Course on Analytical Chemistry
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Module 9
Lecture No 41
Electrochemical Methods - I

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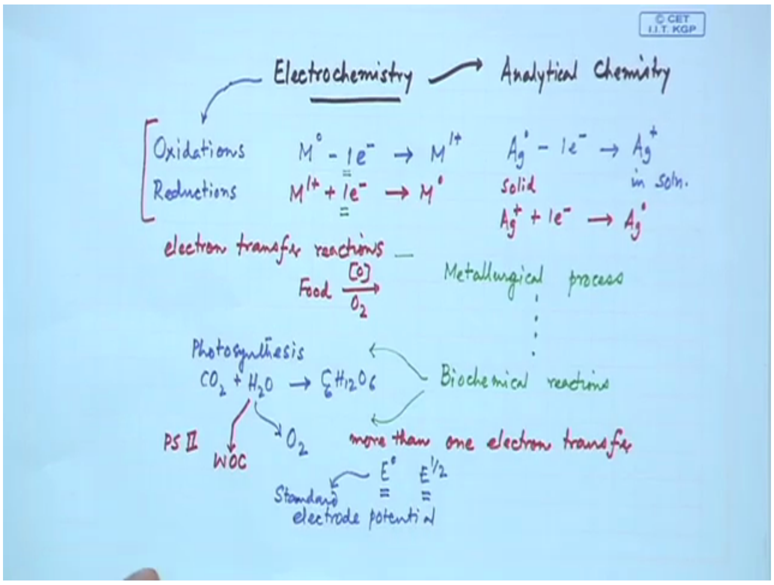

Hello welcome to this class or electrochemical studies where we will talk about the very basic thing what we deal while doing some chemical reactions is electrochemistry so because, so electrochemical studies we can apply that to study something which can be very much useful for analytical chemistry. So we can analyse something in terms of that electrochemical behaviour of a particular species and 2 things we know from our childhood basically that when we study something that means you can have for electron transfer reactions oxidations as well as reductions.

So how we can follow these 2 things and we all know that oxidation for a particular species if it is a metallic species metal is a 0 oxidation state, that means the atom of that particular metal if it loses one electron, it will go to M one plus that means in a positive metal ion in a particular case that means if we have silver in the 0 oxidation state losing one electron to go to silver ionic state in solution, so these 2 things that means what we see that a metallic species that means the atom of the metal and the ions in the solution, so this will be in the solid-state and this will be in the solution.

So we can study the electron transfer reactions, how? That means that particular species that means the silver in the metallic state can have some condense heat to lose its electrons to go to silver ion or is the reverse process that means if we have some species like again M, the same example if I can take plus one electron give you the metallic state M0, so here also that means the reverse one is true that means if you have the silver ion which can accept one electron to give you silver 0.

So this electron transfer reactions for oxidations and reductions we can study very nicely particularly what we will be interested to know about the corresponding number of electrons which can take place for this particular electron transfer reaction. So what we can consider that these 2 species, these are definitely chemical species but they are related in terms of either one electron gain or one electron loss, so they are some kind of chemical species which are related to some different oxidation state this is the oxidation state 0 and then the other case it is oxidation state one plus.

So these electron transfer reactions are very much useful starting from some metallurgical process to some biochemical reactions and 2 more important things what we can see for this biochemical reactions what we know from our school days that during photosynthesis we all know that we can fix the carbon dioxide from air into some useful molecules which is your carbohydrate, so fixation of your CO2 by water giving rise to your C6 H12O6 and at the same time what we find that this water molecule can undergo oxidation to release the oxygen into the atmosphere so this particular release is nothing but the corresponding oxidation of the water molecule and we consider that this is happening in photo system 2 where we have you water oxidation center WOC.

So if we have the water oxidation center where water can be oxidised to your O2 what we get as a benefit for your photosynthetic process and this removal of this oxygen we can consider that there will be a number of electron transfer reactions into it. Similarly if in other processthat means if we have this particular carbohydrate or any other food material in our hand, so food material we want to oxidise it, so again we get back the carbon dioxide and water but this particular food oxidation can take place in terms of its corresponding burning of the food material by oxygen and oxygen is a good acceptor in that particular case oxygen will except those electrons and ultimately will convert to water molecules.

So if we consider that these water oxidation can take place by giving rise to more number of electrons, so more than one basically one electron transfer and take place and now in terms of the silver ion and the any other ionic species and its corresponding elemental state, what we can consider is that we want to know the corresponding E0 value. E0 or sometimes we will consider it as E half when we directly measure by some procedure, the polarographic technique or cyclic voltammetry technique can give rise to the E half value for a redox couple or half-cell as we all know that due to one electron transfer either for the oxidation or the reduction we get one species and these 2 are related to some thermodynamic parameter is your corresponding electrode potential and 0 is for your corresponding standard state, so standard electrodes potential.

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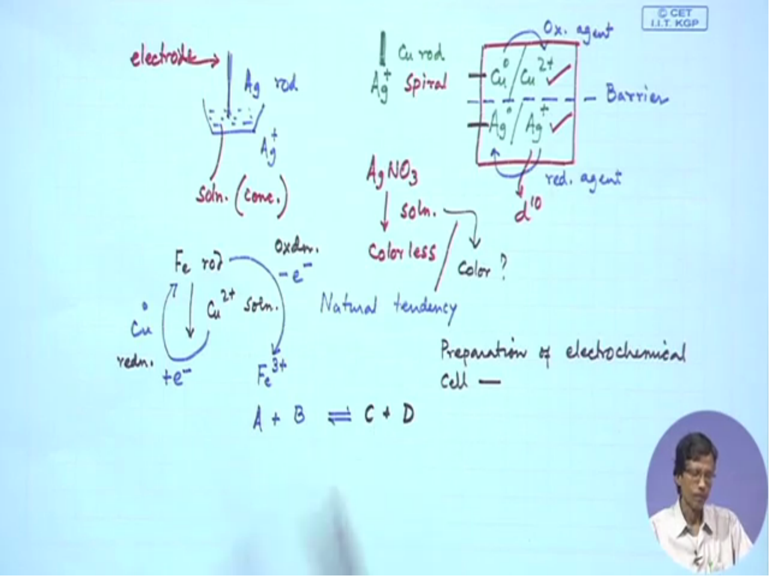

So now we have thisquestion that when we have this that means if we put this that means the solid thing that means if you have a silver rod and which can be immersed in a solution of its corresponding ion. That means these 2 are interrelated I that particular electron transfer reactions so this is the reduced form and this is the oxidised form or if we bring some other metal ion, what will happen whether you can have some competition for handling something that means if we have silver ion and if we dip of copper rod into it that means we are interested to couple between these half-cell reactions or corresponding oxidation and reduction reactions for say copper 0 and copper 2 plus and silver 0 and silver one plus.

So if we can consider that this particular things can take place and if one of the species can function as an oxidising agent and another species can function as a reducing agent, so these 2 can take place together and simultaneously the oxidation and reduction reactions can happen there in the solution state also, so we have this silver as a rod can consider these as the electrode and this is your solution, so when you have the electrode and which can be immersed in some solution so 2 things we can consider there that what sort of electrode do we have and what is the solution concentration if we are considering for copper ion or silver ion into the solution.

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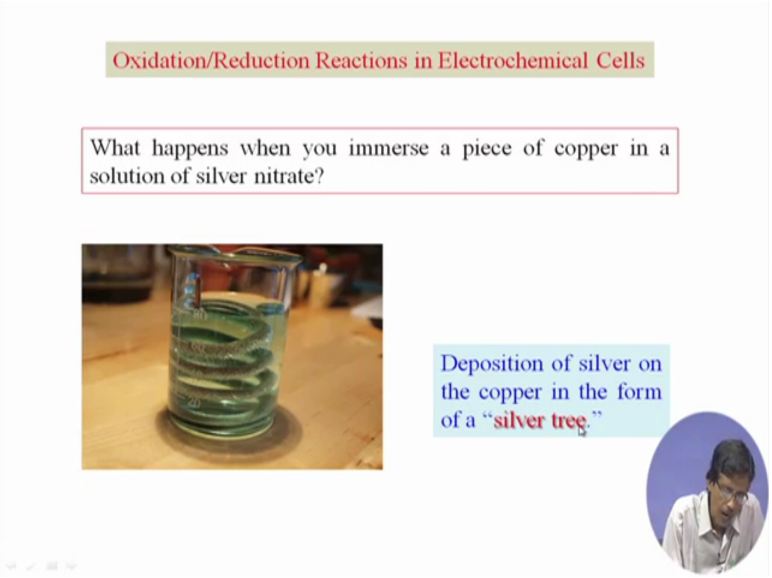

So ultimately these oxidation reduction reactions can give rise to something which we can consider as electrochemical cells, so how we can develop that particular electrochemical cells that we all know from our earlier childhood that a very simple consideration that if we immerse a piece of copper in a solution of silver nitrate, so that means what we are trying to do now as we are bringing copper as the copper electrode and silver nitrate as a solution that means silver ion in the solution.

So what should be the corresponding tendency for this copper electrode and the silver ion to react together such that this thing and happen, so we have the beaker and the beaker has a corresponding solution or some color is there so but the rod is immersed as a (())(11:11) copper that means the spiral thing is your corresponding copper rod and we have a silver nitrate solution and as we all know that the corresponding silver nitrate if we have and its solution which is colourless because silver as the silver one plus we all know that like your copper one it is not copper 2, so is a detained system and is a colourless species, so what we are doing we are dipping a spiral copper rod which is spiral inside a colourless silver nitrate solution, so what we expect?

We expect that whether there is some reaction the copper rod or some reaction is happening for the solution also, so will there be any color change for this particular solution, so solution was colourless. So whether that solution is still remains as colourless or some color is being developed that we can see, so if we very clearly see this picture, what we find that is not a very colourless solution, so it is slightly greener solution is there and the rod is also not looks like to a typical copper rod.

This is the copper rod red brown color of the copper rod is there, so what is happening that this bright white metallic silver tree on this particular copper rod which is red brown in color is due to the depositions of silver on this particular rod from the solution. So silver ions are getting deposited on the copper rod as small silver metallic particle and in the reverse way some of the copper rod is going for dissolution giving rise to the corresponding colouration within the solution.

So that gives rise to a very famous reaction that we get depositions of silver on the copper rod the copper spiral tube in the form of a silver tree. So that is the most important reaction always we can see if we have a over rod or copper wire if we dip inside a silver a silver solution we get this particular type of silver tree reaction. So same thing also happens to terms of the corresponding iron rod when we dip into a copper 2 plus solution, so what happens there that in a similar way that your copper will be deposited on this rod as copper 0 like your silver 0, so your rod it can be rusted also so rust can be covered with a fine layer of metallic copper on it and the same time rod will be losing some thing as its corresponding iron as the ferrous or the ferric iron.

So there is a natural tendency what we see for these 2 reactions, the reaction between copper and silver and copper and iron is that the iron has typical density to be oxidised because this is losing electrons and copper has a typical tendency to gain electrons, so when it loses electrons we can consider and we can say that this is the corresponding oxidation so iron rod has a natural tendency for oxidation in the solution and this copper same time can except that particular electron for its reduction and the corresponding deposition on the iron rod.

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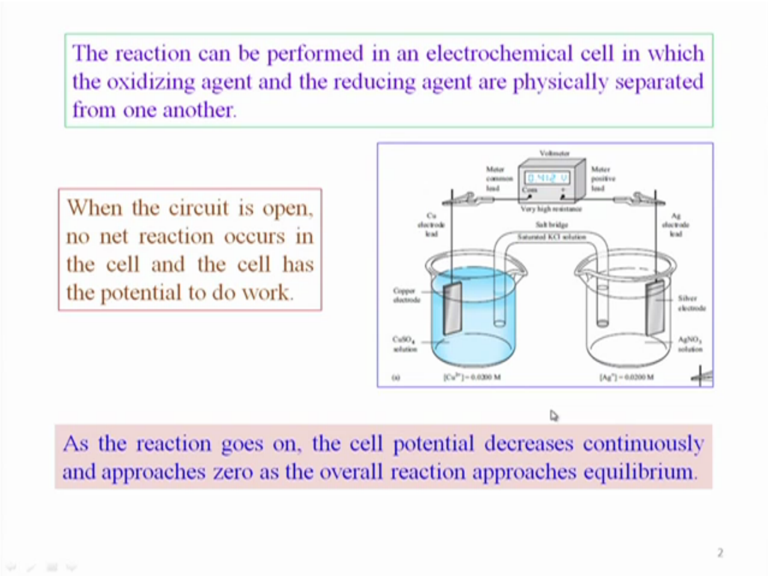

So the silver tree as well as the copper depositions on the iron material can give rise to something we find that a particular reaction can be perform, so a chemical reaction terms of electron transfer we are considering and will be considering that is as a electrochemical cell because the electron transfer is taking place within a cell because 2 of them are confined within a cell like that of your biological cell, so we can consider it that you have developed electrochemical cell in which the oxidising agent and reducing agents are physically separated from each other.

So we will be able to get a particular type of electrochemical cell, so how toarrange or how to prepare preparation of electrochemical cell, how we can make that? So if we have the copper rod as well as the silver rod and 2 solutions, so we have seen that during the reaction that means your corresponding depositions silver on the copper rod but here if you consider that copper rod will be dipped into the copper solution and silver rod will be dipped into the silver solution and we will try to indicate try to evaluate that what should be the natural tendency for this copper 0 or the silver 0 or its oxidation and reduction reactions.

So we can have the responding cell and if we go for a corresponding barrier, so one barrier we can make so if we have a barrier for these 2 solutions, so oxidising agent and the reducing agent because some we have already seen that some will be oxidising and some will be producing. Copper is oxidising to copper 2 plus, so this is the species which is responsible for your oxidation and silver ion is getting deposited as silver 0, so your oxidising agent is this one, so this is your oxidising agent and this is your reducing agent and we separate them by a barrier such that these 2 solutions particularly this copper 2 solution and the silver one solution should not mix up, so when these 2 reagents or these 2 agents are physically separated from each other, we get a construction of a corresponding electrochemical cell.

So now we consider here is that what is the corresponding driving force that particular reaction, so now we have the copper electrode, so this copper electrode lead we consider, so this is the copper strip and is connected by a wire and which has been dipped into a copper solution so the copper electrode dipped into the copper sulphate solution, so this give rise to the corresponding copper 2 plus solution and the copper electrode is dipped inside that and what we consider at the corresponding concentration of this copper 2 plus because this concentration has some effect this particular type of electron transfer reaction.

So is .02 molar solution of copper 2 and so copper electrons is dipped into a (())(19:12) copper solution of strength of 0.02 molar. Similarly on the right-hand side what we do, we dothe same silver electrode so from the silver plate or silver strip, so this silver electrode is dipped into the colourless solution of silver iron of same strain that means .02 molar solution and we connect this in terms of a salt bridge containing some saturated production chloride solution because that will be required for the direction of the electron transfer from one direction to the other.

If electrons moving into this particular direction, so in the opposite direction that K plus and CL minus will move. So when we have a corresponding connectivity in terms of very high resistance meter so voltmeter is then connected and you have a meter (())(20:09) and meter positive lead is connected, so we get some measurement of your potential so in open circuit when you are not drawing any current or we are not putting any current to this particular system for electrolysis, we will be able to record some amount of voltage within a voltmeter.

So voltmeter can measure a potential of 0.412 volt, so measurement of that particular volt is important, when we connect these 2 together that means you can generate or we can develop electrochemical cell giving rise to a corresponding potential which is equal to 0.412 volt. So we have developedelectrochemical cell at particular electrochemical cellwill be useful to measure some potential and that potential will be useful to tell us that which way the electron can transfer from copper solution to copper or silver solution to silver or the reverse. So when the circuit is open at means we are not drawing any current that means no net reaction occurs in the cell and cell has the potential to work.

That means if the circuit is open, we do not allow any reaction to occur as particular cell electrochemical cell has a potential to work or in other words it can rise to the corresponding energy in terms of its electrical energy do some work. So it has the potential that is why the electrode potential what we consider that we have to measure the corresponding electrode potential for the individual half-cell reactions. So when we connect left half of the cell to that of our right half of the cell and for the individual part means the left half as well as the right half have some standard electrode potential and when we add up that particular standard electrode potential we get the corresponding potential for the cell which is equal to e-cell for that particular type.

So as the reaction goes on, so we allow the reaction to go on, the cell potential decreases continuously and approaches 0 as the overall reaction approaches equilibrium, so what we consider, we know that a particular reaction what we see at a particular reaction we can have that A in terms of a very simple reaction not in terms of any electron transfer reaction but only the reaction of A and B giving rise to C+D and when we write a equilibrium sign we consider at any point of time A and B will react to give you C and D another same time the reverse is also go true that means C and D also will react to give you A and B back, but when we consider some kind of electron transfer reaction in this fashion, if the system has reach the equilibrium so the cell will not have any initial to work.

That means we cannot draw any current from that particular electrochemical cell because the thing has reach to an equilibrium. So during this particular process when we get this means something will happen and the concentration of this solutions will change and ultimately those concentrations will be responsible for giving rise to your decrease in E0 value for the half cell. Ultimately both these 2 will be equal and we do not get any potential to be developed or potential to be drawn from the cell when it approaches to a equilibrium situation, okay.

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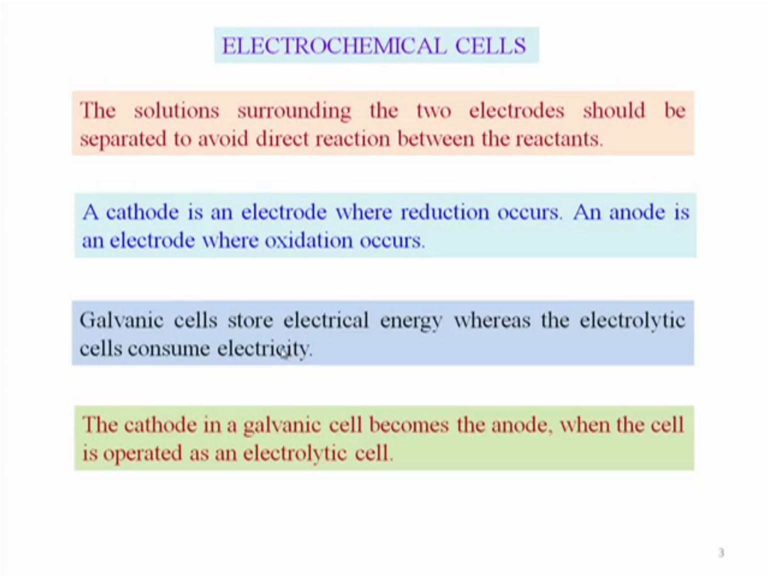

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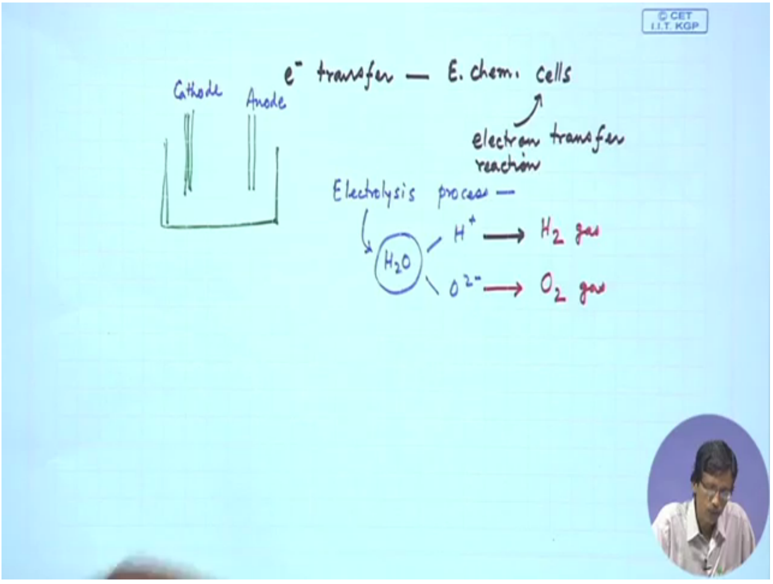

So what we find therefor that how we can develop some kind of electrochemical cells, so in this way it can have some cell can be considered as a typical electrochemical cell. So what we see that we can have the electron transfer within something that means within some beaker or 2 beaker connected by a salt bridge and we should be able to develop some electrochemical cells that means electron transfer reaction and take place within that particular cell, so electron transfer reaction will happen within that particular cell and we will consider that as your electrochemical cell.

So what we have the solution surrounding these 2 electrodes should be separated to avoid direct reaction between the reactant that we have seen, that we must have a barrier in there and that particular barrier should tell us that whether we have the direct reaction in the reactants what we see that, when we insert or when we immerse copper rod within the silver solution but when you separate these that means a cathode will you will get, so what is that particular cathode, so cathode will be there for you have like a electrode where the reduction occurs.

So if we have this 2 electrodes and we find that can have a natural tendency to lose electron and to gain electrode, so where we have the corresponding cathode (())(25:53) where the reduction occurs, so if we find that electron transfer is taking place and at the electrode, when electrons are being excepted, so reduction will occur and the reverse is true for the definition for anode, the anode is an electrode where oxidation occurs. So what we get, we get a galvanic cell, so by definition we will be able to get a galvanic cell which can store electrical energy, so we can draw electrical energy from that particular galvanic cell.

Whereas theelectrolytic cell consumes electricity, so we can have some cell, so 2 types of electrochemical cells we can have, so when we have the galvanic cell due to the natural tendency of its oxidation and reduction reactions of the cathodes and the anode. So if we have a cathode and the anode, so due to that particular tendency of this cathode and anode for oxidation and the reduction reaction respectively.

So we get a natural tendency and when we connect them, we can get some electrical energy to be drawn, but the reverse thing that we know that a typical electrolysis process how it happens that we all know, that electrolysis for water we can do because we know that this has H plus and O2 minus, so they have some tendency to the oxidised and reduced. So when it basically accepts electron that means the reduction of this H plus, so reduction of this H plus can give rise to the corresponding evolution of hydrogen and losing of electron from O2 minus species will give rise to the evolution of oxygen.

So we know that the electrolysis of that particular water can give rise to the hydrogen as hydrogen gas and oxygen as the corresponding oxygen gas but in this particular case we put the electron in to the system that means we go for, we apply electrical energy for that particular process. So we have 2 use this particular electrolysis reaction where the electrolytic cell and consume electricity means if we go for the corresponding oxidation of water molecule, what we do? We put the electricity and we can go for the electrolysis of water or the evolution of hydrogen and oxygen respectively.

So in this particular thing in terms of its corresponding definition the cathode in a galvanic cell now becomes an anode,so if the galvanic cell which is storing electrical energy and by definition what we are talking about a cathode where the reduction occur but a cathode in a galvanic cell becomes anode when the same is operated as an electrolytic cell.

So these definitions of anode and cathode will be completely different when we talk in terms of the galvanic cell as well as the corresponding cell where the corresponding electricity we can give go for the corresponding electrolysis. So electrochemical cells will be of 2 types and we should be very much careful about its corresponding type of whether you have a cathode or the anode and whether we draw electrical energy or whether we put electrical energy for electrolysis reactions, okay. Thank you very much.