oxygen plus 4 H plus, plus 4 electron and the famous situation 2 H 2 O. And if you get the  $E^{\circ}$  value of this, which is plus 1.229 whereas  $E^{\circ}$  prime in the biological module it is plus 0.815.

So, this is where the water splitting happens. So, this is basically you are splitting the water. Now take a simple 1 iron 3 plus, plus electron it is getting reduced to make it f E 2 plus. Now in that situation value is 0.771 as well as 0.771. Now you realize the difference, both are same why both are same? Because the previous case this was the reasons why I want to show you have H plus ions which are involved in it.

So, if you I will give you few examples which will tell you the story, whenever you have the p H involvement is there. The storyline is going to change out here and when p H is not involved there, it will remain the same. So, please appreciate this 2 interesting situation. Now let us get to another one another example in that line.

So, say for example, let us take the case of iodine I 2 plus, 2 electron making it 2 I minus and the changes are  $E^{\circ}$  changes 0.535 (Refer Time: 13:53) 0.535. Now you realize it is similar to the ferrous ferric ferrous.

Now I come to another situation where you have the biological molecule like cytochrome, cytochrome a which is Fe<sup>3+</sup> plus, plus electron it becomes cytochrome a Fe<sup>2+</sup> plus which is getting reduced and the values are plus 0.290 plus 290, because again there is no involvement of any hydrogen ion or any kind of acid base situation.

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$\text{CYTOCHROME a (Fe}^{3+}) + e^- \rightleftharpoons \text{CYTOCHROME a (Fe}^{2+})$	+0.290	+0.290
$\text{O}_2 (\text{g}) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}_2$	+0.695	0.281
$\text{PYRUVATE} + 2\text{H}^+ + 2e^- \rightleftharpoons \text{LACTATE}$	+0.224	-0.190

So, now I will move on to another example which is a very tricky one which is oxygen, gas, plus 2 protons, plus 2 electron making it H<sub>2</sub>O<sub>2</sub> and in that situation your value is plus 695 whereas, if you measure it with E<sup>0</sup> prime the value will be 0.281. Now here is another example of the difference you could see.

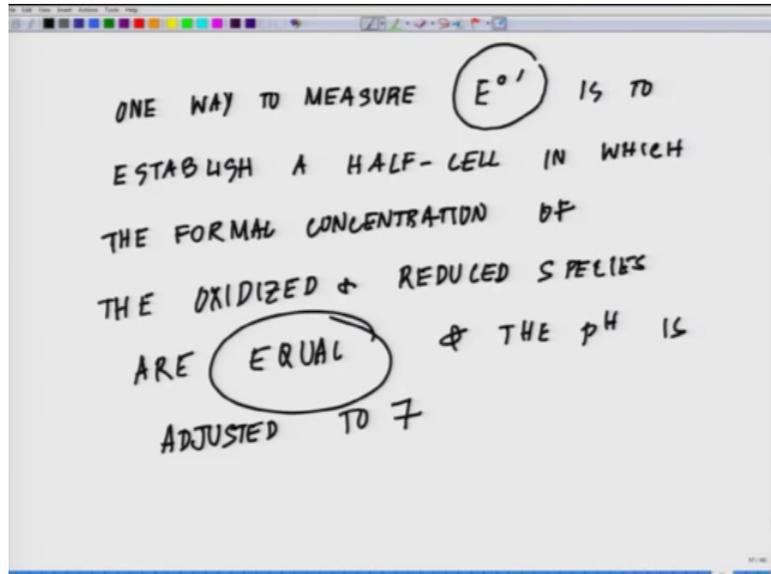
Similarly, you can do it for cytochrome c Fe<sup>3+</sup> plus plus electron to make it cytochrome c Fe<sup>2+</sup> plus you know you will see a plus 254 volt E<sup>0</sup> prime. Similarly let us take another example where say pyruvate, pyruvate to lactate once again pyruvate plus 2 H plus plus 2 electron this is making it a lactate.

Now, if you look at this reaction pyruvate to lactate pyruvate to lactate under standard reduction potential it is plus 2 to 4 whereas, if you use the E<sup>0</sup> prime value it will be 0 point minus now look at this one the difference. So, what I mean I will give you the list of all these things.

What is important for you to realize is for us for bio electrochemist, it is important that we understand the concept of E<sup>0</sup> prime or the formal potential, because this is the

potential, which we will be using in most of the electrodes time and again time and again and time and again.

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So, keep that formal potential in mind and let me highlight another aspect here. So, one way to measure  $E^{\circ'}$  is to establish the half-cell, which is a formal concentration of oxidized and reduced species are equal and the pH is adjusted to 7.

So, keep this in mind one way to measure  $E^{\circ'}$  is to establish a half cell in which the formal concentration of the oxidized and reduced species are equal and the pH is adjusted to 7.

So, keep that in mind and there is another aspect, which I have not dealt as of now and I will be dealing with later is the concentration of the complexing agent. This part is very critical the concentration of the complexing agent will come later with the monoprotic system diprotic system, I am not introducing all those at this point purposefully.

But what I want is you people understand that whenever we talk about the formal potential for the bio for the use in the biochemical reactions. We have to always keep in mind H plus ion concentration ionic strength, it cannot be unity and the concentration of the complexing agent will come later as will move on to the different kind of electrodes.

So, with this we kind of have covered most of the fundamental basics, what you will be needing to understand the electrodes of course, there are much more to it as it we will do it and wherever the opportunities will come I will highlight it, but it is much of a doing things you know once you do these kind of things you realize and much of a can have to think over think through it what is happening in this whole process.

I will close in here and we will continue with a different kind of electrodes in the next section.

Thank you. Bye.