Course on Analytical Chemistry
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Module 9
Lecture No 42
Electrochemical Methods – I (Contd.)

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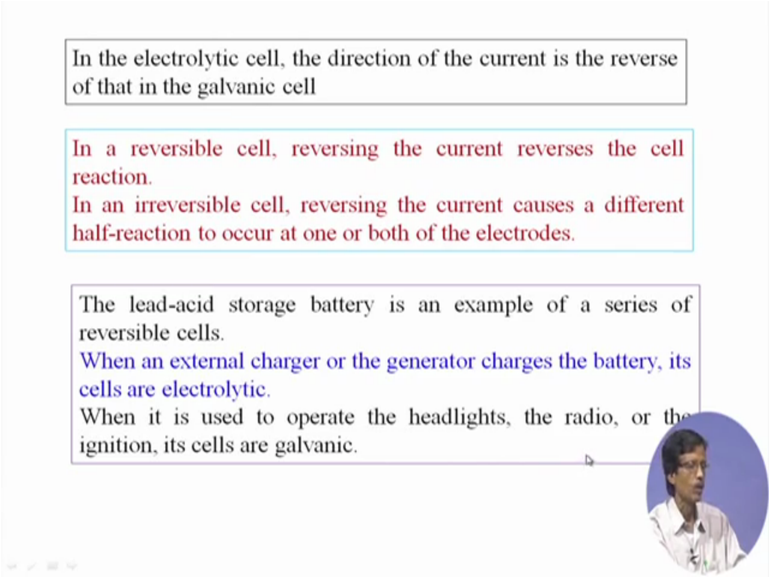

In the electrolytic cell, the direction of the current is the reverse of that in the galvanic cell

In a reversible cell, reversing the current reverses the cell reaction.
In an irreversible cell, reversing the current causes a different half-reaction to occur at one or both of the electrodes.

The lead-acid storage battery is an example of a series of reversible cells.
When an external charger or the generator charges the battery, its cells are electrolytic.
When it is used to operate the headlights, the radio, or th ignition, its cells are galvanic.

Welcome back to this class of electrochemical studies where we are talking about some cells, electrochemical cells and how those electrochemical cells can be applied for your voltage generation or the electricity generation as well as the electrolysis. So we have seen that in the electrolytic cell the direction of the current is the reverse to that of an galvanic cell. So that is why the definition is completely different for electrolytic cell and the galvanic cell.

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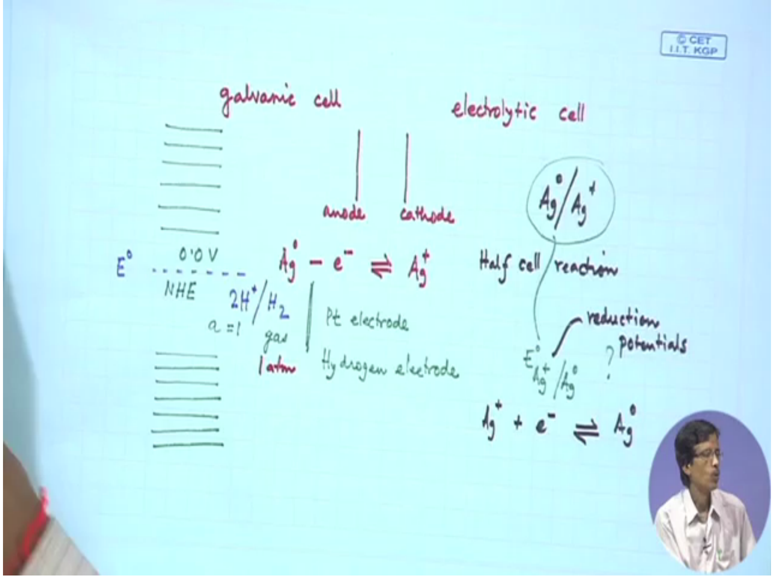

So if we have the galvanic cell and the electrolytic cell, so definition for anode and cathode will be different and anode is required that in one particular case that anode is for the oxidation and cathode is for the reduction but if we do in a different way it means if we draw the electricity from there in the galvanic cell, the anode will supply that particular electrode or cathode will except that particular electron.

So in a reversible cell now, we consider a reversible cell when we get a particular type of reaction that means if we see that silver is there silver 0 which is losing electron to get silver ion for its half-cell reaction, so if some condition can be applied to it, such that you can reverse the reaction though we know that is a natural tendency or this is that, if you find that, there is a natural tendency for this reaction or half-cell reaction.

So this is your half-cell reaction and for half-cell reaction itself also we have a natural tendency if we consider these 2 together, we consider that silver 0 which is kept in presence of silver ion that whether your silver will go for oxidation to silver ion or silver ion will except the electron to give you the silver in the metallic state. So this whether we can reverse it, if we consider that one this is one electrode reaction, the other electrode we can have, so we get combination of these 2 electrons giving rise to the corresponding electrochemical cell.

So if we have a reversible cell, reversing the current reverses the cell reaction. That means the direction of the current in one particular direction will go for the supply of electron. If we reverse that, if we supply electron in the other electrode, we get that the reversing of the current reverses the cell reaction, that means if we go for silver 0 to silver ion, if we reverse it silver ion will go to silver 0 or particular reversible reaction but there are some electrochemical cells which are not considered as reversible cells.

So what those cells will consider name those electrodes cells as a reversible cell and this irreversible cell will behave or will function in a different manner compared to your reversible cell. When we reverse the current direction or when we reverse the current causing a different half reaction to occur at one or both the electrodes.

So we can force it such a way that we reverse the direction of the current to be passed to the 2 different electrodes but if it is an irreversible cell will not be able to get the same reaction what we are expecting for a reversible cell but a different type of reaction at means the coats of reaction will be different at least for one type of electrode or sometimes it is true for both the 2 electrodes.

Such as what we know that the storage battery for the mobiles what we use the lead plates, the metallic lead plates and the sulphuric acid we know that the lead is responsible for its oxidation and something will also there which can be responsible for its reduction but your we have a series of reversible cells that is why it is considered as a storage battery that means during a particular reaction that means reaction of the acid with that of our lead plates gives rise to some energy.

So when energy is basically discharging the thing and its energy potential or the current potential or the voltage potential that particular case is decreasing, so when we draw more and more current it is almost dying that particular battery but when the external charge or the generator, if we put in to the charging device, so the charger or the generator charges the battery, it is cells are electrolytic.

So when we charge it the cells will be electrolytic, it is not a voltaic cell otherwise it will be a voltaic cell when it gives us the power or the electrical energy, when it is used to operate the lights, headlights, the radio or the ignition, its cells is galvanic. So we see that it is a typical example when we draw the current it is the corresponding galvanic cell but when we charge it from external source of electrical energy.

During the charging process it is the corresponding cell will be termed as the electrolytic cell, so that gives us a very good idea so the definition why is the definition for your anode and cathode will also be different if we consider whether we are talking in terms of a galvanic cell or in terms of some electrolytic cell.

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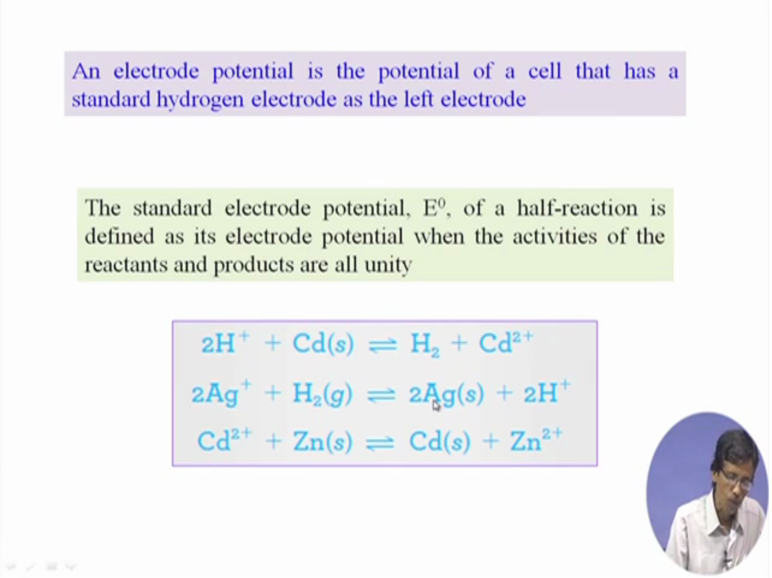

An electrode potential is the potential of a cell that has a standard hydrogen electrode as the left electrode

The standard electrode potential, E^0, of a half-reaction is defined as its electrode potential when the activities of the reactants and products are all unity

$$2H^+ + Cd(s) \rightleftharpoons H_2 + Cd^{2+}$$
$$2Ag^+ + H_2(g) \rightleftharpoons 2Ag(s) + 2H^+$$
$$Cd^{2+} + Zn(s) \rightleftharpoons Cd(s) + Zn^{2+}$$

So thus we get some electrodes and electrodes is dipped inside a solution, so we will be able to develop some electrode potential, so what is that potential? It is the potential of a cell, it can be your half-cell also that has a standard hydrogen electrode at the left electrode, so if we put a standard hydrogen electron as the left electrode and the measured electrode potential will be the corresponding potential for its half-cell reaction.

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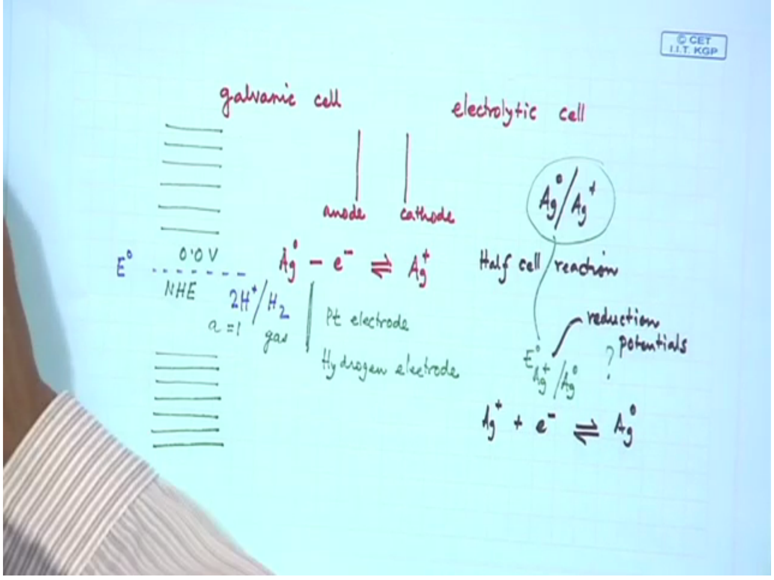

So from our school days also we know that the corresponding level we consider the corresponding E0 value for the hydrogen electrode, hydrogen electron is the corresponding reduction of hydrogen 2 of H plus is reducing to hydrogen gas, so this we consider this particular potential will consider as 0.0 volt and why we consider this as 0.0 volt, is that we can have some electrodes what we consider as normal hydrogen electrodes NHE.

So with respect to the normal hydrogen electrodes that mean you have the hydrogen as the gas and at activity one of this hydrogen ion that means the corresponding acid solution. So activity of that acid solution is also one so we get that on a platinum electrode, so that platinum electrode give rise to the corresponding setup for hydrogen electrode we get and based on this particular half-cell that means the tendency of the hydrogen ion for its reduction to give rise to the hydrogen gas is considered as the standard as 0.0 volt and with respect to that we have all other species we level it that means whether the species have more or less electron transfer activity or tendency compared to your hydrogen electron.

So that is why some of this metal species or the other non-metallic species will be above this hydrogen electrode or will be below the hydrogen electrode depending upon their tendency for oxidation or reduction reactions. So if we consider that whether if you have a half cell reaction of silver plus and silver O, we have a half cell reaction so how we get the corresponding standard electrode potential of these that means the E0 value for AG plus AG 0, how we get that?

So since by definition we are considering that will be talking in terms of the corresponding electron transfer reactions with respect to this hydrogen electrode that means this tendency is a standard tendency whether it accepts electron or donates electrons to produce hydrogen ion from the hydrogen gas is a reference one and with reference to that whether your this half-cell, the another half-cell will be oxidising or reducing that will tell us whether it will be above this 0 level or below this 0 level.

So if we connect this particular one if we connect this cell that means the cell for your silver ion that means we are talking in terms of the corresponding reduction reactions because all these cases will be reporting there is a natural convention or the standard convention is your reduction potential. So what will be reporting is your reduction potential, so this give rise to silver 0 is the typical reduction reactions.

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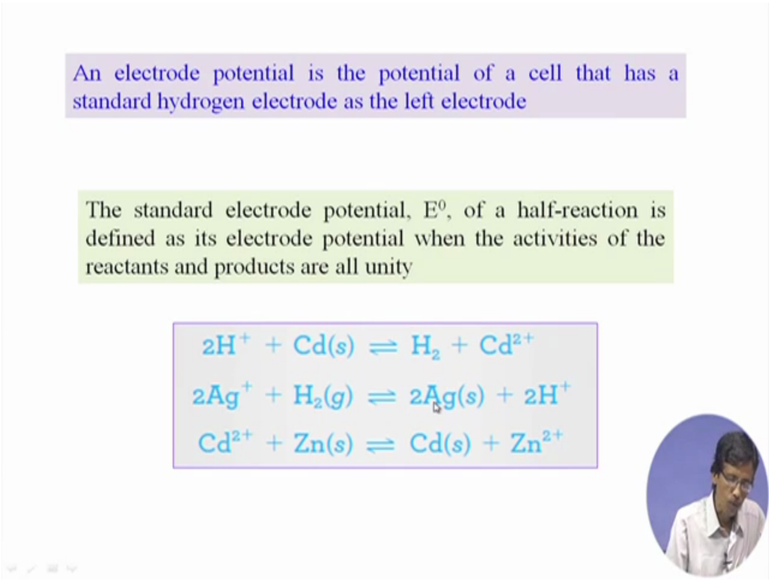

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So that reduction reaction will tell us and how we measure this E a 0 value is very simple that you connect it with a standard hydrogen electron as your left electrode, so the species whose E0 value will be measuring is on the right and the hydrogen electrode will be the left then we get the standard electrode potential as your E0. As a half reaction is defined as electrode potential when the activities of the reactants and products are all unity that means this hydrogen gas if we consider this as hydrogen electrode is at one atmospheric pressure.

So this has a activity of 1 and hydrogen gas is also bubbling on the electrodes platinum electrode surface having a potential of 1 atmosphere so we get these as activities of the reactants and products are all unity. So if we consider their concentrations in that particular term and the resulting E0 value what we will be getting over there is your E0 value for that particular half-cell reaction.

Now we will take 3 consecutive reactions or 3 reactions we will consider one is the reaction of acid with cadmium, solid cadmium that means the cadmium in the metallic state cadmium in this 0 state giving rise to the evolution of hydrogen and cadmium is going to cadmium 2 plus. Then the second reaction will be considering is as your silver ion which is reacting with H2 gas giving rise to silver as a silver solid or silver 0 or the metallic silver and hydrogen ion.

And third one is the reaction between cadmium and the cadmium ion the ionic state of cadmium that means the cadmium in solution and zinc is very similar to that of our thing what we are discussing from our previous class that the dipping copper rod or the copper spiral wire inside a corresponding silver solution will result in the corresponding to the position.

Similarly if we dip zinc rod in the cadmium solution, cadmium will be deposited and zinc will go into the solution. So in terms of electron transfer reaction and all are interconnected, hydrogen is connected to cadmium, the same hydrogen is connected to silver and then cadmium is again connected to zinc. So if you consider out of these 3 reactions that 4 species that is hydrogen, cadmium, silver and zinc and if we try to consider their relatives tendency for oxidation and reduction reactions that we should know very nicely from the reaction if the reaction goes from left to right.

Though we have written this in the reversible sign but what we are considering that it has a tendency that is why initially when these 2 are reacted that means cadmium is reacted with some acid, reaction will go to the right-hand side with the evolution of hydrogen that means cadmium is the stronger reducing agent which can reduce your hydrogen ion for hydrogen gas evolution.

So until and unless you have the corresponding evolution of these things and if we keep together we reach the corresponding concentration that the equilibrium concentration, when equilibrium concentration is reached H2 further react with cadmium 2 plus producing back your cadmium solid and the hydrogen ion but that is not happening when it is beyond or when it is away from your equilibrium situation.

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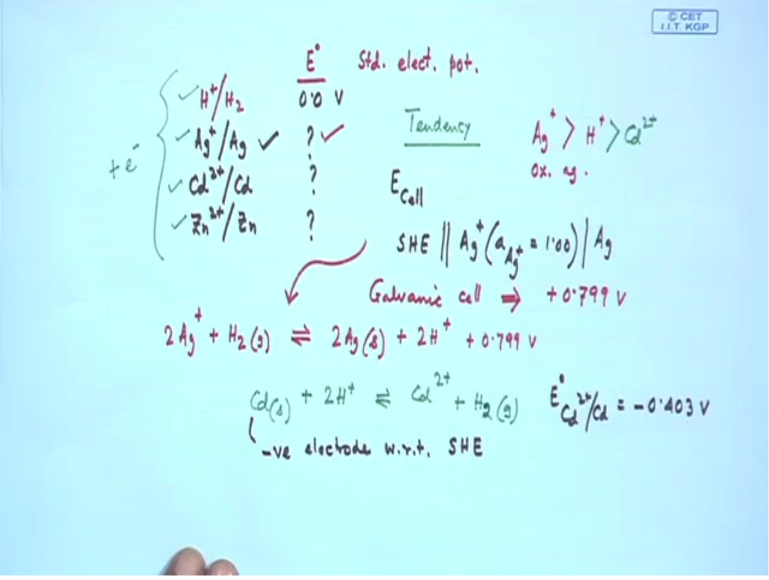

Similarly for the second reaction also when we start from the left we are beyond some equilibrium situation and as we proceed towards the equilibrium your reaction is in the reverse direction and third reaction is also in a similar fashion so if we try to go for this reactions so what we will be looking for basically, will be looking for something where will be considering for this half-cell reactions that means what should be your E 0 value for this which is very important to know and as we defined already by definition this is 0.0 volt versus (())(15:32).

So what will be the other case that means involvement of this, then we have the corresponding silver ion that means silver ion silver 0. Then we have cadmium 2 plus and cadmium and zinc 2 plus and zinc. So what are these values? So by looking at the reaction, we can have some good idea about the tendency that means if we consider these are the pairs on the left you have the species which can be reduced to the species which are on the right-hand side that means all 4 species the left can be reduced to all 4 species on the right.

So the electron transfer reaction or the tendency for some of these species that means if you consider these the cationic species altogether which will be accepting electron that means they are corresponding deduction potential values or in the reverse way if you consider the species on the right-hand side, their oxidising capability (())(16:44) tendency for accepting the electron. So this tendency for accepting electron by going from H plus to H2 AG plus to AG, CD 2 plus to CD and Zn 2 plus to Zn will tell us the corresponding potential in terms of its E0 values.

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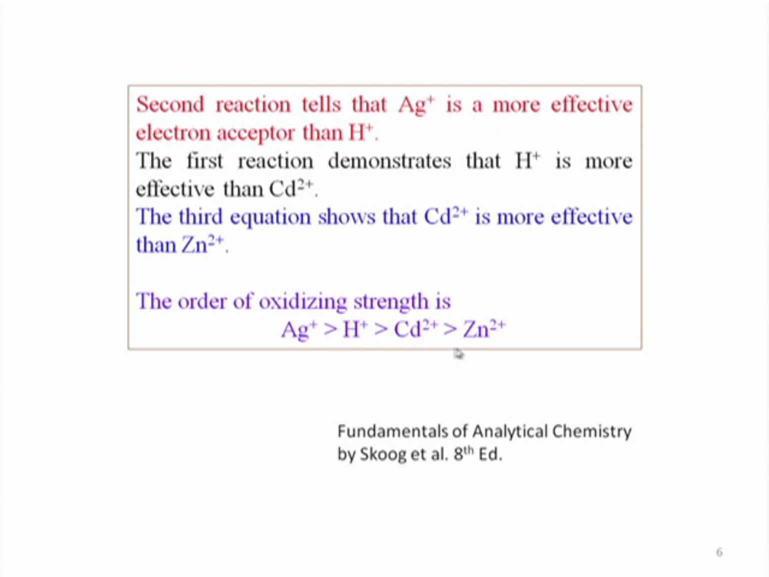

Second reaction tells that Ag^+ is a more effective electron acceptor than H^+.
The first reaction demonstrates that H^+ is more effective than Cd^{2+}.
The third equation shows that Cd^{2+} is more effective than Zn^{2+}.

The order of oxidizing strength is
$$Ag^+ > H^+ > Cd^{2+} > Zn^{2+}$$

Fundamentals of Analytical Chemistry
by Skoog et al. 8th Ed.

So by looking at these things some important information we can gather without knowing the quantitative magnitude of E0 values is that if we consider the first reaction, the first reaction what it tells this is the corresponding reaction of H plus with cadmium, metallic cadmium. So first reaction demonstrates that H plus is more effective than cadmium 2 plus in terms of its electronic acceptance. That means its corresponding electrons acceptance is that it can function as the corresponding oxidising agent that means we are talking in terms of the corresponding oxidising strength of all these species.

So what we are looking for we are looking for 4 species and their corresponding electron acceptance behaviour. If the electronic acceptance behaviour is considered in terms of its oxidising strength, we try to have some order for 4 different species. So the first reaction will tell us that H plus is more effective than cadmium 2 plus that means H plus will have more tendency to except electrons from cadmium and cadmium will go into this solution as cadmium 2 plus and H plus is the stronger oxidising agent to oxidise the cadmium 2 plus to cadmium 2, cadmium 0 to cadmium 2 plus.

So (())(18:38) that means acid is your oxidising agent. Why this acid is oxidising agent? That means in presence of cadmium the acid will be responsible for evolution of hydrogen. Similarly the second reaction tells us that your AG plus that means the silver ion is more effective electron accelerator than H plus. If we go for a competitive situation that means whether silver ion will accept electron or H plus will accept electron, it is the silver ion which is more effective in terms of its electron acceptance.

So we get the oxidising strength order as AG plus is greater than H plus and third equation shows that the cadmium 2 plus is more effective as oxidising agent than zinc 2 plus. That means if we consider the corresponding oxidising strength of cadmium 2 plus bivalent cadmium and bivalent zinc, we consider that anomie will be stronger oxidising agent compared to zinc 2 plus, so cadmium will be responsible for oxidation compared to your zinc 2 plus.

So if we arrange altogether we get this particular order where silver plus is greater than H plus is greater than cadmium 2 plus is greater than zinc 2 plus. So in a qualitative a what we can understand is that the tendency for electron transfer whether it is for oxidising or reducing we can arrange, so if we go for all these species because this this this and this we are talking about corresponding acceptance of electrons that means in minus they are accepting.

That means their oxidising strength we are talking in terms of their thing that how we get the corresponding is 0 values, so this particular thing is there in all standard books and has been taken from your analytical chemistry book of Skoog. So Skoog book will tell you that this particular qualitative information what we can gather arranging this particular cationic species.

Now we have considered these and this as your E0 is your standard electrode potential and that standard electrode potential you have to determine and how we determine that is very simple one that E cell we have to measure and with respect to your hydrogen potential, we have to measure the corresponding one for the second species, that means this one will go or its corresponding reduction that means silver one will go for your silver 0.

So this reduction at means the reduction potential or its corresponding reduction of silver ion to silver can be measured, if we consider the responding standard electric potential for this and by definition what we can do, standard hydrogen electrode not the corresponding normal hydrogen electrode is now standard hydrogen electrode if we attach that means this is the junction then shall with that of our silver ion concentration where the activity of silver ion will be equal to 1.00 or 1 and with silver.

So silver ion is dipped into the silver solution and if we connect the corresponding potential we get and when we almost open is not electrolytic cell but it is the galvanic cell, so the galvanic cell will record the corresponding potential which is plus 0.799 volt. So what we find that this particular one we have seen that compared to your hydrogen that means hydrogen is going for its reduction from hydrogen ion and silver is also going for a silver ion to silver 0.

So what we see that the corresponding oxidising strength of this that means AG one plus that means AG plus is stronger than your H plus this we have seen from our qualitative picture. So this will have the tendency that means the reduction potential of this we can consider so this is a different one so silver one plus is a stronger oxidising agent than your H plus.

So as oxidising agent silver ion is stronger than your H plus but when we are considering this in terms of its corresponding reduction in shall, we see that it is plus 0.799 volt that means it can function as of stronger oxidising agent that means the cationic version that means the cationic form of this species which are engaged in the half cell is the stronger oxidising agent because you have a corresponding positive potential.

So if we consider this as a measured potential the standard electrode potential for the silver half reaction is you can measure. For a particular reaction what we see that now is there for you have this will have more tendency will react with basically hydrogen gas giving rise to the corresponding reduction of silver as solid and 2H plus, so this is the corresponding cell reaction what we get and the measured potential what we will be getting, so now we write the corresponding potential is this one.

So what we get we get this particular entry, so this potential we get from there and we get this potential as your plus 0.799 volt, so this will be your corresponding potential for silver electrode. Similarly if we go for the corresponding cadmium electrodes, so cadmium is as the corresponding solid, so this corresponding one and this comparison we all know that cadmium as solid which can now react with this proton because cadmium on the other side because cadmium is here now.

So this corresponding combination of this things so the the corresponding electrochemical table what we know that the silver in one direction that means if silver is above H plus then cadmium will be below, so the reaction will be different one which is opposite to that of the silver reactions so we get this as the corresponding cadmium as cadmium 2 plus and hydrogen as the corresponding gas.

So what we find from there, the cadmium electrode is now a negative electrode with respect to the standard hydrogen electrode, so this will be now your negative electrode with respect to standard hydrogen electrode. So we get therefore the corresponding potential we can measure and the corresponding E0 value for this cadmium 2 plus 2 cadmium will be a negative potential 0.403 volt.

So you see the position of these 2 will immediately tell us that one is the positive potential and another is the negative potential. So this particular negative potential can be experimentally determine so that is the thing what we are trying to discuss over here is that how we can go for the corresponding tendency and we get this particular cadmium as the corresponding negative electrode.

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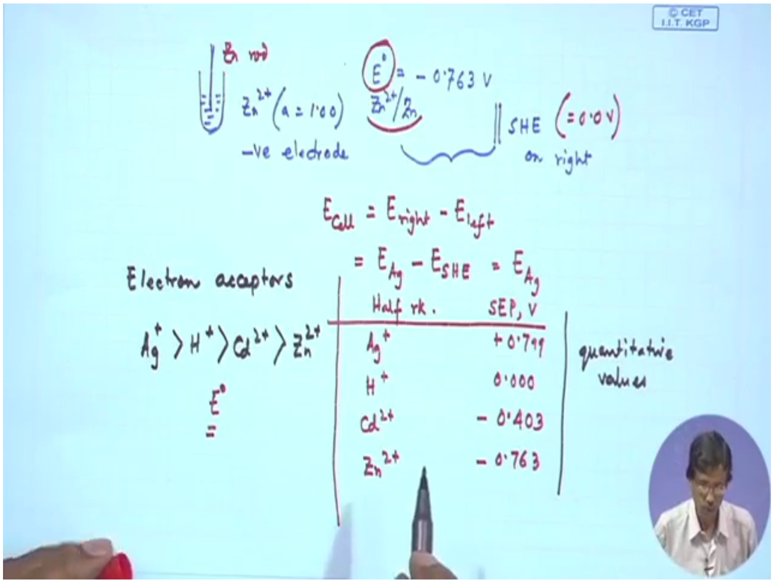

Zn rod

$Zn^{2+}(a = 1{\cdot}00)$ $\boxed{E^{\circ}_{Zn^{2+}/Zn}} = -0{\cdot}763$ V $\|$ SHE $(= 0{\cdot}0$ V$)$

-ve electrode

on right

$$E_{Cell} = E_{right} - E_{left}$$

$$= E_{Ag} - E_{SHE} = E_{Ag}$$

Electron acceptors

$Ag^{+} > H^{+} > Cd^{2+} > Zn^{2+}$

E°

Half rk.	SEP, V
Ag^{+}	$+0{\cdot}799$
H^{+}	$0{\cdot}000$
Cd^{2+}	$-0{\cdot}403$
Zn^{2+}	$-0{\cdot}763$

quantitative values

Similarly we get this particular one as the corresponding electrode for zinc window zinc electron is dipped inside a zinc solution, so zinc 2 again having activity one and this can develop a potential of minus 0.763 volt. Again this can be your negative electrode and this will be your the corresponding potential so the left hand electrode is paired with SHE now SHE will be on the right-hand side.

So what we have seen earlier is your SHE on the left, now your SHE will be on the right-hand side and your cadmium as well as the zinc electrode will be on the left. So what we get so this left hand electrode paired with the SHE on the right so SHE on right the corresponding combination of this and this will be your E0 for zinc 2 plus and zinc. So wherever the position is at the corresponding potential will be writing as a corresponding standard reduction potential and this reduction potential we see we consider that is more negative compared to you cadmium.

So this particular one we get for the total evaluation of E cell is therefore your E right minus E left. So far we are not considering so whether you have the SHE on the left or SHE on the right. So SHE values equal to 0.0 volt we are subtracting or we are just adding, so that will not give us the corresponding problem but when we get that for the silver we have seen at for silver the E0 for the silver electrodes is basically minus E of SHE because the standard hydrogen electrode was there in the left and silver electrode was on the right.

So that basically giving rise to the corresponding potential for the silver electrode, so that way we can generate all these things we can develop all these things and now as we have seen (())(29:53) qualitative picture you can have the corresponding half reaction and the standard electrode potential in volt so that we can arrange all of them that means the silver ion, the hydrogen ion, the cadmium 2 ion and zinc 2 plus ion and we start from here at means this is 0.799 volt, this is 0.000 volt, this is minus 0.403 volt and has been determine as this potential of minus 0.763 volt so it will be minus 0.763 volt.

So that also gives us the qualitative picture from the reaction itself what we have found out earlier is that the ordering, so you have this potential at means you have the 0.799 volt that means if we consider this ordering so this also tells us the same ordering what we have found out earlier at means the silver ion is greater than your proton is greater than cadmium 2 plus is greater than your zinc 2 plus.

So these are therefore the conformation and the quantitative values we get, so these are your quantitative values for standard electrode potential and these are universally true for applying this potential or any chemical reaction, so the related strength of the different ionic species as electronic acceptors that means oxidising agent in decreasing order that means zinc is the weakest and silver is the strongest.

So your ionic species are there that means these we are considering as their electron acceptors. So we see that starting from the very concept of your galvanic cell or the electrochemical cell then what we do that the same thing we are doing the dipping of a rod inside the solution is developing something where we basically get the corresponding values of E0 value.

So these are fundamentally levelled with the thing that if you have a standard electrode we can develop then the standard electrode potential we can generate where you have the corresponding zinc electrode zinc rod is dipped inside the zinc solution, so this is your zinc rod so that zinc rod is dipped inside the zinc solution of (())(32:41) activity is giving rise to some potential.

So these potentials are therefore very much useful to tell us that whether you are this particular zinc as the metallic zinc can function as a reducing agent that is why because zinc 2 plus is a weaker corresponding weaker oxidising agent. Similarly this particular silver ion will be the stronger oxidising agent having a potential value, standard electron potential value of 0.799 volt.

So qualitatively the order what we got earlier can also be established in terms of the corresponding different E0 values and all these things. So in our next class we will be trying to develop all these things based on some equation which is known as Nernst equation and from those Nernst equations where we can calculate out the different E0 value and how those E0 values will be useful to understand any electrochemical reactions that we will see. Thank you very much.