Bio-electrochemistry

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Lecture - 05
Galvanic Cells-II

Welcome back to the fifth lecture of Bio-electrochemistry. So, in the last class I will started with the galvanic cell and I give you a classic example of zinc copper electrode and how the cell is formed. So, one of the challenging part of offering a MOOC lecture is that you do not have a classroom in front of you. So, that kinds of prevents you from getting bombarded with questions which are very genuine and which confuses the students all the time and with these kind of electrochemical cells it always remain for several students to figure out like you know how the electron is flowing, how the ion is flowing.

It is very interesting while I was sharing this lecture with the TA of the course miss Himanshi Jangir. She pointed out something very interesting. What she told me is that in our lecture we have not really highlighted how the electron flow and the ion migration or diffusion is happening. So, what I decided is that in this lecture I will again revisit the galvanic cell though this is a last lecture of this week. So, kindly do not get worried I have one of the 15th lectures and I am moving slowly because once this basic fundamentals are clarified then rest of the story will become much more easy. But if there is even one a small doubt remains in the fundamentals than you will always have problem all throughout and again you will have to revisit all the fundamentals.

So, today we will revisit the galvanic cell again with a different form of electrodes. So, if you remember yesterday when we talked about the galvanic cell using copper and zinc electrode we talked about. So, there is a semipermeable membrane and copper is deposited in its corresponding salt sink is deposited in its corresponding salt and zinc is behaving as an anode, where oxidation is taking place zinc is losing its electron and becoming zinc ion and that electron is flowing through the circuit to the copper electrode so on and so forth.

Today, we will take two cases in one case we will talk about the first case what we will be talking about is a cell where there is a common electrode without having that semi permeable membrane. And then we will take another situation where it will be having two different electrode mixed together without having the semi permeable membrane. And in the third case we will talk about what is the need of the semi permeable membrane or what we call as the salt bridge I have an introduced the salt bridge. So, this is what we will be covering today.

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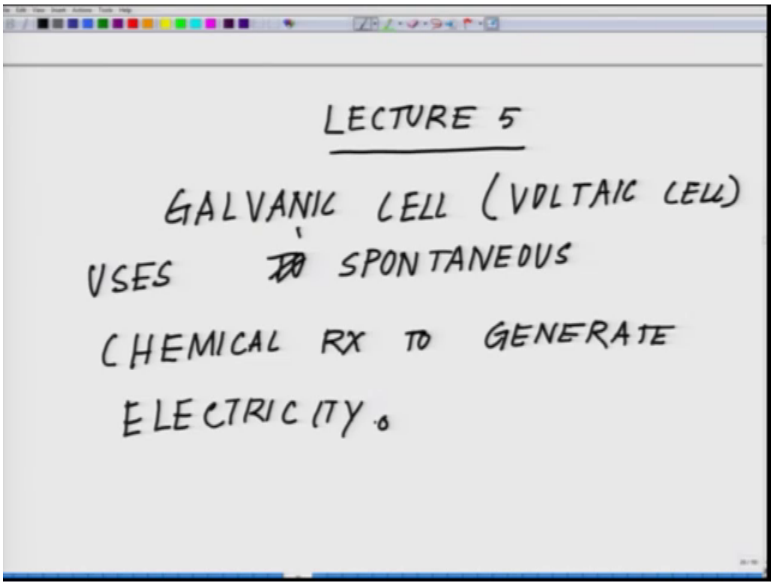

LECTURE 5

GALVANIC CELL (VOLTAIC CELL)

USES ~~TO~~ SPONTANEOUS

CHEMICAL RX TO GENERATE

ELECTRICITY.

So, let us start a lecture 4, lecture 5 sorry, lecture 5. So, let us again revisit the definition of the galvanic cell or the voltaic cell, galvanic cell this is also called voltaic cell sometime it is a special case called Daniell cells it uses spontaneous chemical reaction to generate electricity, the spontaneous chemical reactions to generate electricity. So, this is our basic fundamental definition.

Based on this definition there are few conditions to accomplish this in order to accomplish this, this feat could be only accomplished when one reagent must be oxidized must get oxidized whereas, the another one the second reagent must get reduced this is our basic fundamental.

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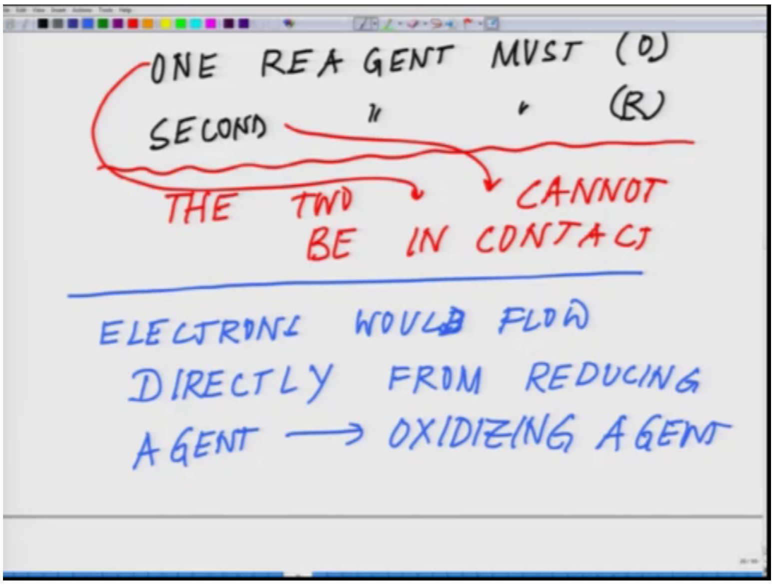

ONE REAGENT MUST (O)

SECOND " " (R)

THE TWO CANNOT BE IN CONTACT

ELECTRONS WOULD FLOW DIRECTLY FROM REDUCING AGENT ⟶ OXIDIZING AGENT

And the next most important thing what we will be dealing today the two cannot be in contact, the two which is this one and this one cannot be in contact. Contact means I am talking about a physical contact with each other they cannot be in contact because if in that case the electrons would flow if say for example, if they are in contact, let us assume a situation if these are in contact in that case the electrons would flow directly from reducing agent to the oxidizing agent and we will talk about such a situation directly from reducing agent to oxidizing agent. So, you have to prevent the physical direct contact and how we achieve that.

So, we will take two cases studies which will tell you how that is happening. Instead oxidizing and reducing agents are so, oxidize zing agent and reducing agent are physically separated, they are physically separated from each other and the electrons are forced to flow through an external circuit.

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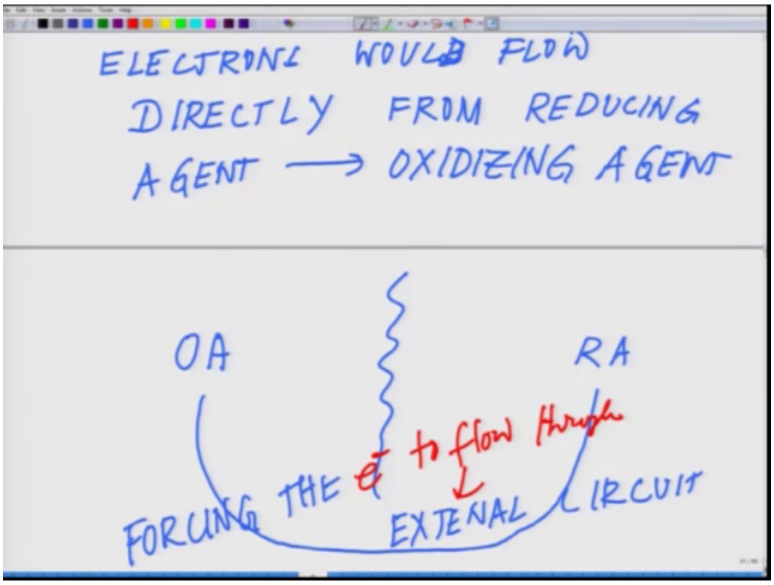

ELECTRONS WOULD FLOW DIRECTLY FROM REDUCING AGENT ⟶ OXIDIZING AGENT

So, essentially something like this. There is an external circuit where you are basically forcing the electron to flow through. So, you are keeping a physical barrier between them and they flow through the external circuit to go from one reactant to another.

Now, there are two terms which I have used an I today which to highlight which will come very handy in future when you talk about batteries where you will find a lot of applications of this or the fuel cell. I am just giving a small hint and then I will again carry over from here.

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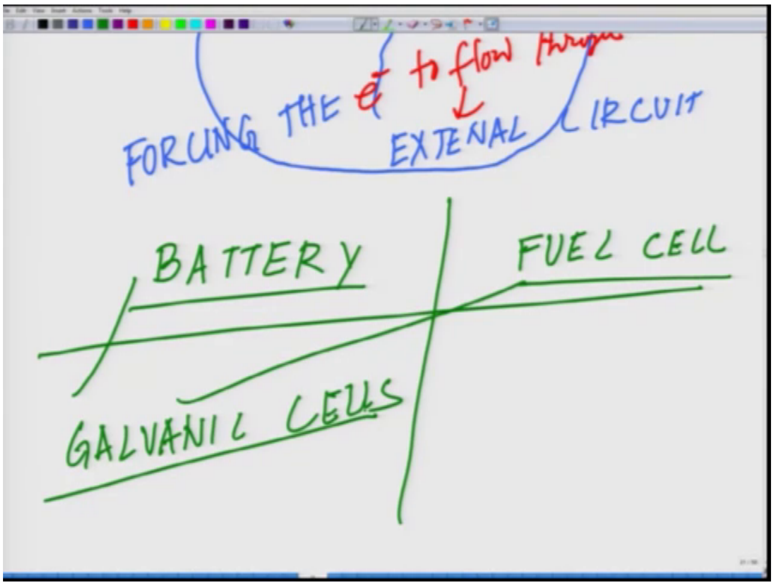

So, when you talk about battery essentially it is a galvanic cell then consume the reactant to generate electricity both of them are galvanic cells by the way, both these are examples of galvanic cells, but there is one small difference in terms of the amount of substrate which are present.

So, when you talk about a battery, in case of a battery so that is the situation when we talk about a static compartment filled with reactant, it is an static compartment filled with reactants.

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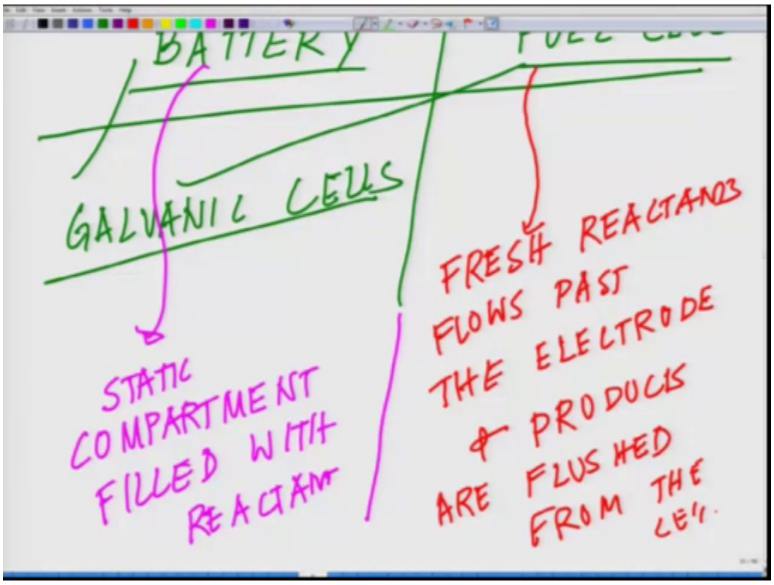

BATTERY

FUEL CELL

GALVANIC CELLS

STATIC COMPARTMENT FILLED WITH REACTANT

FRESH REACTANTS FLOWS PAST THE ELECTRODE & PRODUCTS ARE FLUSHED FROM THE CELL.

On the contrary if we talk about a fuel cell fuel cell, in case of fuel cell the fresh reactant flow past the electrode. So, you are continuously supplying fresh fresh reactants flows past the electrode and products are continuously flushed from the cells, are flushed from the cell. So, keep this in mind, these are two very important applications.

So, in other word when we talk about a fuel cell essentially what we are talking about is you are continuously there is an input of the reactants. So, there is electrode, there is a input of the reactants and the product which is coming out is getting flushed out whereas, in the case of a battery it is a static chamber where the reactions are continuously happening without much shift.

So, keep that in mind because these galvanic cells will come very handy and that is one of the very basic reason why I am spending more than stipulated time for you people to understand this. If you understand this understanding battery understanding fuel cell by fuel cells everything will become much more easy you will be able to know break up the system in terms of anode, cathode, electrolytes, reactants, products and everything. So, let us carry over.

So, now let us draw another. So, we talked about the copper and the zinc in the previous class. So, today we will talk about a different kind of electrode where it will be a cadmium and AgCl. So, it is start off with. So, let us draw a galvanic cell where you have an electrode which is cadmium electrode Cd and you have a AgCl electrode which is Ag and here you have, so here you are having the electrolyte and this is kind of coated with AgCl. So, this is an AgCl silver chloride electrode.

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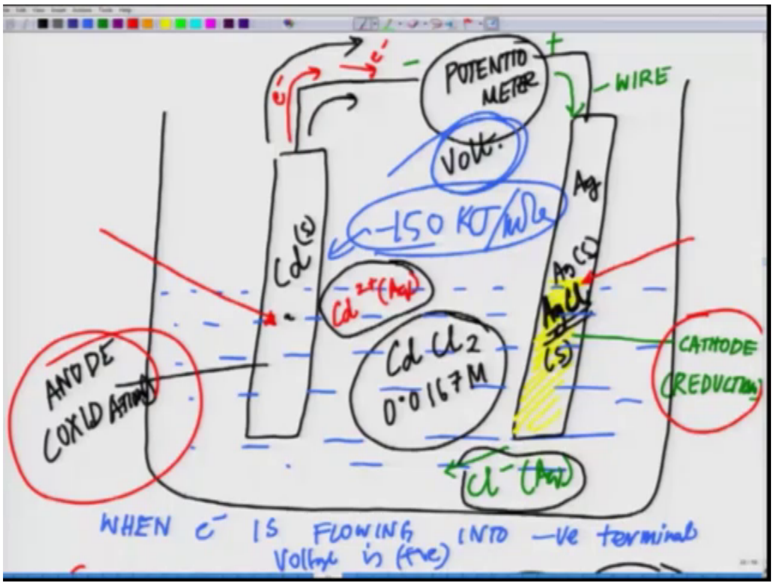

WHEN e⁻ IS FLOWING INTO -ve terminal Voltage is (+ve)

So, silver chloride electrode this is a solid electrode here cadmium, this is also a solid electrode here and this is connected to a voltmeter or potentiometer to measuring the voltage across it and cadmium in this case is the one which is. So, what is the electrolyte? Electrolyte is cadmium chloride. So, you are seeing I have not put any separation out here and for your interest this is around this much molar, which has been standardized over a period of time and in this case your cadmium is the anode and as you remember anode is the place where the oxidation is happening.

So, in other word add the anode what will happen? Cadmium 2 plus we will go to the aqua solution. So, in that case there will be an electron which will be generated which will be traveling in this circuit like this. Whereas, on the AgCl solid electrode which is this case is an cathode where essentially reduction is happening in this case the chloride will come out into the solution Cl minus in the aqueous solution the chloride will come out and here you are having the AgCl solid electrode. So, this electron which would be coming, so in that case this polarity will be positive here it will be negative and this is that external connection the wire and the electron is coming and reducing and the Ag plus which is generated because silver is leaving behind and coming into the solution. So, you know sorry in other word the chloride is coming into the solution leaving behind the silver with additional positive charge which is being nullified by the electron traveling from the cadmium side. So, let us talk about it.

So, this is basically a simple galvanic cell potential that measuring the voltage and it has a positive and negative terminal and the when the electron flows into the negative terminal as elect as the illustration the voltage is positive. So, keep that in mind. When electron is flowing or electron flows into the negative terminal into negative terminal as in this illustration the voltage is positive. So, there is a positive voltage which is good, so this is an axiom by which we define these kind of situations.

Now, having shown this now we will talk about what are the reactions which has happened, that is the important part for us that is the what we have to take into consideration.

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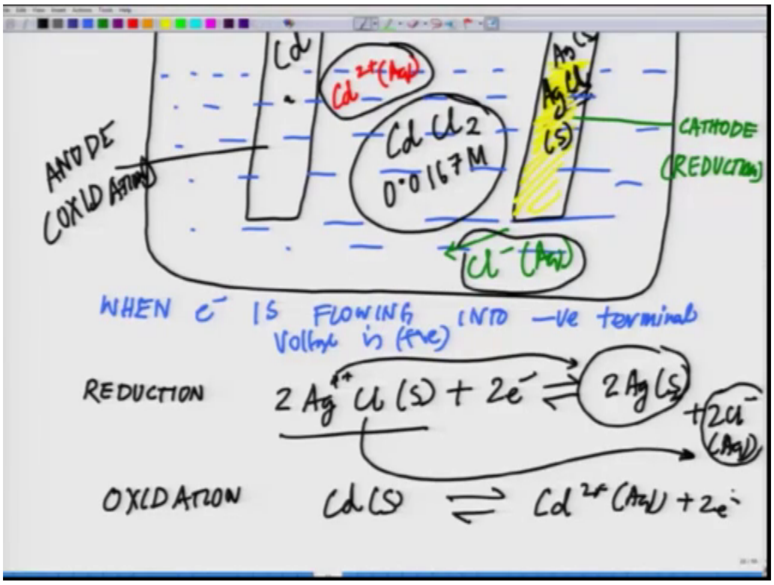

There are two reactions which are happening and mind it there is no semipermeable membrane here. So, there is a reduction reaction where 2 AgCl which is your solid and you have to mention always which is solid, which is aqueous plus 2 electrons which are traveling from cadmium after cadmium getting oxidized making his 2 Ag which is solid plus 2 Cl minus which is in aqueous.

Now, tell it here is that let us start with this term. Here you are having the chloride aqueous 2 Ag. So, this is your AgCl electrode on the edges Cl electrode you are having Ag solid second term, talking about the two electrons which are traveling. So, here you are having those electrons which are travelling from cadmium. So, AgCl, so chloride is getting lost into the aqueous solution and 2 Ag which is left with a positive charge is getting reduced out here to make Ag metal. So, there is a deposition of Ag metal and you are continuously losing the chloride from it.

Now, what is the oxidation reaction which is happening? The oxidation reaction you are having the cadmium which is the solid you see that solid cadmium out here and the solid cadmium is getting oxidized becoming Cd 2 plus in the aqueous system. So, you see this, this is the aqueous solution and it is losing those 2 electrons, those 2 electrons are shown here these are the electrons which are traveling.

Now if we add up this reaction out here what you are going to get in this redox reaction? You have net reaction you have cadmium which is solid plus 2 AgCl which is also solid making, so there is a there is a migration of cadmium 2 plus or cadmium ion into the aqueous solvent plus 2 Ag which is on the solid deposition and 2 Cl which is the aqueous. And you remember we use cadmium chloride as the electrolyte out here. So, this is what is happening in this situation.

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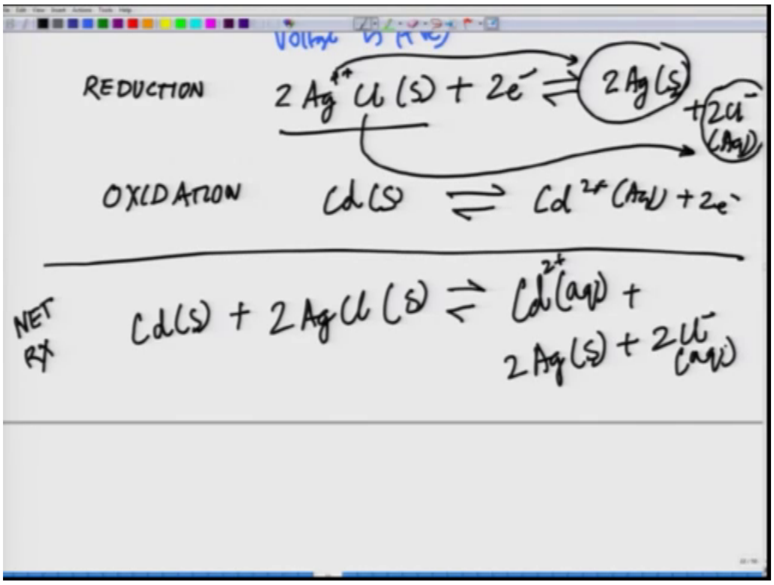

Voltage is (+ve)

REDUCTION $2\overset{+}{Ag}Cl(s) + 2e^- \rightleftharpoons 2Ag(s) + 2Cl^-(aq)$

OXIDATION $Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2e^-$

NET RX $Cd(s) + 2AgCl(s) \rightleftharpoons Cd^{2+}(aq) + 2Ag(s) + 2Cl^-(aq)$

So, if we summarize it out here. So, the oxidation of cadmium metal to Cd, Cd, so basically the oxidation of cadmium metal to Cd 2 plus in aqueous solution provides electrons which flows through outer circuit to the Ag electrode or silver electrode and on the silver electrode at the surface of the, at the Ag surface at silver surface which is basically the AgCl.

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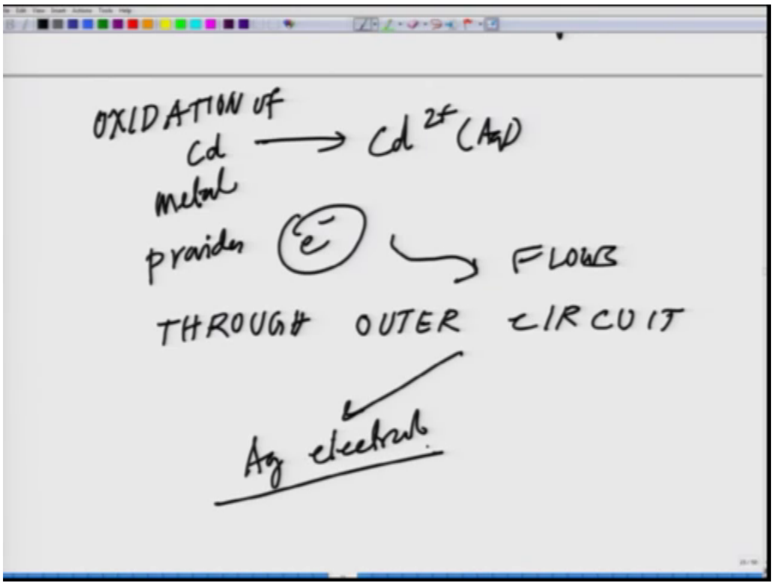

OXIDATION OF Cd metal $\longrightarrow Cd^{2+}(aq)$

provides e^- FLOWS THROUGH OUTER CIRCUIT

Ag electrode

So, keep in mind it is not the pure Ag its AgCl from AgCl is reduced to Ag solid and chloride from keep in mind this is a chloride chloride from AgCl goes into solution.

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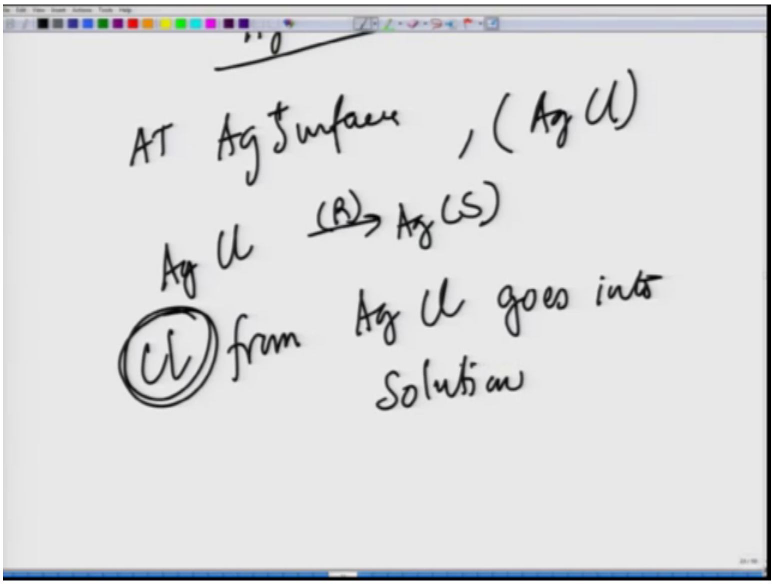

AT Ag Surface, (AgCl)

$AgCl \xrightarrow{(B)} Ag(S)$

Cl from AgCl goes into Solution

So, keep this all these things in mind. And here is the important part you might be wondering where I was talking about all this free energy. So, the free energy change for this net reaction, the net reaction what is being shown here out here for this whole reaction the free energy change which is happening is minus 150 kilo Joule per mole of cadmium.

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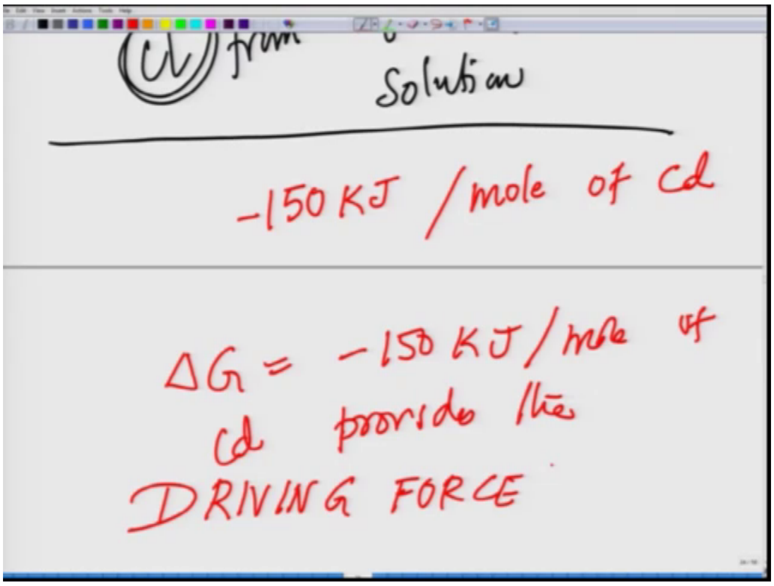

Cl from

Solution

-150 KJ / mole of Cd

ΔG = -150 KJ/mole of Cd provide the DRIVING FORCE

So, this is the free energy change or delta G is equal to minus 150 kilo Joule per mole of cadmium provides the driving force for this reaction to occur, driving force for this reaction to occur.

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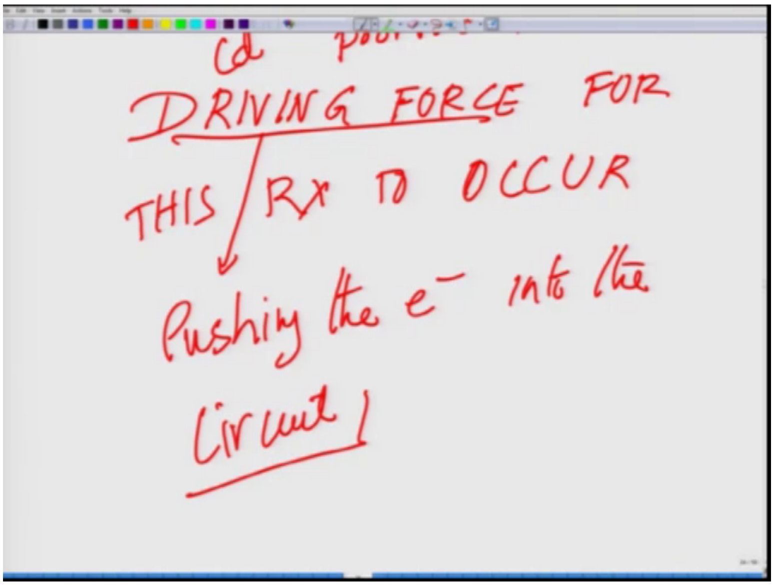

Cd

DRIVING FORCE FOR THIS RX TO OCCUR

Pushing the e^- into the Circuit!

Now, in other word it this is the driving force that pushes the electron into the circuit, this is the driving force pushing the electron into the circuit. So, keep that in mind. So, this is where the electron is coming.

Now, if you remember the formula what I taught you earlier could you calculate the voltage. If you remember, the formula was delta G is equal to minus n F E, where E was the voltage. So, what we have to figure out is the E right. So, E is your unknown parameter.

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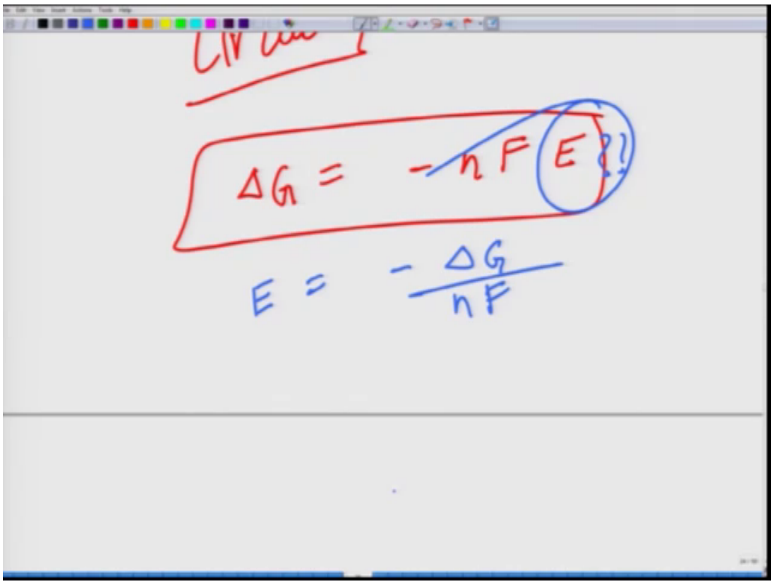

$$\boxed{\Delta G = -nF\,\boxed{E}\,?!}$$

$$E = -\frac{\Delta G}{nF}$$

Now, if you put it like this. So, E is equal to minus delta G upon n F. Now, if I plug in the values now you will see what is the voltage. So, what we are essentially trying to find out what is the voltage value you are going to see. So, you have other parameters, so you know this reaction will happen at minus 150 kilo Joule per mole of cadmium is getting consumed.

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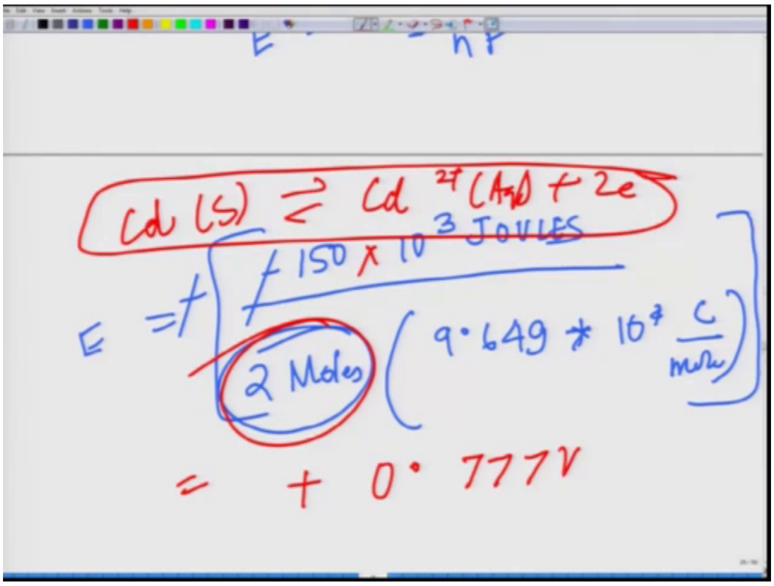

$$\boxed{Cd(s) \rightleftharpoons Cd^{2+}(Aq) + 2e}$$

$$E = \cancel{-}+\left[\frac{\cancel{-}150\times10^{3}\ \text{JOULES}}{\boxed{2\ \text{Moles}}\left(9.649 * 10^{4}\ \frac{C}{mole}\right)}\right]$$

$$= +0.777V$$

So, if this is the situation then the value of e will be minus 150 into 10 to the power 3 Joules, so that was in kilo Joule. So, I am converting that into Joules divided by 2 moles

2 moles multiplied by f which is n F Faraday's constant which is 649 multiplied by 10 to the power 4 coulomb per mole. Now, if you calculate this value this will come as, so there is a minus already here and this equation is also comes with a minus. So, this minus minus canceled. So, this is what it is and by the way I have not mentioned that, so basically what you are calculating is the voltage produced by the chemical reaction.

So, now what you are having is that you might be wondering why I put 2 moles here. Now, if you recollect the reaction what happened in the reaction of the cadmium so that will clarify why I put 2 moles there because if you see the reaction. So, if you see this generate 2 electrons. So, we assume this those 2 electrons are basically 2 moles you can always say 2 electrons or 2 moles of electron because you cannot really calculate the number of electrons here, so 2 moles of electrons that is why I put it as a 2 moles.

So, that this value the 2 moles what you see should not confused you it is because in that reaction. So, you should always remember the reaction the first reaction what you saw was Cd solid, so cadmium becoming 2 plus aqueous plus 2 electron. So, this is the reaction which is governing this whole flow of electron. So, 2 moles there, so minus minus becomes plus and as I told you. So, 150 multiplied by 10 to the power 3 and if you do this whole calculation or by yourself what will be generating is plus 0.777 volt.

So, this is a spontaneous chemical reaction negativity delta G produced produces a positive voltage. So, negative delta G producing positive voltage and this is an spontaneous reaction. So, vice versa if there have been would have been a positive delta G which is non spontaneous reaction you would have got a negative voltage.

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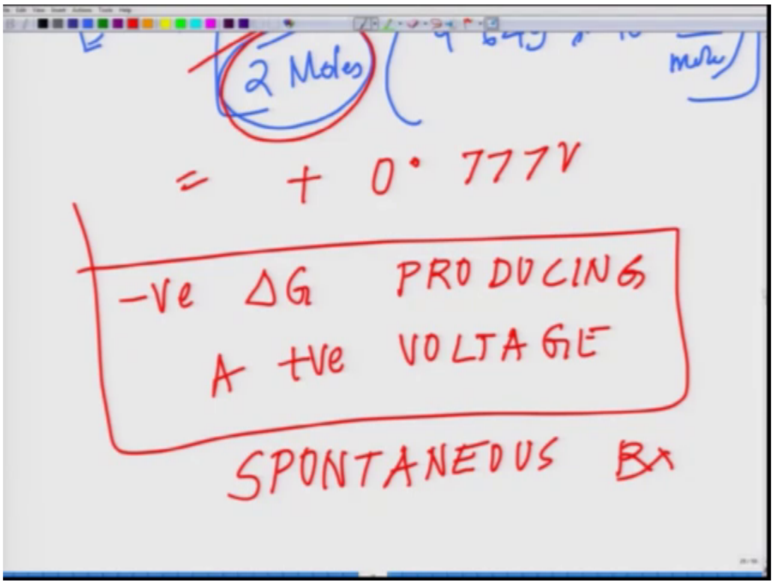

So, keep this in mind and we have already talked about the concept of anode and cathode where we told you that anode is the one where there basically electrode the oxidation occurs and cathode is the one where is the reduction occurs. So, in this case in that situation your this is your cathode and this is your anode because this is where the oxidation is happening ao and cr which is cathode the reduction to remember cr ao, ao is anode where the oxidation is happening and cathode where the reduction is happening.

Now, from here we will move on to a situation which is slightly complicated than this and that is the whole reason to you know invest another class on it. Now, a situation where we will be talking about another cell now let me draw the cell and that will clarify everything.

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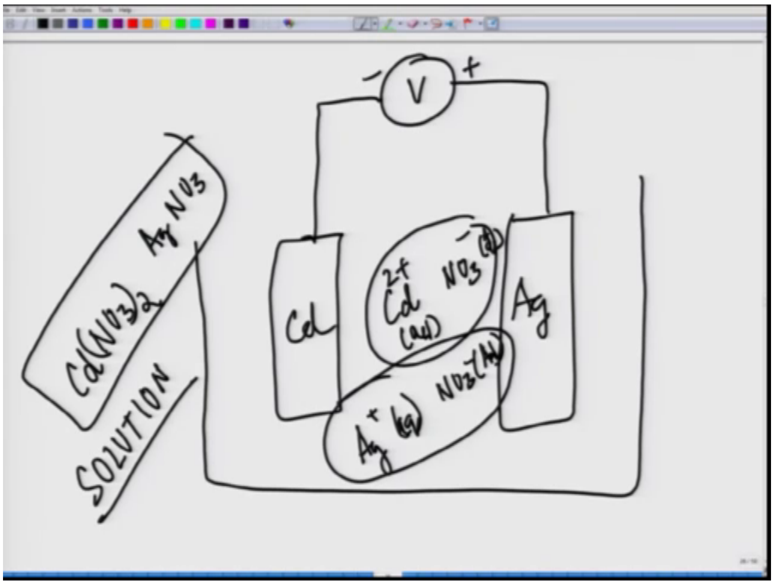

So, here you have the voltmeter sitting and you have a cadmium electrode again a cadmium electrode, but this time I have a silver electrode no more Ag Cl I have a silver electrode sitting here. So, it is a positive is a negative as we evolved earlier should and now I am putting two different electrolyte into that Cd NO 3 which is a aqueous and Cd is again this is a aqueous which is plus NO 3 minus Cd 2 plus 3 minus whereas, the other electrolyte I am mixing is Ag NO 3 Ag aqueous it is positive plus NO 3 minus which is also a aqueous 1 now having 2 electrolytes which are mixed together.

In this situation, this situation contained Cd NO 3 2, Ag NO 3. These are the two solutions the solution contain these or in other word these are the electrolytes. So, I am not putting, now here is a situation if you remember when I started the class I told you I could have 3 situation, in one situation where I have a barrier as I have discussed in the previous class where you have the copper and the zinc electrode separated by a barrier. Second situation is that I do not have a barrier which I just now explained before earlier than this we have cadmium and AgCl electrode in cadmium chloride.

Now, third situation I am talking about I have two different electrolyte and I am mixing them together. Two different electrolytes are cadmium nitrate and Ag NO 3 silver nitrate, and my electrode are cadmium and silver. Now, what will happen in this situation? Now, this is a very tricky situation. So, this is the situation what I am going to now discuss is the resultant for this, so let us write down the reaction first because in order to understand all these things you have to write down the reaction.

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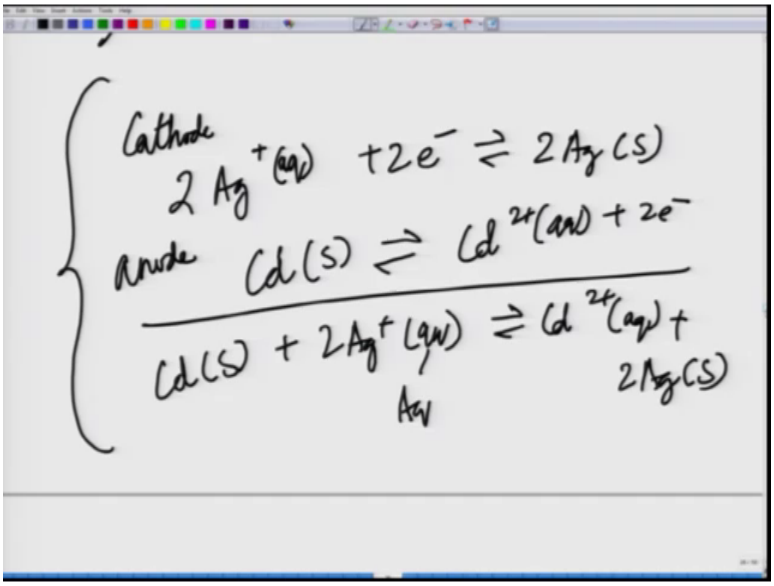

Cathode

$$2Ag^{+}(aq) + 2e^{-} \rightleftharpoons 2Ag(s)$$

anode

$$Cd(s) \rightleftharpoons Cd^{2+}(aq) + 2e^{-}$$

$$Cd(s) + 2Ag^{+}\underset{Aq}{(aq)} \rightleftharpoons Cd^{2+}(aq) + 2Ag(s)$$

At the cathode where the reduction is happening where basically 2 Ag plus aqueous plus 2 electrons will make 2 Ag solid. Whereas, at anode what is going to happen is cadmium solid cadmium 2 plus goes to the aqueous plus 2 electron and the net reaction what is happening is cadmium solid plus 2 Ag plus aqueous, once again, aqueous Cd 2 plus aqueous plus 2 Ag solid. So, this is the overall reaction which is happening.

And in this reaction what will happen, the net reaction is spontaneous, the net reaction is spontaneous but little current will flows through the circuit because Ag 2 plus is not forced to be reduced at silver electrode.

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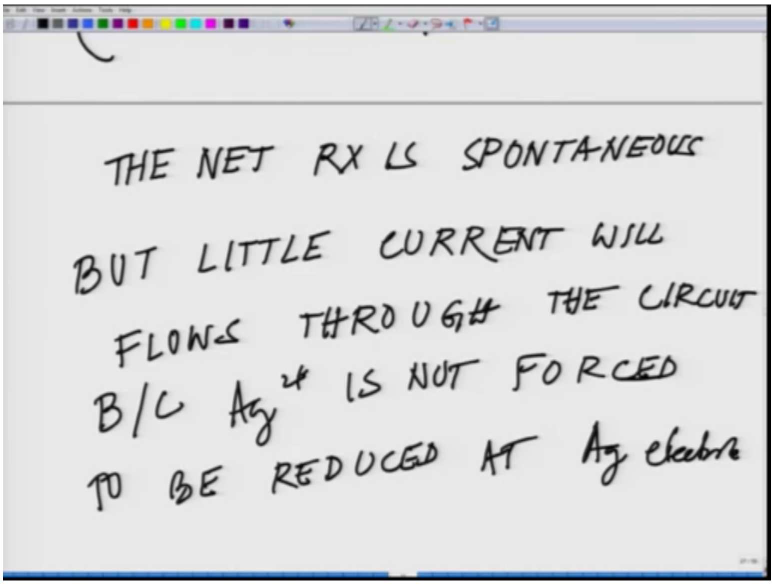

THE NET RX IS SPONTANEOUS

BUT LITTLE CURRENT WILL FLOWS THROUGH THE CIRCUIT

B/C Ag^{2+} IS NOT FORCED TO BE REDUCED AT Ag electr

So, aqueous Ag plus can react directly to the cadmium solid surface giving same net reaction with no flow of electrons which is e’s transfer electrons through external circuit.

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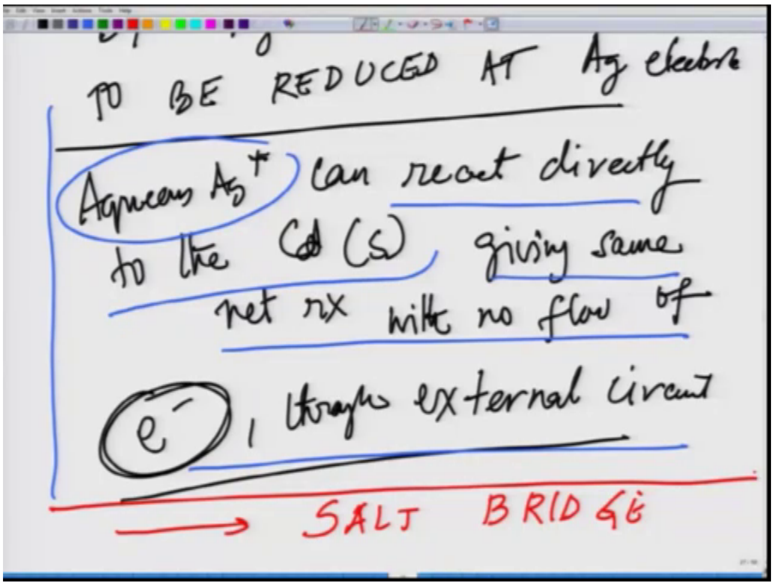

TO BE REDUCED AT Ag electr

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

→ SALT BRIDGE

This is a classic situation where if you think of it this Ag which is coming out from here as Ag plus can directly react on the cadmium surface and that is exactly what I was trying to highlight here if you look at it. Aqueous Ag plus can directly react to the cadmium solid surface giving the same net reaction with no net flow of electrons through the external circuit.

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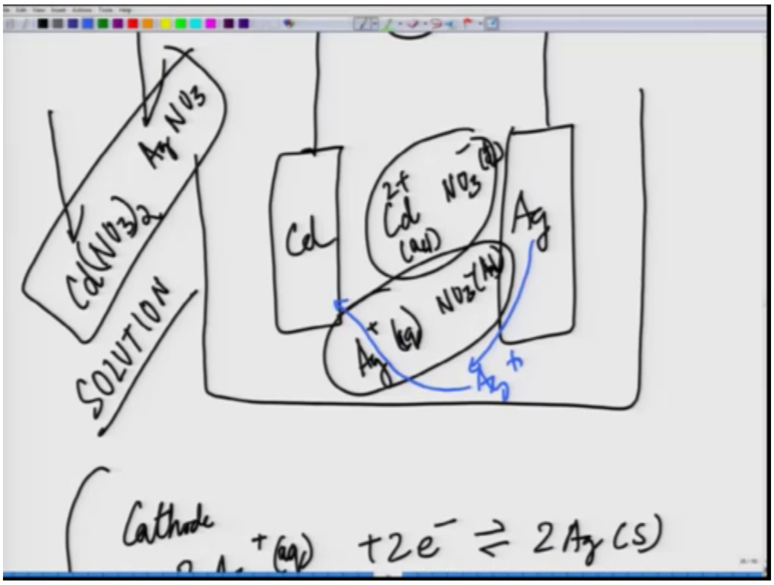

So, essentially this is where the catch is the cell that will not work a solution containing two different electrolytes it is not going to work and this basic fundamental is needed to be understood because once we understand this then we will move on to our next class we will talk about the why we needed the salt bridge and what is the role of salt bridge.

So, what I will do I will close in here and in the next class we will be exceeding a little bit further in the next class we will talk about a situation of salt bridge, why salt bridge is need needed. Why in the first case, if you remember the previous class when I introduced a semipermeable membrane, why the semipermeable membrane has to be introduced? What was the need for that semipermeable membrane?

We will talk about that semi permeable membrane in the next class that will kind of give you the fee of a situation where a galvanic cell can work with a single electrolyte. But if you mix two different electrolytes what will happen and if you separate both of them how you can force the electron to move into the circuit instead of a close in contact which prevents it to do any meaningful work.

Thank you.