Bio-electrochemistry

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Lecture - 06
Salt Bridge

Welcome back to the second week of for Bio-electrochemistry. So, in the previous week we are supposed to finish all the way up to Nernst equation and electrode potentials, we could not really reach there because I was concentrating exclusively on the fundamentals. So, we will have a little spill over this week which will continue will be slightly delayed, but kindly do not worry we will compensate it may have extra lectures or eventually we will you know kind of make up for the delay what is happening at this stage.

But what is most essential is your fundamental should get very clear at this stage because once we will be talking about the biological systems they are far more complex than these inorganic salts and inorganic solutions. So, that is why I am devoting all my time at this stage to clarify all the doubts. So, just a small recap when we talked about in the last class about the galvanic cells we put up a definition there which I wanted to again revisit.

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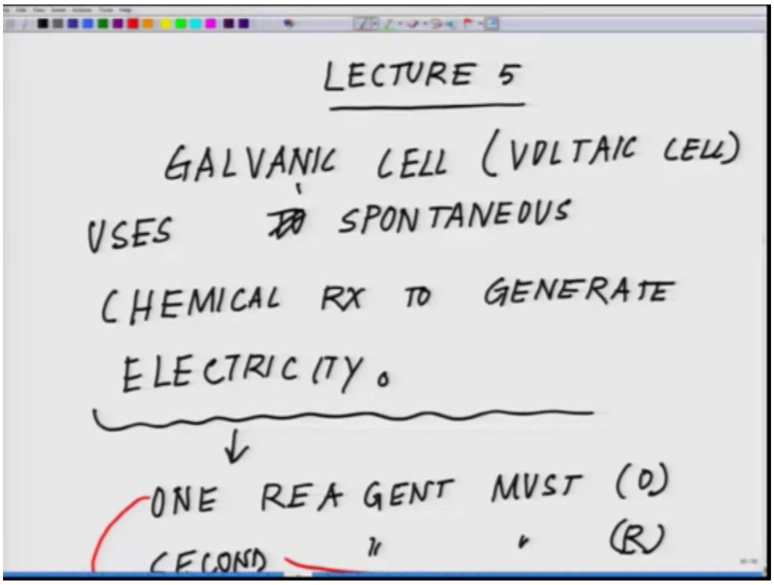

LECTURE 5

GALVANIC CELL (VOLTAIC CELL)
USES ~~TO~~ SPONTANEOUS
CHEMICAL RX TO GENERATE
ELECTRICITY.

ONE REAGENT MUST (O)
SECOND " " (R)

So, galvanic cell which is a voltaic cell using a spontaneous chemical reaction to generate electricity and I mention two things here. So, one reagent must oxidize the second one must get reused and the two should not be in contact.

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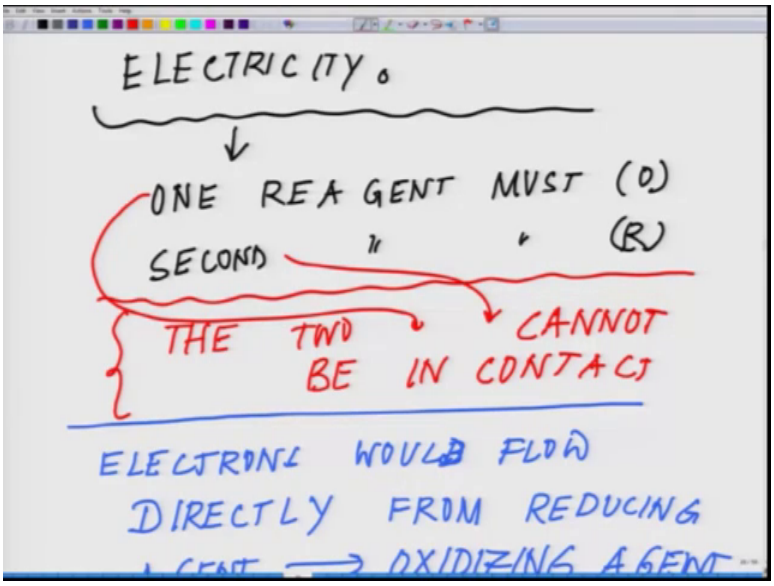

ELECTRICITY.

ONE REAGENT MUST (O)
SECOND " " (R)

THE TWO CANNOT
BE IN CONTACT

ELECTRONS WOULD FLOW
DIRECTLY FROM REDUCING
AGENT → OXIDIZING AGENT

So, we talked about a situation where the most classic situation of Daniell cell where we talk about the zinc and the copper electrode, we are zinc getting oxidized and copper receiving those electrons generated by the zinc and they are being separated in two different compartments zinc in, zinc sulfate and copper and copper sulfate so on and so forth.

Then we talked about a situation where we had a common electrolyte which is cadmium chloride and we had a cadmium electrode and a silver chloride Ag AgCl electrode which is essentially on an Ag or the AgCl coating where oxidation occurs at cadmium electrode. So, cadmium moves into the aqueous medium as Cd 2 plus and the electrons which are left behind are forced to travel and being received by the AgCl electrode because chloride from the AgCl electrode diffuses into the cadmium chloride solution and so there is a dearth of electrons there those electrons travel all the way from cadmium electrode to the AgCl electrode and there is a deposition of the silver on the AgCl electrode right.

And in order to drive this reaction which the spontaneous reaction the delta G is minus 150 kilo Joule per mole of cadmium getting consumed and we calculate the voltage what you will be observing, if you remember it. So, we talked about delta G is equal to n F E, remember the formula what we discuss in the very early 3 classes. So, delta G is equal to n F E, but minus delta G is equal to n F E. So, in this situation it was minus delta G the value of delta G was minus 150 kiloJoules per mole. So, essentially minus minus makes it plus. So, delta G value becomes 150 kilo Joule per mole on the left hand side is equal to n F E, where n we considered as this cadmium solid becoming Cd 2 plus into the aqueous plus 2 electron. So, we considered those 2 electron as here 2 moles of electrons your n becomes electron moles of electrons.

So, 2 moles of electron multiplied by the Faraday's constant if you remember the Faraday's constant. The amount of charge on an electron multiplied by the Avogadro's number that is what is the Faraday's constant. So, we multiply the Faraday's constant you are left with E. So, 150 kilo Joule per mole divided by n which is 2, F which is Faraday's constant and 150 kilo Joule, you convert that into Joule intermittent multiplying by 10 to the power 3 and the value what he was getting was around I think 0.777 or something, if we just this is the value which you obtain.

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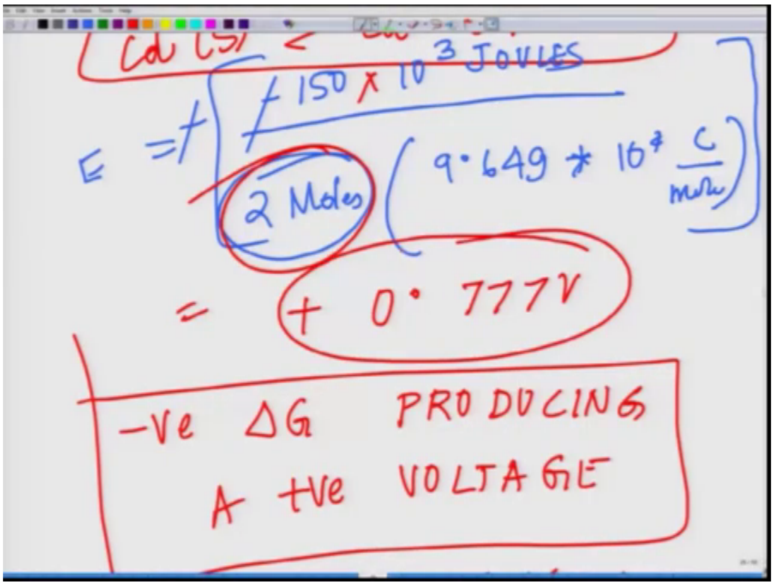

Then we talked about a third case scenario where we talked about silver electrode and a cadmium electrode no more silver chloride, remember silver electrode and a cadmium electrode and we dissolve them in two different electrolytes Ag NO 3 and Cd NO 3, cadmium nitrate and Ag NO 3 and Cd NO 3 2.

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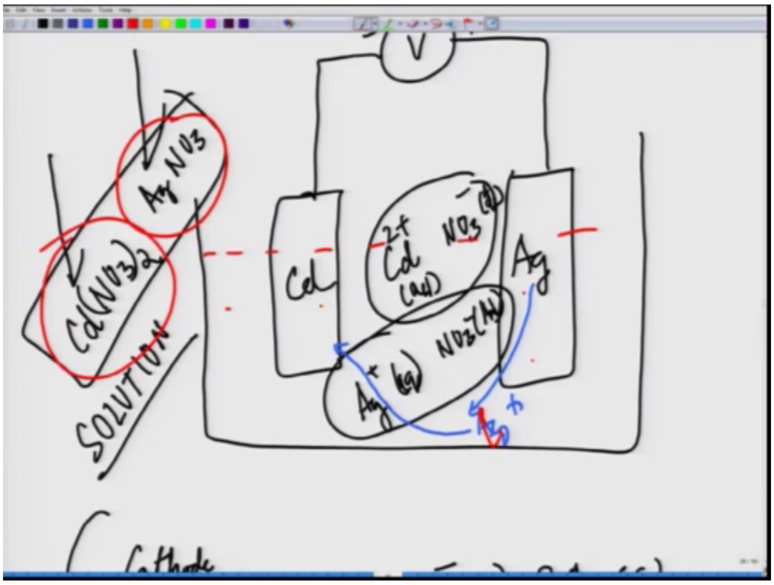

Now, here is a situation where we realize that there will not be any flow of electron per se because what will happen, Ag which is the as the chloride is moving out into it sorry as the chloride will be moving out into it the net reaction is a spontaneous, but little current will flow through the circuit because Ag 2 plus. So, this is not chloride I am just slight mistake Ag 2 plus is not forced to be reduced as the Ag electrode because the Ag plus is not forced to be reduced at the Ag electrode whereas, aqueous Ag plus can react directly to the cadmium surface or cadmium solid surface of the cadmium giving the same net reaction with no flow of electron through the external circuit.

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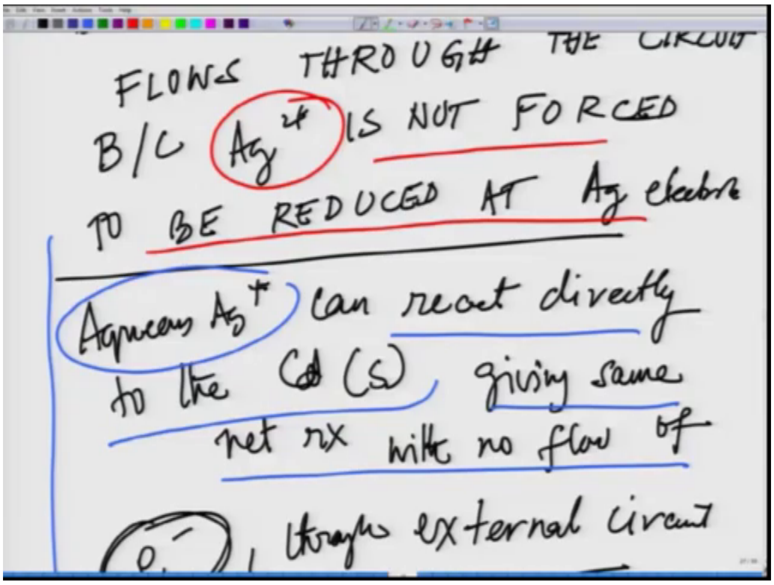

FLOWS THROUGH THE CIRCUIT
B/C Ag^{2+} IS NOT FORCED
TO BE REDUCED AT Ag electrode

Aqueous Ag^+ can react directly
to the Cd (s) giving same
net rx with no flow of
e^-, through external circuit

So, this was a very tricky situation. So, there will not be any effective work. Now, that is the point where we talked about we are introducing the salt bridge.

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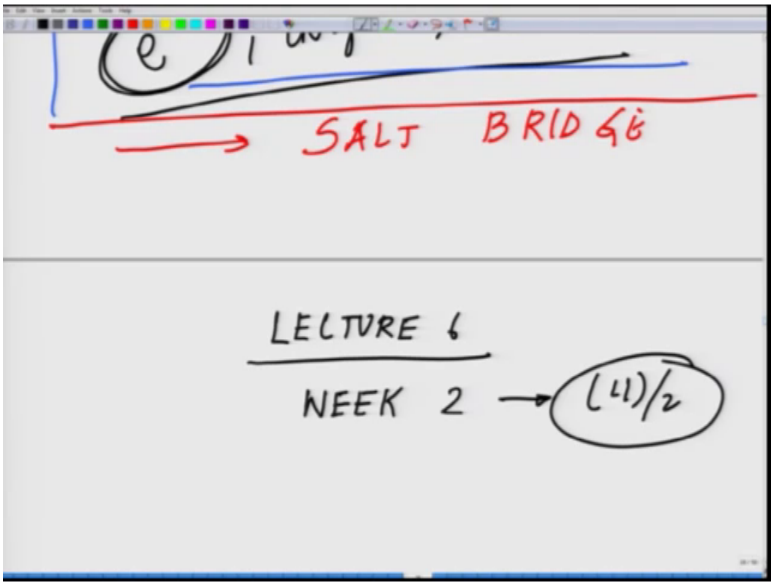

SALT BRIDGE

LECTURE 6

WEEK 2 → (L1)/2

So, we are into lecture 6. So, we are into week 2 and for week 2 this is lecture 2. Try to put it like this week 2 lecture 1.

Now, I built a different kind of cell today where we will be talking about the salt bridge, the concept of salt bridge and why there is a need for salt bridge, need for salt bridge.

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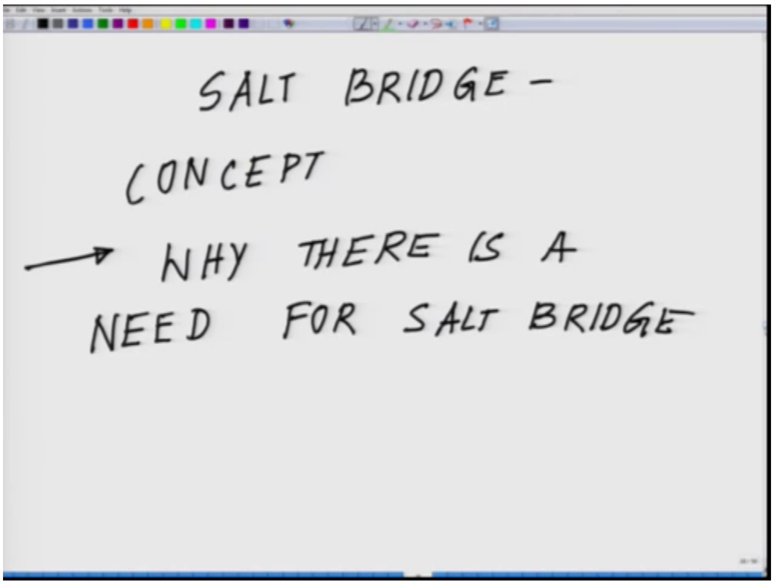

SALT BRIDGE -

CONCEPT

→ WHY THERE IS A NEED FOR SALT BRIDGE

Let us draw the situation where we did not get any net work done.

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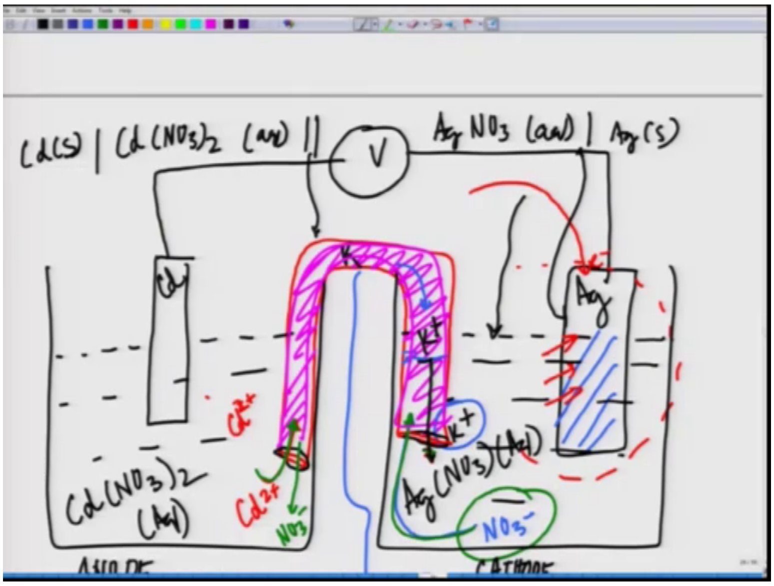

So, here you have now we have two different beakers coming through. So, you have the cadmium you have the voltmeter sitting here or potentiometer sitting here, we have silver electrode here Ag, we have cadmium electrode here and the solution it is dissolved in is cadmium nitrate Cd NO 3 2 which is an aqueous condition whereas, Ag is kept in a G NO 3, which is also aqueous.

Now, this is your anode where the oxidation is happening, whereas Cd solid moving to Cd 2 plus aqueous plus 2 electron. So, this is one side of the reaction. The other side of the reaction is at the cathode where you have 2 Ag plus in the aqueous plus 2 electrons 2 Ag solid. And if you remember the this Ag which is coming out from the Ag electrode out here from this Ag electrode this was the one which was migrating that Ag 2 plus was migrating on the surface of the cadmium and was consuming the electron and was becoming Ag solid and getting deposited in cadmium you can use this for electroplating you can quote a cadmium with silver on top of it like that. So, that was the reason why there was no external flow of electrons and that is where we talked about that will be introducing the concept of salt bridge.

Now, we will be introducing the concept, the basic fundamental of salt bridge. So, here we have a salt bridge now what is a salt bridge and what is its role. Now, this salt bridge is a very interesting concept and let us before I get into the salt bridge we talked about we can separate the reaction into two half cells. We have separated the reaction or the reactants you can say in this case into two half cells.

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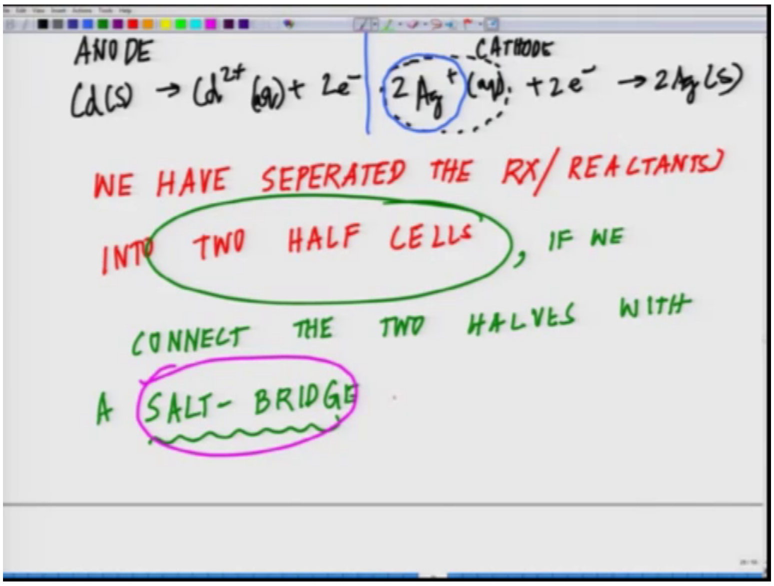

ANODE | CATHODE

$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$ | $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$

WE HAVE SEPERATED THE RX/ REACTANTS) INTO TWO HALF CELLS, IF WE CONNECT THE TWO HALVES WITH A SALT- BRIDGE

So, here we are introducing the concept of the half cells. So, please be very careful this will come very handy the concept of half cells. If we now, if we connect the two halves with a now here we are introducing the fundamental of salt bridge with a salt bridge, with a salt bridge as we have shown in the figure here this is your salt bridge, this is the salt bridge we are talking about and I will talk about that what you are feeling filling the salt bridge with salt bridge what is the salt bridge. Now we are defining the salt bridge.

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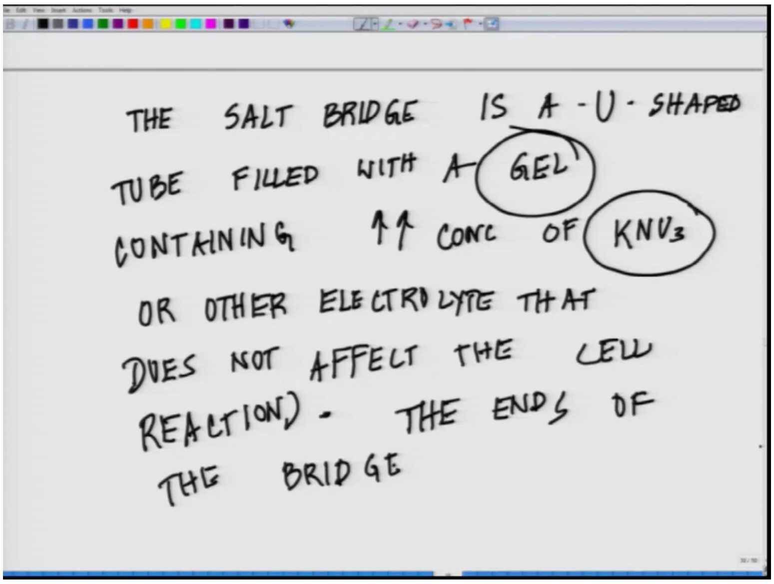

THE SALT BRIDGE IS A - U - SHAPED
TUBE FILLED WITH A GEL
CONTAINING ↑↑ CONC OF KNU_3
OR OTHER ELECTROLYTE THAT
DOES NOT AFFECT THE CELL
REACTION) - THE ENDS OF
THE BRIDGE

The salt bridge is U shaped tube filled with a gel. So, here is the gel containing a very high concentration of KNU 3. So, my need this, this will change according to the cell type KNU 3 or other electrolyte that does not affect the cell reactants or the cell reaction, that does not affect the cell reaction the end of the bridge.

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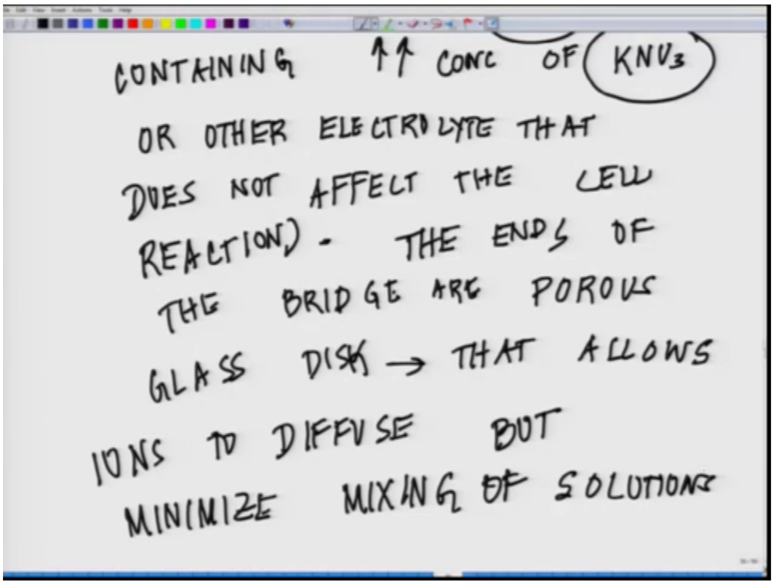

CONTAINING ↑↑ CONC OF KNU_3
OR OTHER ELECTROLYTE THAT
DOES NOT AFFECT THE CELL
REACTION) - THE ENDS OF
THE BRIDGE ARE POROUS
GLASS DISK → THAT ALLOWS
IONS TO DIFFUSE BUT
MINIMIZE MIXING OF SOLUTIONS

So, we are talking about these parts these are the ends we are talking about these are filled with porous material. End of the bridge are porous glass disc that allows ions to diffuse, but minimize mixing of solutions, minimize mixing of solutions inside and outside the bridge.

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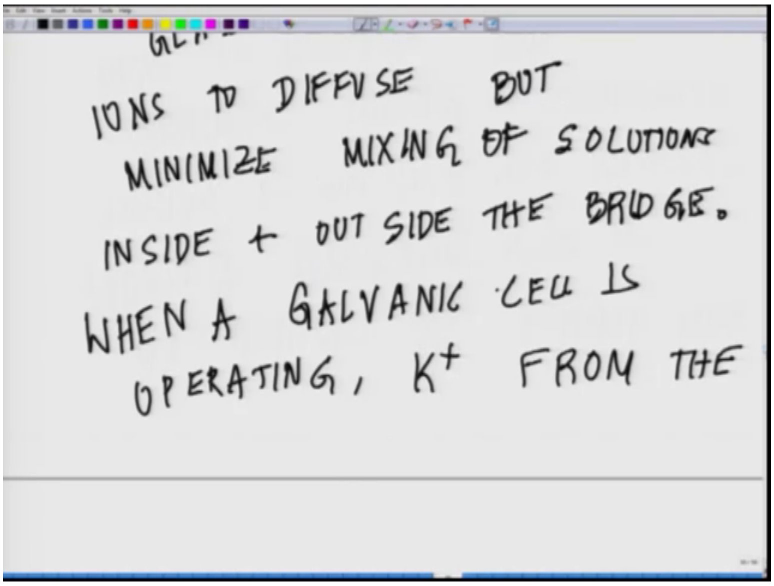

IONS TO DIFFUSE BUT
MINIMIZE MIXING OF SOLUTIONS
INSIDE + OUT SIDE THE BRIDGE.
WHEN A GALVANIC CELL IS
OPERATING, K^+ FROM THE

So, it will not allow any further mixing. So, when galvanic cell is operating then potassium ion potassium from. So, I have an introduced this I will complete the drawing potassium from the bridge migrates to the cathode chamber to the cathode compartment and small amount of NO 3 minus migrates from the cathode to the salt bridge, cathode into the bridge.

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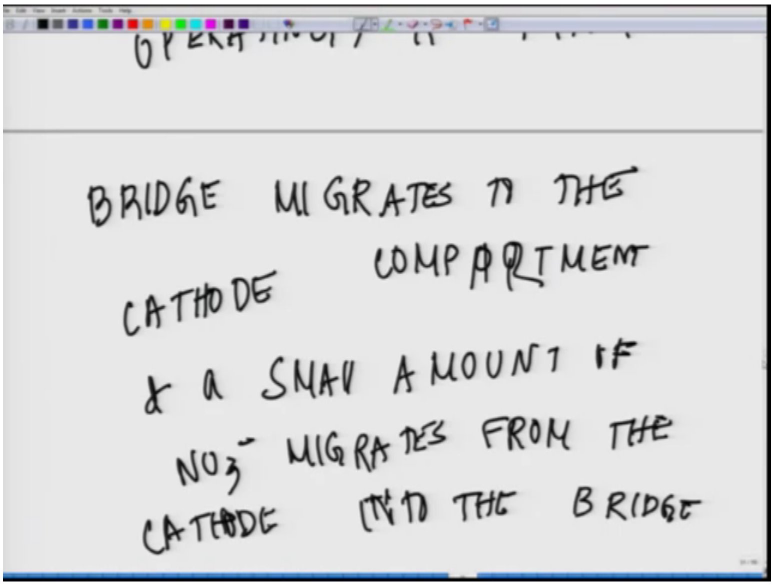

BRIDGE MIGRATES TO THE
CATHODE COMPARTMENT
& A SMALL AMOUNT OF
NO_3^- MIGRATES FROM THE
CATHODE INTO THE BRIDGE

Now, let us see the picture revisit the picture what is happening. So, now here it is filled with potassium. So, let us draw it that will make more sense. So, you are having a salt bridge which has lot of potassium salt in it, out here what is happening at the cathode side which is this side. So, there is a movement of some of the potassium ions coming onto this side.

So, from here some of the protections are moving into this side whereas, some of the NO 3, NO 3 minus is moving out there. So, this is the small amount of movement of ion which are happening somewhere out here. It does not proceed further this is where some of these potassium are moving onto the cathode side. On the contrary if you look at the anode side something very interesting is happening.

So, as the cathode is pulling out some of the positive charges in order to maintain. So, why it is happening? Because out here what is happening if you look at it this Ag plus is getting reduced by the electrons which are coming from the cadmium side. So, there is a dearth of some of the positive charges out here. So, just you have to imagine what is happening on this side. So, out here on this side of the story there is a dearth of positive charges those positive charges the dearth is being, so in order to maintain the potential difference there is some positive charges in the form of potassium ions which are positively charged they are moving percolating into this side. A little bit not a whole lot of migration happens.

On the contrary if you look at the cadmium side which is the anode side what is happening? On the cadmium side there is an excess of cadmium which is getting into the solution. Now, this excess cadmium which is Cd 2 plus. Now, because there is a dearth of positive charges because some of the potassiums are coming here some of these cadmium get into it Cd 2 plus, from the anode chamber move slightly into the cathode chamber and in return some of those NO 3 which become excess here moves out here.

So, on the cathode chamber if you look at it, the negatively charged ions and ions they migrate it onto the slide there is a small amount of migration which took place into the salt bridge whereas, positively charged ions from the salt bridge potassium ions. They slightly migrated to the cathode side. On the contrary the positively charged ions from the anode side move slightly inside the salt bridge which is your cadmium 2 plus whereas, some of the negatively charged ions NO 3 minus from the salt bridge migrated into the anode side. So, what are the consequences of this kind of movement? That is very important for you to understand.

Now, if we go back where cathode into the bridge.

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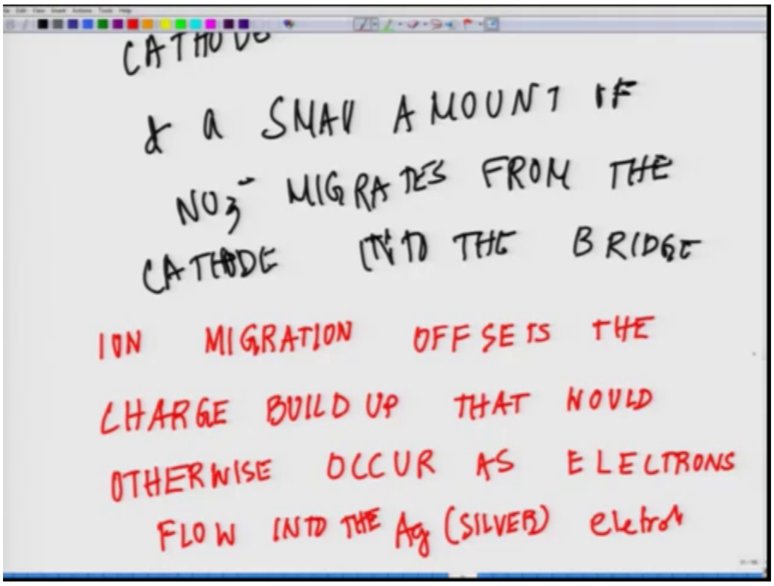

CATHODE

& A SMALL AMOUNT OF NO_3^- MIGRATES FROM THE CATHODE INTO THE BRIDGE

ION MIGRATION OFFSETS THE CHARGE BUILD UP THAT WOULD OTHERWISE OCCUR AS ELECTRONS FLOW INTO THE Ag (SILVER) electr

So, this part is very important, the ion migration why this ionic migration is essential. Ion migration offsets the charge build up that would otherwise occur as electrons flow into the silver or the Ag electrode. Because you are realizing that there will be a huge amount of charge offsets which will be happening because there will be a lot of electrons which are traveling out here and there will be a movement of the Ag 2 plus on the Ag electrode to get reduce and there will be a dearth or positive charges in the solution which is being compensated by those positive charges in the form of potassium plus which slightly migrates from the salt bridge. So, it is kind of doing a balancing act in order to maintain the potential difference across the 2 electrodes this part this concept has to be clarified.

And then next what is happening out here if I come back out here. On the other hand the migration of ions out of the bridge is greater. So, here let us highlight this part.

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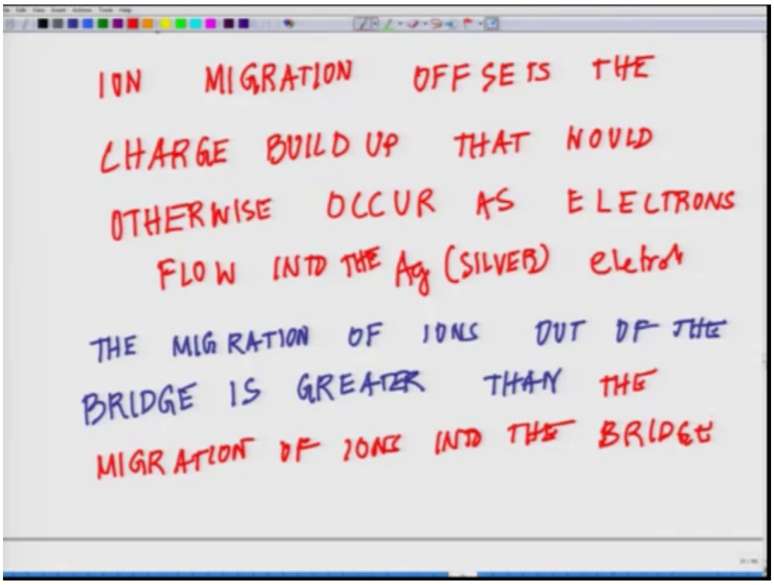

ION MIGRATION OFFSETS THE CHARGE BUILD UP THAT WOULD OTHERWISE OCCUR AS ELECTRONS FLOW INTO THE Ag (SILVER) eletrod

THE MIGRATION OF IONS OUT OF THE BRIDGE IS GREATER THAN THE MIGRATION OF IONS INTO THE BRIDGE

The migration of ions out of the bridge is greater than this keep in mind than the migration of ions into the bridge than the migration of ions into the bridge or the salt bridge here of course, into the salt bridge because salt concentration in the bridge is much much much higher than the salt concentration in the half cell.

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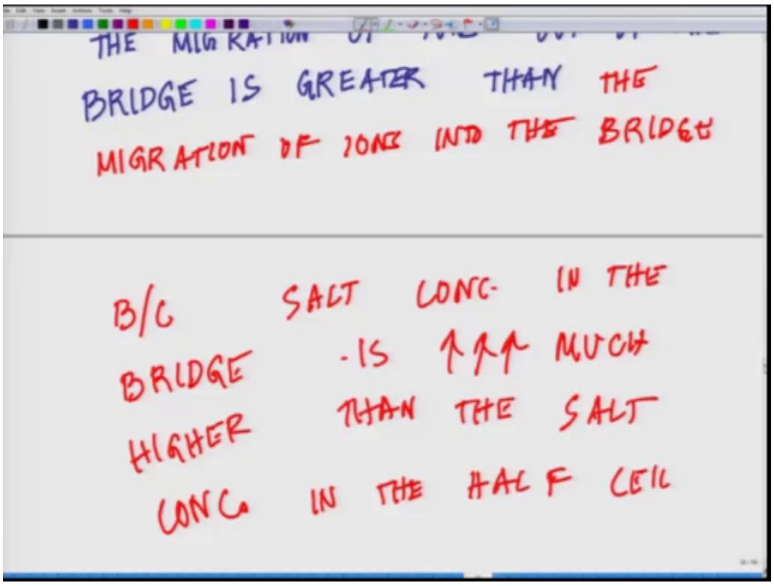

THE MIGRATION

BRIDGE IS GREATER THAN THE MIGRATION OF IONS INTO THE BRIDGE

B/C SALT CONC. IN THE BRIDGE IS ↑↑↑ MUCH HIGHER THAN THE SALT CONC. IN THE HALF CELL

So, that kind of tells you that why there will be more diffusion from the salt bridge as compared to the, into the salt bridge.

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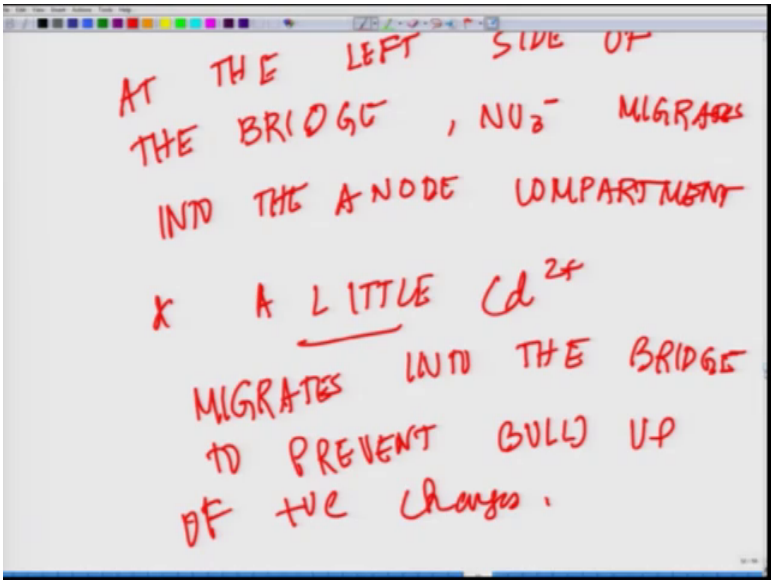

AT THE LEFT SIDE OF
THE BRIDGE, NO_3^- MIGRATES
INTO THE ANODE COMPARTMENT
& A LITTLE Cd^{2+}
MIGRATES INTO THE BRIDGE
TO PREVENT BUILD UP
OF +ve charges.

At the left side of the bridge which is now we are talking about that anode side, NO 3 minus migrates into the anode compartment. We have already mentioned it I am just putting it down into the anode compartment and little Cd 2 plus migrates into the bridge to prevent buildup of positive charges on the anodic side.

So, thus in order to prepare a salt bridge what you have to do this is a practical side of it what I am going to discuss now. In order to prepare a salt bridge for a reaction that, so you have to be very careful that these reactions should not these kind of salt bridge should not affect the reaction on the half cells instead they are only used to maintain an offset. As we will proceed further in the practical application you will realize why these are so significant.

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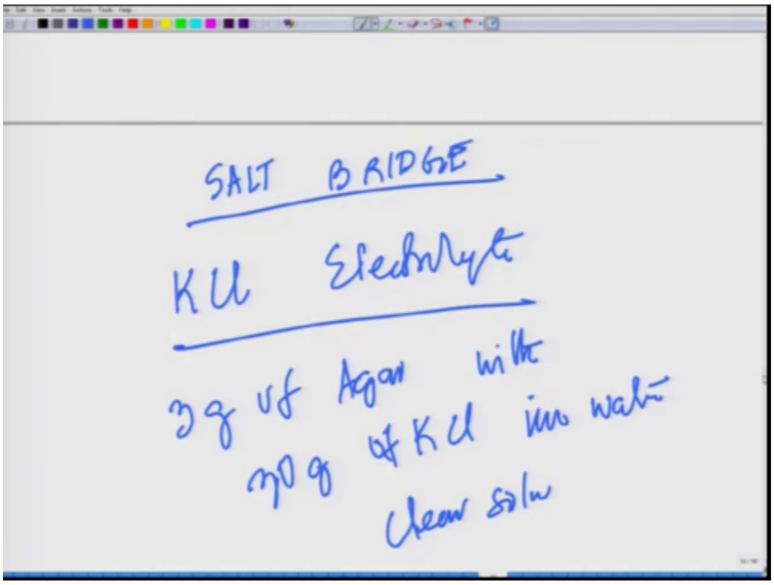

SALT BRIDGE

KCl Electrolyte

3 g of Agar with

30 g of KCl in water

Clear soln

Now, coming back to the salt bridge. For the reaction that do not involve silver or other species that react with chloride the salt bridge usually contain KCl electrolyte and a typical salt bridge is prepared by 3 gram of agar with 30 gram of KCl in water you can prepare this till you obtain a clear solution and the solution is poured into a U tube to allow it to gel. So, you prepare the solution and pour this solution into the u tube till it becomes a gel.

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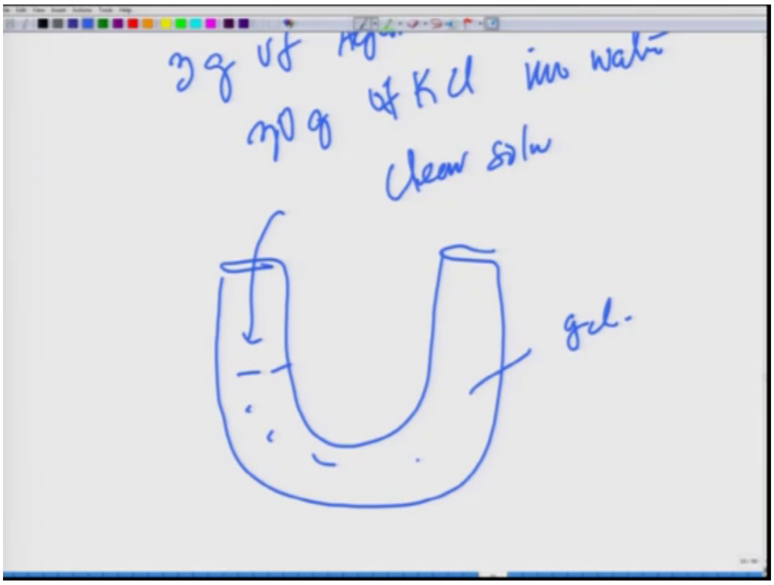

3 g of Agar

30 g of KCl in water

Clear soln

So, this is how you prepared these kind of salt bridges what we talked about; and talking about the line notation, here single line showing the phase boundary and the double line showing the salt bridge.

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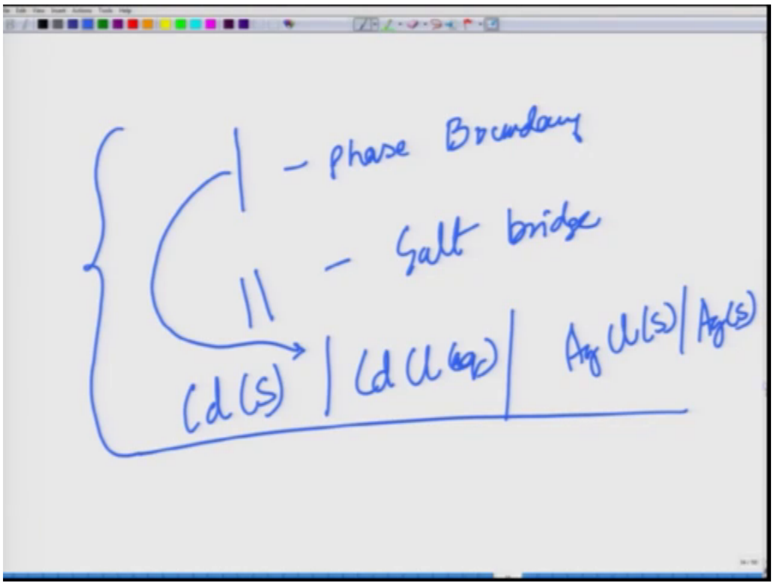

| - phase Boundary

|| - Salt bridge

Cd(s) | CdCl(aq) | AgCl(s) | Ag(s)

So, the cell in this case cadmium solid Cd Cl which is the aqueous, this is the phase boundary between cadmium and cadmium chloride and this is that electrode what we talked about earlier where you do not have any separation you have the AgCl solid, Ag solid. So, this is where with a single electrolyte we could achieve it. So, this is essentially the case of, this is the case.

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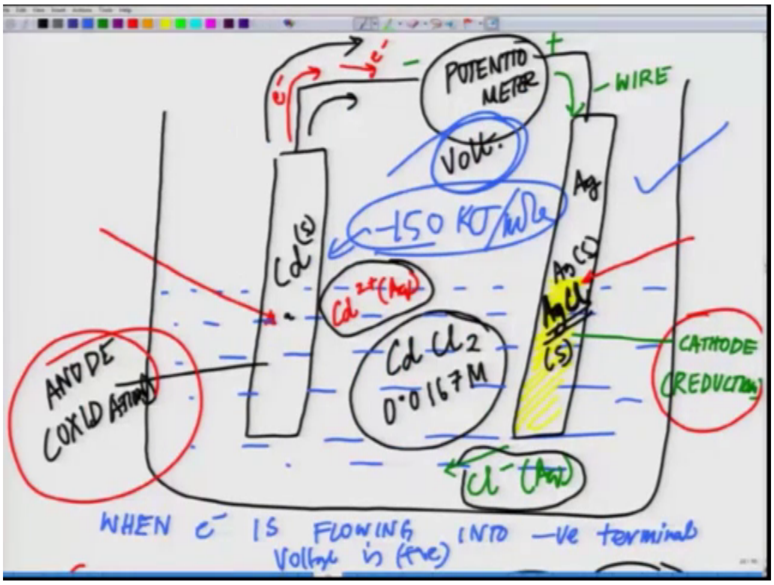

Now, if we talk about this current reaction then this will be Cd solid cadmium solid, Cd NO 3 2 aqueous.

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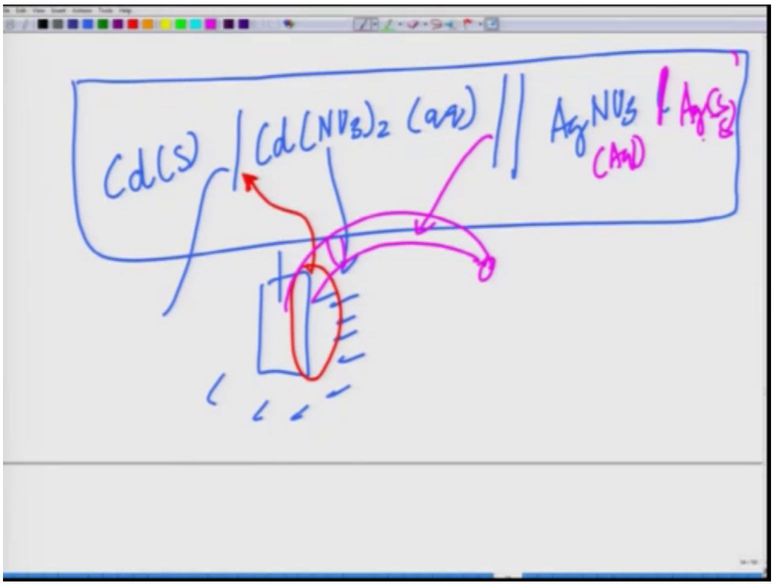

Now here is the salt bridge Ag NO 3, let us have the line notation for it where you have cadmium solid, so cadmium nitrate. So, this is the first phase boundary we are showing which is cadmium nitrate is the electrolyte in which it is. So, you have the cadmium electrode and in contact with cadmium nitrite. So, this is the phase boundary which is shown by this one line and then you have this pickup another color. So, you have this salt bridge which is shown here. So, you have Ag NO 3 which is your aqueous phase AG NO 3 with the phase Ag solid.

So, this is essentially the reaction what we just now discussed how you are going to write in a notation of line notation. This is what this reaction should be written. Again I am rewriting it cadmium solid, Cd NO 3 2 which is your aqueous double line which is your essentially your salt bridge followed by your Ag NO 3 which is aqueous which is this one with the phase boundary out here you are showing Ag solid.

So, that brings us to a situation where we have covered all the different aspects of the galvanic cell. That give you a compact idea how one can force the electron to flow into the external circuit, how you have these salt bridges which are compensating for much of this movement and the mass moment of the ions, how they are helping you to create an offset because of the charge buildup positive charge or negative charge buildup.

So, I will request you these last 2 lectures, 3 lectures are extremely important please go through them listen to them very carefully. If you have doubt please put them up in the forum. I tried to cover as much as I can by spreading 3 classes on galvanic cells because I felt that this is very important that this clarity of thought comes in your mind and I am thankful to the TA who pointed out this point. So, from here we will move on to the standard potential in the Nernst equation and we are slightly lagging behind, but do not worry we will cover it up ok.

Thank you.