Advanced Chemical Thermodynamics & Kinetics
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Lecture-38

Electrochemistry: Insights into electrode processes, Ionic conductivity – Part 01

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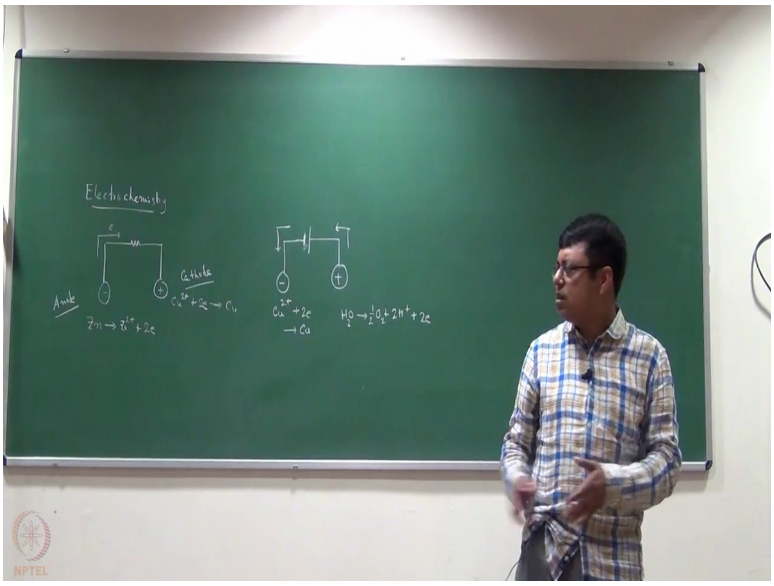

Now, already this is the high school stuff like you already or all of you know like galvanic cell and electrolytic cell, right so, just again just to recap you, ok. So, like a galvanic cell is something like. So, let us take an example, we draw it (Refer Time:0:40) And this is the kinetic cell right, ok. So, what is the galvanic cell? Galvanic cell is basically.

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Louder, there are two kinds of cell, right galvanic cell and electrolytic cell. Now what is the galvanic cell?

Student: (Refer Time: 01:22)

Is for basically producing electricity.

Student: (Refer Time:01:28)

Right now, the thing is that if I just connect this of course, you know that there is a half cell, right and I have to basically get the total cell potential. We have to basically take e right minus e left, there is a convention right by thing here is that. As you can see that I have oxidation here, right. So, wherever I have oxidation that electrode, I denote as anode, right. So, and then what will happen this zinc, ok. So, suppose this is zinc metal and it is coming to the solution, the zinc two plus ions leaving the electrons here. So, this becomes a negative electrode right and this becomes a positive electrode. So, that the electron actually flows from like zinc to zinc electrode to copper electrode, ok.

But if I actually reverse a concept in the sense that of a, I am writing the same thing. Here, we have defined the electrode potential, this equal in this case actually what happens like, as you can see like what is happening, water is getting oxidized here right and electrons are deposited here. Wherever I have a oxidation that I will call as always anode, ok. So, valve per valve ok, but here the only difference is that from the galvanic cell and the electrolytic cell is that in galvanic cell when negative electrode here is the anode. Whereas, here actually as you can see here also when I have the which one method (Refer Time: 03:47) copper and then zinc just one I have.

So, water is getting oxidized. So, ye electrons will flow, but in this common cell what happens is that we always write plus and minus for anode and cathode, ok. So, anode always you keep in mind that irrespective of the type of the cell whether it is a galvanic cell or a electrolytic cell, ok. It will be always that electrode that actually have while actually oxidation happens, ok. And cathode is basically the ion electric, ok. Now as you can see that the, I can actually use or suppose for example, what is electrolysis, ok. Now all of you know this thing. So, electrolysis means suppose, I will like supplying electricity, and let something deposit on something, right.

Suppose I want copper plating, which, which cell I should use galvanic cell or an electrolytic cell? Actually, I can use anyone if I use a galvanic cell, where actually this reaction is spontaneous, right. And actually use a electrode along with copper where actually copper will be deposited, or I could have actually used a potential external bias, to get that opposite reaction happens, ok. So, that way also I can do electroplating of copper, ok. So, electrolysis does not always mean that you have to do electrolytically insert, ok. You can also do it in galvanic cell; it only depends on the difference in the potential.

Now, this is a standard thing which everybody starts with right the Daniel cell and other things, but the thing is like and this is a very like common thing, common thing in the sense that usually, you will always have two half reactions, right two half cells and then we will connect it, ok. Now, which means actually we will have basically two electrodes to begin with, right. And then there is a electrolytic solution that is the all the thing, right. Now the thing is like what could be these electrodes, all of you know that most of the cases the way I have shown here is basically the metallic electrodes, right like platinum hydrogen all those things, right.

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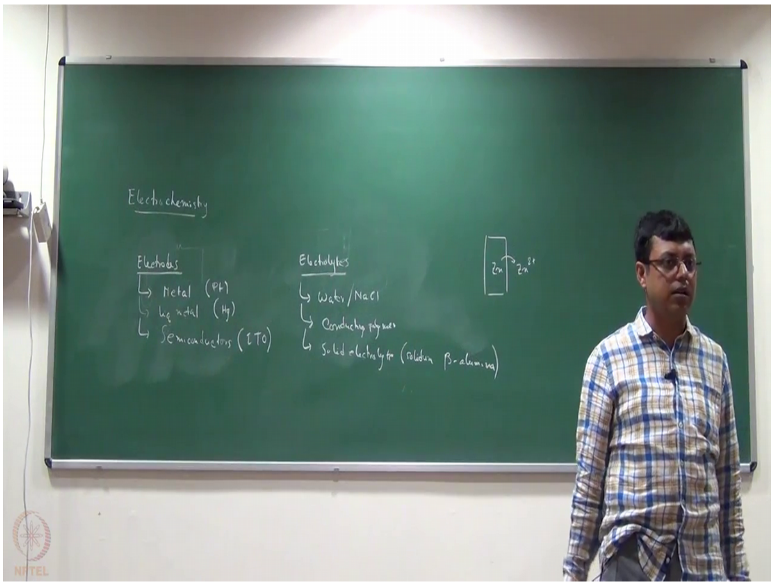

So, I electrodes can be of metallic in nature, ok. They can be also liquid metal for example, like anyone liquid metal, any among them let us say mercurous; so, we can have actually liquid metal, ok. Not only metal we can also have semiconductors like ITO indium tin oxide, right. Say mercury (Refer Time: 06:45) something like that, ok. And similarly, for the electrolytes, I will also have like usually it is aqua solutions like also water and some soluble salt, like it can be like NACL or something potassium chloride whatever, come to the example solution. It can be also let us say, conducting polymers also like in solars, also you will never use actually any solid liquid solution because the volume will be match, ok.

So, by conducting polymer it can also be solid electrolyte, ok. Anyone solid electrolyte like all your mobile phone batteries, right those are depending on solid electrolytes, lithium ion batteries all those things, right where actually it happens basically the lithium ion moves in and out, of like intercalate structure, ok. And then pass cycle basically this intercalated structure, the composition and all things the, get degraded, that is why mobile phone battery also has a life time. And the entire like current technology is based on that ok, but there are also sodium based batteries which are being developed. So, an example is sodium alumina beta alumina electrolyte.

Now, thing is ok, I have basically electrodes, I have electrolytes, ok. And the overall function of a cell will depend on basically how the electrodes and electrolytes are basically functioning, ok. Now what happens and the electrode and electrolyte is basically some electron transfer will happen, right we know. Now of course, (Refer Time: 08:55) the electrode electron transfer is happening, but in the solution phase what is happening the ion transfer, right. So, both are important like electron transfer as well as the ion transfer, I should say is not only electron, it is electron or a hole that mean the way you want to see, electron and hole transfer. So, electron and hole are actually mobile carriers for the electrodes as well as external circuit, ok

We usually do not talk about that when we talk about electro chemistry, because we usually use like standard definition like a copper wire is attached ok, ok, because copper wire has a perfect a particular standard resistivity, ok. So, do not focus on, on that part, or this is the mobility of electrons that definitely, the mobility of electron matters at a interfaces meaning as I, as I said that I have basically zinc and I have zinc 2 plus here, right. So, when the electron transfer takes place, there of course, it is it matters a lot, and many I mean like investment has been there, in developing the surfaces and interfaces.

So, all these electrochemistry thing is actual pretty much an interfacial phenomenon which we discussed like surfaces and interfaces, but this is the surface electrochemistry now, we are talking about, ok. The very specific nature of the surfaces also matters see an example totally, ok. Second thing, the mobility of the electrolytes is also matters, right like how there are mobile and we will be talk about it in like a later class, how basically I can connect the ionic mobility, to something known as conductivity of ions and conductance number and all these things, right.

Now, these two things matter of course, now the question is how these two things are connected, or meaning basically what have all of you know that if I am actually having a electrode inside a solution, ok. There is always a potential difference, ok. Now the question is, how we can actually quantify the potential difference or what is the basic nature of the potential difference, ok? Now usually one we talk about electrode potential, ok, we usually write all these half cell reaction standard half cell reactions, right with respect to some standard electrode. And all of you know that, that is standard electrodes are of can be of (Refer Time: 11:20) the most like widely accepted one is the standard hydrogen electrode, right.

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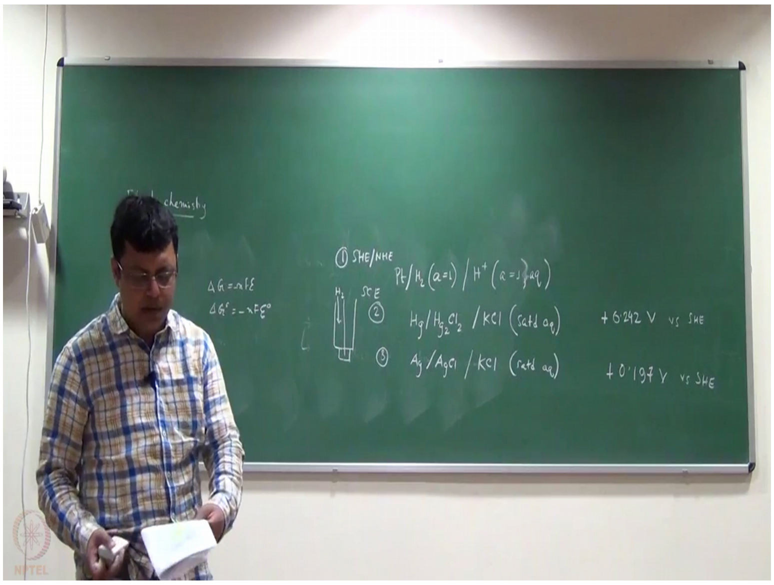

Now, there actually we have up the electron is actually platinum right and the way we know is widely as I have platinum something would actually write it as a vertical bar, ok. Why because these bars is basically represent the two phases ok, because this is the gas phase and this is the solid phase, ok. Now once, I have the gas phase thing, they let us say I am just writing platinum and hydrogen how it will look like? So, basically I have a platinum electrode, and of course, like it will be inside the glass wire tube, I have hydrogen gas, ok.

Now, as you can see that I am assuming that everyone knows Nernst equation, ok. Now it will be it only, I am taking about platinum right and write basically a cell reaction where I have a e 0 plus concentration of the species, right. Here, the species is basically metal. Now ideally, I cannot write concentration, because already talked about it for electrolytes. Particularly, we have to write in terms of activity, ok. Now if I replace it by activity metals, pure metals always have activity equal to 1 to this test right problem is the here hydrogen right, it is a gas. So, I have to use basically either fugacity or activity some kind of concept.

So, by definition, I always choose that these activity is basically equal to 1, ok, because this cell right any cell we have a e 0 standard thing plus rtln all this stuff ok, but that terms I am actually making 0 for the standard definition. How to make it 0, basically I am making it to 1 platinum, I am never write activity to be 1, because it is already a metal, ok. And then of course, I have what my the aqua states, I have basically H plus, because a fundamental reaction is H plus getting reduced to H 2 right. So, that H plus again I have to write an activity, ok. So, by default actually we choose the activity choose to be equal to 1 and of course, I have to write it that it is in aqua state.

Now, this represents a cell diagram, a notation a shorthand notation where actually I am describing the half cell, for the standard hydrogen electrode, ok. And we take the standard potential of this term to be equal to 0, I will measure everything with respect to that again. We usually do not use this thing, it is called actually standard hydrogen electrode or normal hydrogen electrode, but usually we do not use it because of practical purpose. We always have to keep the hydrogen activity to be equal to 1, we have to always pass hydrogen gas, ok. So, it is also not very much like portable, right you have to basically transfer hydrogen gas. So, for that actually, we have alternate electrode which is known as what is this calomel electrode right you know, this thing.

So, Hg is nothing, but mercury mercurous chloride, in KCl, that this KCl, it is what is KCl, it is a potassium chloride aqua solution, but then activity cannot be equal to 1, because it is a solution, ok. So, like so, all you can say is that this KCl maximum you can take as a saturated solution, ok. So, instead of writing A equal to 1, we write it as a saturated aqua solution for potential of that, with respect to the standard hydrogen electrode is something like 0.242 volt, ye clear. So, this is one of the practical electrodes, ok.

Thus I have a practical electrode which is silver, silver chloride electrode and the potential is. So, when I said plus 1 9, 7 it is good to write like verses is standard hydrogen electrode, ok,because you always measure the potential, ok. How do you measure the potential in what is measure the electromotive force of a cell right and each cell has two half cells, you always measure the differences in the Gibbs free energy delta g right, you are not measuring the absolute Gibbs free energy, you cannot actual.

So, the delta g is the difference and that is why you always talk about the differences, ok. That delta g is of course, you know it is minus nFE, or I mean the standard state will be defined as minus n f will, will be very, but not in this thing just give you a very interesting introduction (Refer Time: 16:56) introduction to this. Now, suppose I have a like cell like this, I have suppose platinum, I mean these are basically the standard electrodes. This is known as.

Student: (Refer Time: 17:11)

It is called saturated calomel electrode,. The reason is basically, I have saturated solution, ok. And similarly, I have the silver electrode, alright. Now the question is, suppose I have what will be my like arrangement, experimental arrangement, I have basically two electrodes, ok. And I will just basically dip it into the solution and I have an external circuit, ok. Now think about it, I have suppose just think about all one thing that I have process like a one particular electrode. So, what I am doing is that I dip the electrode, ok. So, I know that there is a potential developed, ok. Now always keep in mind that the potential is developing only across the interface, ok. So, that is why interface is also important. Now, I am suppose applying some voltage to it, ok. So, what happens? So, ideally like when you talk about electron transfer, right.

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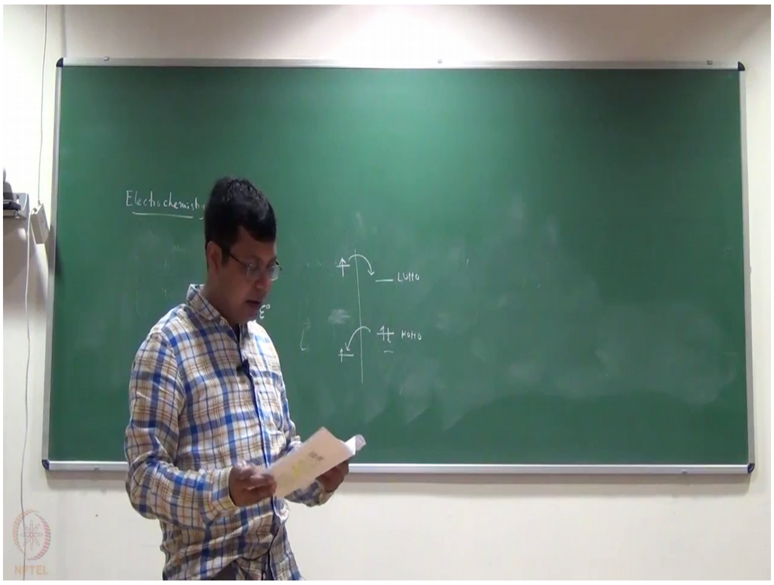

So, the first thing which the way (Refer Time:18:10) think is that like I have electrolyte, and this electrolyte has some molecule, it can be say ion also that zinc 2 plus or something, ok. And when basically all the electrons up to the homo (Refer Time:18:27) and there is a(Refer Time:18:31) lumo, ok. Now what happens is that I have my metals potential, somewhere here, which I can change. How will you change it? Basically, I can choose a particular electrode or actually I can take a particular electrode and apply potential. If I apply potential I will basically tune the potential like this, ok.

And suppose an electrode means something like you always represent it by one electron. Why I am showing it as one electron, because I am saying that it has a basically conduction line where actually it can accept electron. As well as, it can donate an electron ok, it is not really an one particular electron, because it is a basically a continuous band, it is a metal in it ok, but only point is that it is, it can still accept or donate electrons, ok. Now what can happen is that like suppose if the if, I can position my electrode here, or if I scan the potential ok, I can have a electron transfer from here to here, ok. Alternatively, as you can see if I have the potential scan here, ok. I could have the electron transfer for the solution to the electrode ok, because it is still have like valent, ok. So, meaning this is usually known as so, what is happening here as you can see the electron is leaving the electrode, ok.

So, it is kind of an anodic process, verses this is the kind of cathodic process, ok. Now I am giving an overview, if I do this thing suppose I have fixed electrode and I am just basically scanning this potential, ok. What will happen, at what point like I will have how the current will flow. So, basically all I am trying to understand is that if I scan the potential external, and tune basically the energy level of the, it is not energy level it is basically the electric potential of the metal with respect to the solution, ok. So, that I can facilitate this electron transfer or this electron transfer something like that, ok. Then of course, once the electron transfer happens then the circuit gets completed right then I have current flow, right.

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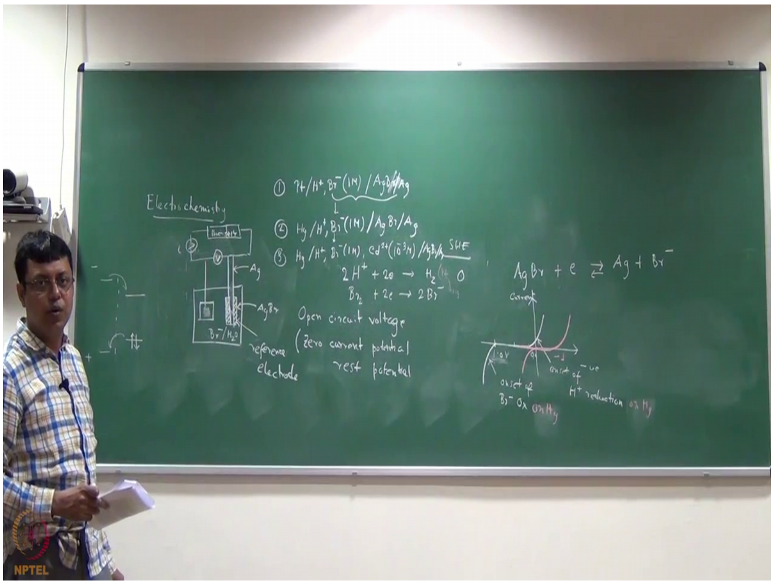

So, all I am looking at is basically if I scan the potential how the current changes, ok. And I have a very very let us say very like interesting set up here. What is that? Suppose, I have something like some solution, ok; I have just dip platinum electrode here, ok. This is not a standard hydrogen electrode; this is just a platinum metal, dipped in a solution. On the other side I have suppose some electrode which is the silver electrolyte electrode, ok. So, it is basically, let me just first draw it. So, I have basically a piece of metals which is silver, and outside I have silver chloride or silver bromide.

Remember, that when I write a Hgcl or Hgpl, there also activities by default one, because this is also solid, ok. It is in solid clear, I need a solution suppose I have, I should have one, I should have some kind of ion, right. And suppose, I am taking here let us say some bromide solution of some say activity, and then what I am doing is that I am basically connecting these two. And I am asking this question how much is the potential drop between them, ok? I can have a power supply and also measure the say this is a current, ok. So, what I did is basically I have two electrodes ok, one side actually I have some standard half cell ok. And other side is just a metal and this also aqua solution in the sense that it is Bromine Bromide water. So, let us a kbr whatever, ok.

And then what I am doing is that I have plused a potentiometer between what is a potentiometer? It is basically, I should have a panel connection right and a potentiometer by definition should have infinite resistance. So, that I mean practically no current flows through it before we need, ok. And then I have a some kind of ammeter while I can actually look at the current flow. And I have a power supply what actually I can apply say positive voltage as well as the negative voltage, clear this is my circuit. Now what I am doing is that I am basically scanning the potential, and trying to see how the oxidation and reduction reaction as they are occurred in ok, how the current flow is happen, ok.

Now, think about it there are many things can happen first of all actually there is water, ok. Now, water can actually like basically there will be a H plus and water can at equilibrium like whatever trying to say is that there will be some equilibrium like this, right. So, this reaction will happen at some point now every reaction as I know has basically e 0, right. What is basically the standard reduction potential? So, when I am scanning the potential, when the potential actually reaches around the value of the potential corresponding to a particular reaction then the reaction happens, ok. It is basically the other way of thinking; however, just keep in mind this cell is a very special cell in the sense that on one hand, I have like thermodynamic equilibrium, you will say silver, silver bromide all these thing.

But here I do not have, because I am not (Refer Time: 24:49) hydrogen again it just a metallic electrode, ok. It is not actually in that cells or two half cells just one half cell is present ok, but you can still measure the potential, ok. Now, in this configuration if I just attach the, if I just connect the voltmeter, ok and if I just do not just start it off ok, say zero power supply or something like this zero potential, ok. I might still some residual current ok, because there is a, could be and net potential difference that is acting and that is causing a current flow. So, I might actually have to supply some current to stop sorry, supply some apply some voltage to stop the current, ok. So, that voltage which is required to get a 0 current is called actually 0 current voltages or 0 current potential or more commonly as open circuit voltage, ok.

So, basically open circuit voltage corresponds to a voltage or potential where actually my current will reserve, ok. So, it is not always necessary that the zero potential will give you the zero current, because always I will have a residual potential difference, alright we will see actually here open circuit voltage is like different ok. And it has a some alternative elements, it is sometimes called linear zero current potential, potential or sometimes it is called a rest potential. And the name (Refer Time: 26:34) is obvious, right. Why it is called zero current on the not the rest potential, ok. Now just think about it what is happening. So, I have basically this thing when I am actually applying voltage, ok. So, what can happen is that I have the H plus ion that can (Refer Time: 26:52) hydrogen, or I can also have bromide here.

So, I can also have another electrode reaction which is something by if I write it in the reduction, ok; I have to write it in this way. So, this reaction can also happen clear ok. Now whenever these reactions are happened, these are happening at which electrode platinum electrode, right and there will be always a counter reaction in the other electrode, ok. Now usually these electrodes as we said that this is we call it as a reference electrode, like standard hydrogen electrode that is the reference electrode right, because I am measuring everything with reference to that or say like this is also a standard electrode, ok. So, silver bromide electrode that has a particular potential with respect to standard hydrogen electrode, this is called as secondary reference electrode, but what is the meaning of the reference, ok.

So, this I am saying actually this is the reference electrode. Now think about it what kind of reaction will happen in the reference electrode, the reference electrode that have basically silver bromide, right. So, I have silver bromide is basically silver is oxidized here. So, if I have one electron here, ok. So, I have silver so, this will happen, ok. So, when I have a oxidation there I have reduction here. When I have a reduction here I have a oxidation here. It has to happen all the, this thing cannot go undergo oxidation, because circuit will not be complete, right, you will you know that, right?

But the interesting is that once this reaction is happening, think about it. What is happening? Silver bromide is going to silver, or the other way silver is going to silver bromide, ok. And then if I just write the Nernst equation for this half cell ok, what will be the half cell Nernst equation, I have a e 0 half cell plus some rtln reductant by concentration of reductance reduced basically (Refer Time: 29:00) species that way, but think about it when I am having this reaction, silver bromide is going to silver, but both side the activities equal to 1. It does not matter like if the 10 molecules of silver bromide is giving me silver does not change the activity still 1, because both are solid only change can happen in the bromide ion will appear and disappear.

But if I assume that the bromide has I have excess concentration of bromide that also does not change. So, that part the rtln that factor is basically essentially does not change, ok. As I am using this thing this reaction so, basically the reference electrode is not contributing too much change in the potential. In this reaction it's potential is not changing, it is still e 0 clear, ok. It is actually contributing only the e 0, but not the other part, ok. So, all the other part is now actually taken care of the platinum. So, I am actually, do not need to actually consider what is happening in the other electrode in the reference electrode, that is why the reference electrode have chosen in such a way, ok.

Usually a solid with reduced or the oxidized form which is another solid ok, but of course, you will have a mobile phase in the sense that you will a you need an ion ok, but if I also use the ion in excess and assume that the ions concentration is not changing much, ok so, that is also constant. Then my easy I mean like total electro motive force is also constant for the half cell, that is why it is known that a reference electrodes are those electrodes where actually during the electrode reactions its own potential is not changing clear, alright. Now think about it suppose everything is happening in the platinum, ok. And then I am basically scanning the voltage, I am basically applying power here.

Now, usually as I drew this thing, I will just draw it once again, ok. So, like usually the convention is somewhere I wrote this image, right. So, like it is, it is homo and it is lumo, right; homo and lumo of a species which is in solution, ok. And then I have basically the electrode which and there has a interface and across the interface the electron (Refer Time: 31:25), right. If I apply a negative bias usually the potential or the energy level is basically getting everywhere gets everywhere, ok. And then I have a metal energy level which is much higher, ok. So, then actually I have facilitate this process, ok. On the other hand if I just draw the potential and I can facilitate this process. So, the idea is that usually the negative bias, is shown at the top and the positive bias is shown at the bottom, ok.

Now, when I am write my x axis here basically I am scanning the voltage, I usually write the positive voltage here and the negative voltage in this direction. It is the (Refer Time: 32:09) that is the convention ok, because actually it has a very direct and also with this ok. And as why usually we write the standard reduction potential convention, we never write the standard oxidation potential convention clear, ok. So, suppose I am scanning the voltage and then what I will have I have basically one monitor, what is the current,

current flowing in the circuit; that is basically given by this ammeter and I was scanning the voltage that is a simple experiment, ok. And I can assume under this condition all the reactions or all the potentials in this happening at the platinum interface ok, because the other interface does not really participate. It is a standard electrode clear, ok.

Now, what will be the curve or the nature of the curve how it will look like (Refer Time: 33:06) plot it (Refer Time: 33:14) Now think about it now, when I am scanning right the voltage I am going to say more negative side, which means actually this side I am suppose scanning, so, this reaction can happen. Now this reaction is happening with respect to what, with respect to platinum, ok. And that we have already taken it to be kind of zero right, but it will not occur exactly at the zero why, because there is no hydrogen present, ok. If hydrogen is present at one active, unit activity and then platinum is there then that potential is basically zero, it will be slightly off from zero, ok.

So, if I scan the potential at some point I will see the all of a certain current will rise, ok. At what point? That point where basically the potential will match the standard reduction potential of one of this clear, ok. So, I have a basically curve like this and I will this (Refer Time: 34:14) like shoot up in the curve, ok. It means a very small change in potential which means that I have reached already that you know. So, this thing actually basically marks the onset of this reduction H plus reduction clear, ok. So, as you can see here basically the H plus is getting reduced or in other sense the electron is getting transferred into the solution which make sense, because I have actually increased the metals energy level, ok. So, the metal is basically supplying electron to the species in solution what is the species in solution H plus protons.

Protons are getting reduced, but it is an oxidation process basically, because actually the electrode surface once it is a kind of oxidation process electrons are giving, ok. Now similarly, if I actually reduce it of course, there will be reduction process, ok. Then I am actually scanning this thing, ok. And then what will happen basically, it will nicely match with may be some other thing this case actually it will match this potential, ok. And if it matches at some potential it will again show a curve, that this time a curve will be the other direction make sense, because actually we are reverse the direction of potential, ok. And that will happen in a something which is (Refer Time: 35:47) scale this something like 1.0 here, ok. And here, here actually I have something like this, and here I have onset of if I call these as an onset, ok. So, this is basically onset of Br minus oxidation, ok.

If I think it like this it is a reduction process on probably, right you can think it a reverse direction it is basically Br minus oxidation, ok. So, onset of bromide solution ok, but H plus reduction bromide get oxidation on platinum surphase, ok. These are all platinum, the other reaction is also happening in other electrode has to right, but I do not care I am only focusing on the platinum surface there, fine. Now this is already obvious thing, right. So, this will be something like this ok, but there are few things what are the few things? Think about it, ok? So, this is basically the current, right and as you can see that there is a range of potential where actually even for scan the potential ok, I am not basically getting any cut and all of us are needs and as you can see that is basically (Refer Time: 37:12) rising, ok.

So, what happens is that you can think in a very classical way in the sense that I have electron and nuclear bound, right in the middle and then I am applying a potential. So, what it is doing is basically it is trying to make it polarizable right, it is making polarized. Now, it will depend actually these atoms in the metals how polarizable they are, ok. So, like I am actually applying voltage, applying voltage, applying voltage and at a some threshold voltage the electron is actually lift off ok, that is what is happening, ok. So, if the polarizablity of the metal at the exact it the opposite processes is happening in this case, ok. Actually I am trying to push on electron, and electron cloud in the metal is basically opposing, opposing, opposing, but at some days actually it is the electron is going inside, right.

So, these (Refer Time: 38:05) which is basically describing me how polarized is the metal and we will see actually. So, like the more the polarizability of the metal I have this range actually I can broaden it ok, alright. Now think of a slightly different processes, slightly different (Refer Time: 38:26) that I have the similar electrode, but instead of like platinum. Now, I am actually changing it to the mercury electrode ok, let me actually write the half cell reaction just a minute. So, I am only replacing this platinum by another just better which is just mercury (Refer Time: 38:55), ok.

So, what I have you know this earlier I have this thing platinum and what I should have and, and basically H plus, right there also hydrogen it is not a (Refer Time: 39:11) standard hydrogen (Refer Time: 39:12), it is just a metal dip there, ok. And then I had outside the cell (Refer Time: 39:19) bromide, let us say I make it as 1 (Refer Time:39:24) and then I had another interface which was Agbr, ok. So, this was my first experiment, ok. Again this is proper half cell, but the other one is not a proper half cell, ok. And second thing as you can see that in this is basically the liquid phase or solution phase, ok. So, solution phase species usually that we had it as common ok, but then again there is another interface which is the interface which is the silver boron and then we can (Refer Time: 40:02) silver, ok. Now volume changing is basically not the left hand side whereas, actually instead of platinum I have just mercury then everything else is same, ok. Now I am doing this same experiment once again what will happen that is the question, ok? Now as I said that just think about part the onset of H plus oxidation sorry H plus reduction, that actually happened close to zero, this is basically let us say the 00.0 of potential as well as zero of cation, ok.

And again as you can see the basically. So, this potential where actually it is like just started overshooting, ok so, that I can actually call as the open circuit voltage this voltage circuit. Now think about it like what is going to happen, ok? Now they are I could gave a logic that it is the H, H plus reaction and I as I know that with respect to the standard hydrogen electrode, the potential of this guy is always zero, because that was the definition, ok.

Now, interestingly if you do this experiment keeping actually with instead of platinum. If I just do it say on mercury, oxidation on say mercury what you see is that this thing will come somewhere around minus 1. And other thing the reduction will be something around here closed to here, ok. What has happened? It is a same reaction, ok. So, it is basically H plus is getting reduced and the other half is basically Bromine is getting oxidized, ok. So, now, the thing is whatever you described here H plus 2 electron, this is the actual reaction what is happening ok, but you defined it with respect to a platinum and hydrogen that was a standard hydrogen electrode definition.

So, when you are using platinum as a electrode, then the same reaction is does not differ to much from the standard hydrogen electrode that is why I am (Refer Time: 42:20) shooting them; however, when you are using mercury, the potential has changed comparatively, ok. So, what I am trying to say here is that just by the reaction looking at the reaction you cannot say that reaction this is the standard reduction potential, you have to always mention, ok. And what condition I am using what electrode ok, in this case actually H plus is going to hydrogen, but hydrogen actually we never use. As a case, it is usually absorbed on electrode standard thing was platinum, but I am sure that moment I make it mercury ok, this is very different actually.

So, which means actually the nature of the interface is extreme important ok. Now what is here doing, here is that the actual thing is there is a kinetic (Refer Time: 43:15), ok. The reaction for the absorbed hydrogen on mercury surface are much more kinetical inert and that is why the reaction does not happen, ok. So, this is a kinetic inertness of electron transfer at the mercury interface, ok. Now let us see even more interesting thing. So, when I just say is that this entire potential thing, ok. You need always define a basically a particular interface otherwise you cannot like tell anything about it, ok.

Now, let us do one more thing. So, I had suppose so, this was my first experiment where I dis this thing. Second is for (Refer Time: 44:00) basically did the same thing with mercury, with this electrolyte H plus everything else I kept constant, ok. Now I am making another change, what I am doing is that I am basically adding some trace amount of cadmium ion to it, ok. What the cadmium ion will do? Cadmium ion itself will create another I mean like redox coming and everything, ok. So, what I am doing I had mercury, I had H plus, ok. In the solution phase specifically I have H plus I have Br minus 1 molar. And I have suppose cadmium, but cadmium is suppose 1 mole is suppose the (Refer Time: 44:53) whatever rest itself, rest itself means same thing Agbr Ag, ok. So, what I did, I had platinum, I have change it to first mercury, ok. Now I am adding also little bit amount of cadmium, ok. Now, interesting thing is that I can apart from these two reactions.

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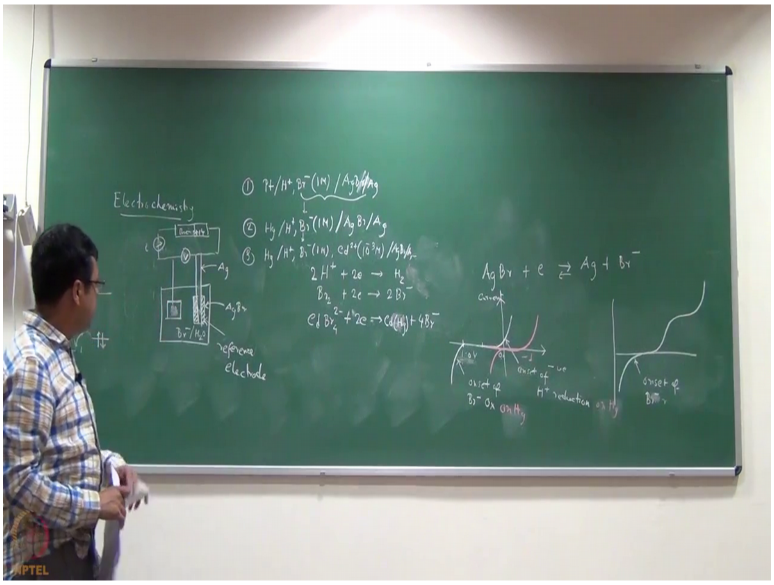

Apart from these two reactions, I can also have a third reaction which is something like this Cd Br 4 2 minus 2 electrons and then Cd plus. Once this Cd is formed, it is basically in presence of the mercury, right. So, it basically gets dissolved in the mercury I mean it basically forms a(Refer Time:45:58), the metallic Cd, alright. Now actually I have another redox coming, ok. So, what is happening if I scan, now the voltage I am basically have another onset kind of thing, because I just showed it for 2, like one reaction, the second reaction, one reaction and the second reaction.

But now actually what I am expecting that I will basically have another onset at some point, ok. And the nature of the curve will drastically change something by I can say by the picture so, sometime so, the actual drawing. So, it will be something like this and where this is the onset of this is onset of Bromine just a minute. So, once I have this kind of reaction, like I said that for the first case, ok. I have basically these two reactions; right let me actually write it all the reactions.

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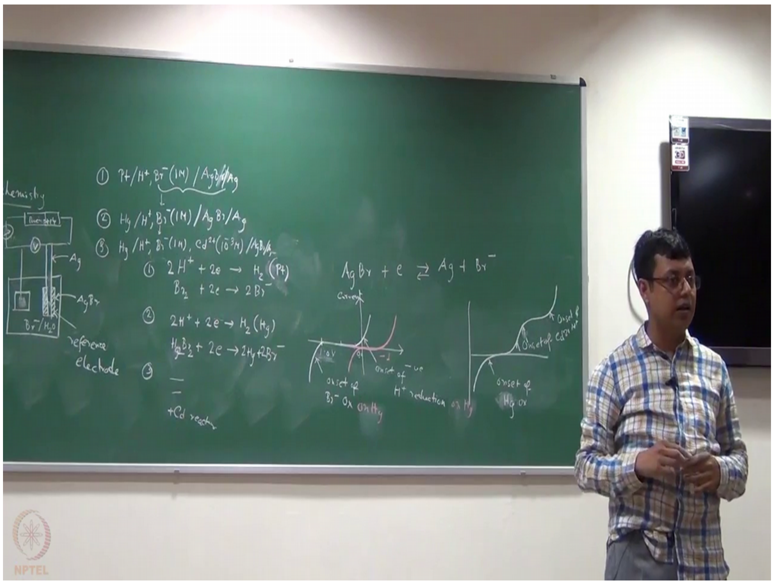

So, this was for the case number 1, I had only 2,, case number 2, what I have (Refer Time: 47:31) mercury. So, this is in platinum. So, I still have this reaction 2 H plus, plus 2 electron giving hydrogen, but this hydrogen will be on mercury, ok.

The second reaction it will be something like H 2 Br 2. So, think over it earlier what I had, I had basically Bromine evolution kind of thing at platinum interface, right. I had excess Bromine and that is going as a Bromine right, but in this case when I changing to mercury, actually it will be H 2; that means, the chemical species is different. So, these two reactions were happening. So, what I wrote here, it is not actually the onset of it is tells us the same thing, it is onset of Br minus, but here actually it is written as like this will be Hg B r 2. Now as you can see it is basically the reduction of mercury, ok.

Now, what if you think in the reverse way it is basically the oxidation of that you know. So, this will be actually onset of oxidation of the Hg ye oxidation of mercury ok, clear, because when I am actually changing the curve, so, this actually comes up, ok. Now you can ask this question what happened to the other reaction? Does Bromine come out? It is, you can actually compare these two, it is basically what I am trying to say is the in the presence of mercury amalgam, ok. I basically have the Bromine getting connected to basically mercury (Refer Time: 49:32) Bromine, clear ok, because the reaction is changed. It is a completely different reaction, right now, ok. And in the third case I have this thing, this thing plus this other reaction which I just wrote the cadmium reaction.

So, here I am basically have onset of mercury in oxidation right, these curve are actually as I can see here, ok. Now actually I have the onset, this is the onset of the cadmium reaction, ok. And this is basically the onset of the H plus reaction, ok. Now you see this kind of curve actually is known as potential wave, say (Refer Time: 50:22) actually having a wavy reaction, ok. Now I actually talked about two things, two different things one is that I have discrete potential steps, just to (Refer Time: 50:33), ok. I have basically possibilities of the hydrogen evolution or I have the possibilities of the Bromine oxidation reaction, right.

Then I said moment I switch to mercury the Bromine get some changes little bit it is a different reaction, ok. And the hydrogen thing actually occurs in a very different potential ok, because actually there is a kinetic inertness, which is basically not varying. This reaction have plus I make down the thing even more complicated I am saying if I actually add one more thing, what will happen? So, then I have actually three kind of steps like this, like this ok. So, the (Refer Time: 51:14) short what I am trying to say here is that if I actually sweep the potential ok, it will depend on two things how many species are there ok? And the second thing is that very, very exclusive nature of the interface (Refer Time: 51:30), ok.

It can be the same reaction like the H plus is going to H 2 ok, but it depends whether it is a platinum or it is a mercury clear. Now let us just trying to try to rationalize the entire thing entire thing, rationalization means I actually want homo, lomo kind of picture where I am I will start with some potential for the metal, ok. And I am scanning and I know that in the solution, I have different species; each species has a standard reduction potential, ok. And this potential is getting scanned when actually it will match with one standard potential, ok. I will have that also be shown and that is how basically you use in potentiometer basically I have seen this cyclic photometry and other things, right.

So, I basically sweep the voltage and monitor the current and there actually you have a onset of a basically current, when basically this potential is matching you are scanning the potential or the voltage, ok. And then I have basically multiple like redox species. Now I will show you one particular diagram here this numbers you do not need to remember, it is just for your understanding.

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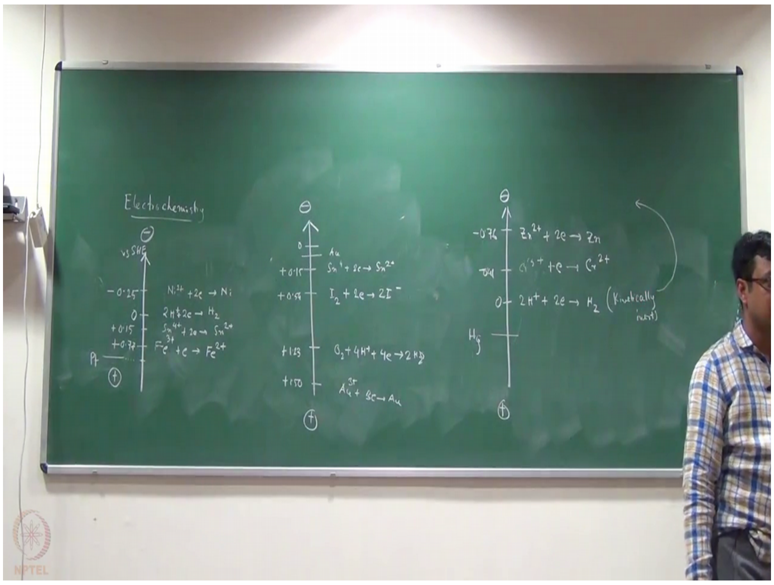

Now, what I was showing in that picture usually the horizontal axis, I show the potential. Here actually I am showing the vertical axis as potential remember that, I am basically scanning the potential as if, right.

And here in the condition is that positive potential is at the bottom, the negative is at the top, ok. So, if I suppose start with the platinum electrode, and then suppose I have a iron compound, fe 3 plus electron going to fe 2 plus what is the potential plus.70, it is plus.77 and then around 0, ok. Of course, I have the hydrogen thing, ok. If I have say 2 H plus plus 2 electron going to H 2, I am just (Refer Time: 54:01) writing see the reduction potential ok. And suppose I have in my solution some tin ion also sn 4 plus going sn 2 plus the potential is plus 0.15,ok. And also I have suppose some nickel ion ni 2 plus plue 2 electron giving ni potential is 0.25.

And this scale is of course, the potential scale verses the standard hydrogen electrode, because that is why the standard hydrogen electrode is same, ok then if I start with the metal which is platinum. So, the first thing is that why I am starting with, ok? This point is basically corresponds to a voltage where the current is there. So, basically so, basically this is the open circuit voltage for a system where I have one side platinum dipped ok. Other side some standard electrode, it can be the silver (Refer Time: 55:14) whatever I do not care, because that does not change much and I have different ions say I have ion, I have tin, I have nickel, ok.

Now, what will happen if I just sweep the potential first I have a rise, ok. Due to this compound clear actually it is basically coming from the bottom, because it is the other (Refer Time: 55:36) as you can see, right. It is basically the oxidation will happen first, ok. This kind of cut then I have another one which is due to the tin which will be close to the 0 1, ok. Why because the standard hydrogen electrode is introduced the 0 1 clear, ok.

And then as standard hydrogen electrode you can have a rise then it will be flat for sometime again I will have a rise for the nickel. So, I have a multiple slope, but try drawing this it is very easy like I have already told. So, basically this is that somewhere from here, as it was carrying the potential, ok. How it will look like?

So, as you can see that 0 of current corresponds to here, ok. What was 0 of current? Current was my y axis, ok. So, this is 0 of current, ok. So, basically in this case I am starting from here already, ok. 0 of current and everything will be above it there is nothing below it, ok, because I already told you that the platinum's like potential will begin with, I am starting from somewhere which is basically corresponding to this 0 of current, ok.

Then this guy will first encounter this thing oxidation, because I cannot stepwise rise and all these thing, but I know that once the standard hydrogen thing will go, ok. I will basically have 0 of voltage. So, the standard hydrogen oxide should be somewhere here right. So, before that I will have rise due to this thing the tin, ok. And before that I am also another rise due to the other thing, ok. So, it will have something like this and then again it will have something like this, this will be the oxide for nickel.

So, this is nickel, this is basically the hydrogen oxide ok. This is the tin and this is the iron. So, that is how is the, the potential, ok. So, this is the direct kind of correlation, one to one (Refer Time: 57:47) between how I am scanning the potential, of the metal and the electrode solution interface. Again potential is always acts as an interface and scanning it, but again always there is a another electrode, but we do not care about it, because it is conditions are not changing during each step of oxidation or reduction, clear.

Let me give you another example, alright. So, this is basically scale will always be like positive (Refer Time: 58:41) at the bottom, and negative will always be at the top, ok. And we are writing everything with respect to the standard hydrogen electrode, ok. Now what I have here is just 1 minute ye, I have basically the gold electrode this is this is 0 sn (Refer Time: 59:23) sn 4 plus, plus 2 electron sn 2 plus that has plus 0.15 ye, alright.

Now, this is very interesting. So, this is (Refer Time: 1:00:24) with respect to the standard hydrogen electrode, with respect to standard hydrogen electrode. If you start with the gold, metal in presence of all these ions ok, it is potential actually starts from here it is very interesting ok. Potential starts from here means actually this is the potential where I am getting 0 value, ok. And then if I actually sweep the voltage to the negative side (Refer Time: 1:00:49) nothing, ok.

In this case actually I have to sweep it only to the positive side, it is the other way (Refer Time: 1:00:59), ok. And then I will explore all these oxidations actual, because it is the reduction equations are written ok, but I will see basically, but as I move in the positive reduction means actually I am going the down, down means actually I was seen the reverse of this reactions, ok. I will see all these oxidations happening one after another, ok.

Now, this again does not include one possibility and this is 0 which is 2 H plus 2 electrons H 2 again with respect to (Refer Time: 1:01:55)51 this is chromium minus 141 minus 0.76, this is zinc. So, what I did here, is basically position of mercury (Refer Time: 1:02:31) at 0 of current.

Now suppose I am sweeping now, once we sweep this thing you will find that this reaction although thermodynamic is suggesting that this will should come anode 0. It will never come, because actually this is kinetically, ok. And in reality what you will see that these actually comes I showed you right minus 1 kind of thing. So, these actually experimentally will come somewhere here when I am scanning this thing. First I will see this thing, second I will see this thing. And then I will see the at a very high potential I will see the, this reaction is happening, ok.

One first this reaction is kinetically inert for mercury interface clear. So, although as a thermodynamics is predicting me that these should be the steps, that should occur one after another, ok. There can be actually kinetic inertness which can actually slow down this reaction and you will see this reaction happening at a much, much higher potential clear, ok.

Now, what it basically means is that the explicit nature of the interface has to be studied, ok. Now the question is as I just told you that that there could be a long range where actually I am applying the potential, but no current is flown, ok. And that basically dictates the polarizability of the metal, ok. So, we have a term here. So, it is called Ideal polarized or polarizable electrode.

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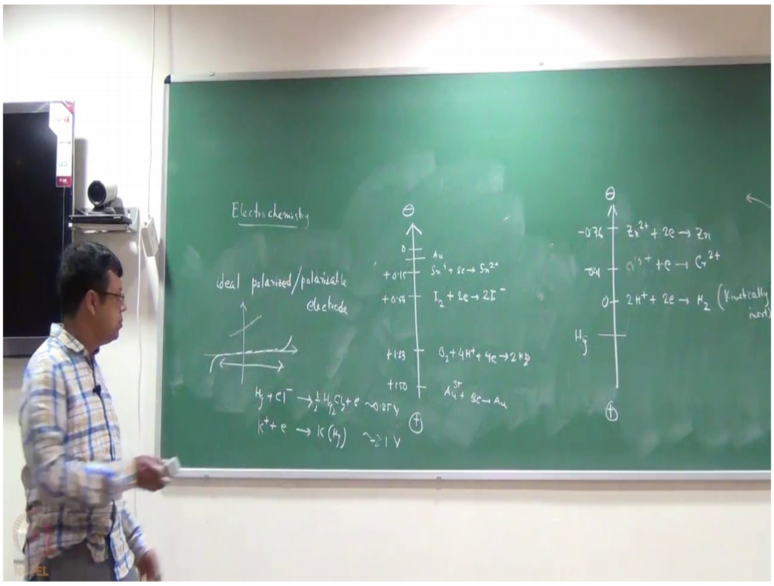

What is an ideal polarizable electrode ideal polarizable electrode means suppose this is the voltage and this is the current, ok. So, this thing should be very, very wide over a long range of voltage ok. I am not basically getting like trying to I mean I have not being able to strip of or add the electrons, ok. So, that is the kind of ideal polarisable electrode and there are some examples. So, that so, right if I have mercury plus chloride again you do not need to remember all these thing H g 2 C l 2 plus electron. If I actually take the mercury electron, it will show around 0.25 y and then as a counter electrode as a potassium 2.1 y. As you can say that what I did here it is an suppose I have mercury electrode and in the solution I have basically potassium chloride.

So, there are two possibilities I can actually for mercury a square which is basically the oscillation of that potassium, actually have reduction of potassium making the potassium parameter by this two steps happened at a very very widening gap. What is happening is 2.1 sorry, actually minus 2.1, ok. And the above one is a 0.25, ok. And you have a over a many at a long range, we do not have much change, right. Now why do you do not have much change, what is happening here actually?

So, do not have much change in the sense that there is no current flow ok, meaning as I said like you can think of that electron pushing and reaping off is basically very difficult ok, but in another way what can have any surfaces ok. There can sometimes you can see a very very small card flowing through it, which is not exactly like short race it is not a oxidation or reduction, but what I am trying to say is that this thing may be, if you can join it see it is slightly slope is there, ok. Now what happens is that apart from the oxidation and reduction, ok. There are also other processes what are those process I was suppose this thing is getting reduce, ok.

Now this thing is the solution, this should first get adsorbed on omega, ok. So, this adsorption process is all these process also happen, right. So, which means for a long time ok, if you think that there is no things are happening I am actually it what, what is this process? Basically I am trying to charge the interface, but it is not charging, which means the interface is now behaving as an kind of insulator in the sense it is where I am charging something and charges have been stored, it is behaving as a capacitor, like there is a dielectric in between I have to place I am basically charging all of you know, what is a capacitor, ok?

Since this is the dielectric there is no covalent there is no electron flow, ok. So, at the first it is basically behaving as a capacitor, ok., there may also this interesting processes one I have the electrons getting transfer whenever the electrons get transfer I will have a current flow. And have a spy this processes are known as faradic process, you have heard this name faradic and non faradic processes, ok. Non faradic process are those processes which are actually happening, but not neatly contributing to an electron flow, ok.

Nevertheless those are also important. So, which means actually the interface is not simple like that charge is coming and then just giving it is electron, ok. There are also other steps and all the steps are happening during this time, but not get transfer is happening which means there is a by I have a electrode here,.

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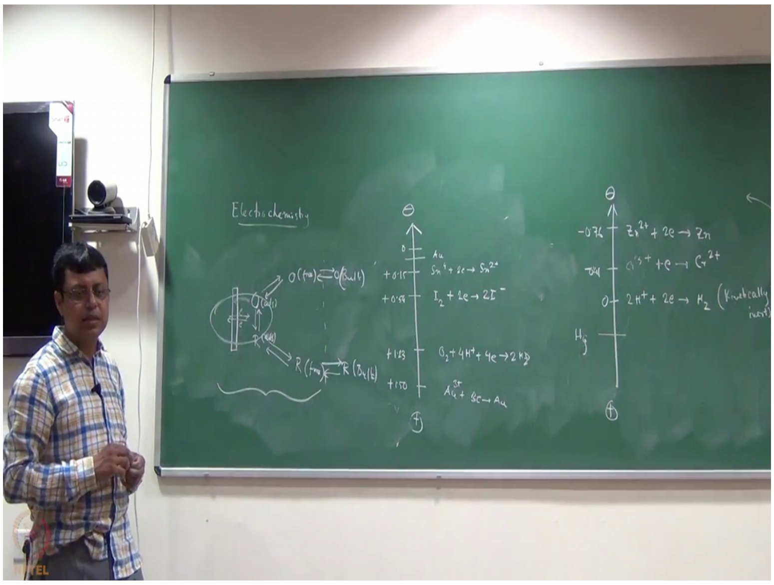

And then it is not going this which I was writing by the ion is coming and then the electron is getting transferred, ok. First it has should come it has to adsorb and all these things should happen, right. So, what mean means actually are the electron surface this processes will happen in a sequential manner, right. Sequential manner in the sense that I have suppose something by n it is (Refer Time: 1:09:34) thing, ok. Suppose I have some oxidants, and then I can have actually mega electron ok. So, what is a ion having oxidant would and not basically they can flows in and out in and out, ok. And this also that we have an supposing we get ok, but what I am saying here this oxidant, should be absorb or a surface as well as dissolve, ok.

Similarly, this reactance also should adsorb and dissolve, ok. And then basically I have adsorb oxidants and wave sorry adsorb reactant, ok. And this is basically free oxidant and free reactant, ok. And these are this can actually the viscidity of the electrode finally, this should also diffuse with the bulk an oxidizing bulk and reactant bulk, ok. So, this is actually what is going on ok, there is a region which is close to the electrode which I can found this region and then there is a bulk, ok.

So, from the bulk actually, there is a equilibrium which is coming nearer to the electrode. And then getting adsorbed and all these things are happen after adsorption only electron transfers, ok. So, when I am talking about say the reduction or oxidation, or basically kinetics of a process just like I showed that within presence of mercury I that reaction is very slow, ok. So, this is not the only factor all other things will also become very- very important ok. For example, this things also very important which is known as (Refer Time: 1:11:23) transfer then from bulk if I have a very higher which is extremely (Refer Time: 1:11:27), that have been move very slowly, ok.

So, even if I am actually applying voltage to make this process faster like more electron transfer,. I may not see, because this bulks does not reached here, because it is a very heavy thing, ok. So, all this electron process are very much actually inherent to all this individual steps. It is not only this things which we are so, much clear, plus there can be issues here itself like this electron transfer may not be (Refer Time: 1:12:03) ok. There may be some like inherent structure of the surface that is must get preventing electron transfer to happen, clear.

At usually this is (Refer Time: 1:12:13) in a very- very simplistic model which is known as a layer model which is known as electrical double model in the sense that is a, that it is electrical thermodynamics one. Here is you basically have a electrode, and then you have ions, ok.

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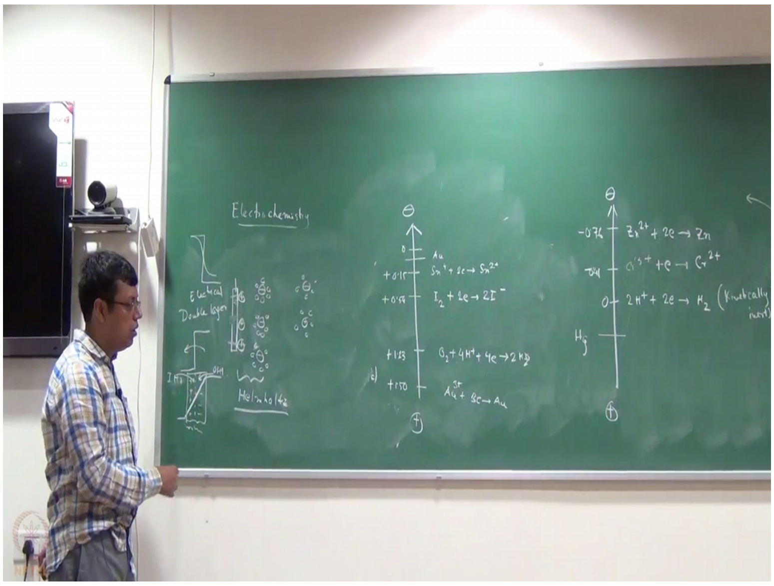

Now, what is says is that these ions some of them are basically very much attached to a electrode, ok. Suppose a positive like negative whatever it is, ok. So, I am trying to say is that suppose the electron is at a timing is a negative electrode, ok.

So, that positive ions are basically move out on the surface of electrodes, ok. And there were also electrons which are basically solvent negative ions ok, because once you have excess positive charge, it will act as some of the excess negative charge annually, but this negative ion actually sitting on the electrode. Why? Because they cannot sit on the electrode because it introduce already slighting (Refer Time: 1:13:17) If I put positive on the plus minus sign will be reverse, ok.

And then of course, there is bulk actually (Refer Time: 1:13:24) negative ions as well as (Refer Time: 1:13:28) is positive ion clear, ok. These two things is known as basically double layer; so, which is simply spirally Helmholtz, ok. He said that usually a very much nature ok. If I just span, if I just draw the, I will there, and I will ask this question, what is potential, how it is changing? If I just cross this interface, ok.

So, electron to solution if I just go one can think, there will be there was a jumping in potential. It can increase or it can decrease depending on whether this has a positive potential or it has a negative potential.

In that way I am drawing this, a basically negative potential with respect to the solution. So, the potential is jumping, but Helmholtz was actually does not happening the skipped jump like this it will have a smooth rise, ok. And in this smooth rise what I was see here and have a region before reaching the bulk. In the bulk if I move and say charge electron that exponents has no change in potential. Once it has reached the bulk, ok. How we measure potential, you basically, use a, you need positive textures, ok. And you just know it if I move it within the metal nodes it is called uniform potential that is why I have flat line here, but the question is how it is changing in between then Helmholtz saying that actually does not change in a jump, ok. In basically changes gradually where actually I have a region, which is known as basically electrode.

Bulk interface, but this region is not like infinitely thing something like also we are discussing whether we are discussing the surface tension, right. So, it is said that there is a excess thing which would be present. If you remember, right this is not like a step function like this similar concept, but beside that these thing you can actually think about composed of two different x 1 is with a electrode is negative to give a node, ok. I will have a excess positive charge kind of layer, ok. And then immediately around it due to electrostatic attraction and (Refer Time: 1:15:36) the excess negative charge kind of layer.

And then there would be bulk where positive and negative are on line so that electron and metal sorry metal and the solution interface, ok. There is not just only one potential, there is a double layer potential, this is known as basically electrical double layer,. In text book like (Refer Time: 1:16:04) or anything you will see that they always write it as a I H P and O H P, this for inner Helmholtz plane outer Helmholtz plane, ok. So, this is just a model to understand how basically the potential changes across (Refer Time: 1:16:23) actually (Refer Time: 1:16:25) limits a positive text judge across the interface from say metal to the solution, how the potential changes so, it is not an (Refer Time: 1:16:34) change.

There will be at least a double layer to begin with of course, there can be multiple layers, but at least the minimum model size that there has to be a double layer otherwise you cannot explain many other things. So, we will see actually what are those many other things, and second thing which is (Refer Time: 1:16:51) and the second thing here is that always remember that there is many, many processes which are associated for this (Refer Time: 1:17:00) cell reaction. It is not just the electron transferred and flow of electron ok, but I has to first come from bulk sit there where it absorbed, ok.

Transfer the electron gets desorbed. So, that a new ion also can come and sit on it, ok. So, all these individual (Refer Time: 1:17:19) will press the (Refer Time: 1:17:21) institute a model, right. One of them is largest then the other one left is actually gets slow down due to that if there is an indeterminate step, right exactly that is what is happening in the mercury case that is why the mercury although that standard potential thermodynamic system. It should happen ion 0 in reality, we never see term 0, ok, because there is a kinetic eagerness ok, alright. So, we just stop here and next class, we will just talk more about the thermodynamics of this process.