

**Indian Institute of Technology Kanpur**

**NP-TEL  
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On  
Technology Enhanced Learning**

**Course Title**

**Environmental Degradation of Materials**

**Lecture – 02**

**Broad Subject: Forms of Degradation,  
Thermodynamics of Corrosion**

**By**

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So today is the second lecture on this course Environmental Degradation of Materials. Here I will be talking about Thermodynamics of, thermodynamics understanding behind environmental degradation of materials, mainly the corrosion aspect of degradation.

Now in the last lecture we have seen that it's very important to study the mechanism of environmental degradation, the reasons because it involves lot of money. Degradation in the sense its loss of material, loss of properties, loss of appearance, and all this loss finally lead to a lot of money loss associated with this Environmental Degradation of Materials. So we need to have a greater look at this subject.

Now in the last class we have also seen what are the core structures and then we have already started the electrochemical aspect of material degradation, and we have seen that there are different forms, and those forms are associated with the forms, there are many factors which decides those forms of degradation. For example one is oxidation, one is corrosion, and corrosion can also be divided into several parts, for example aqueous corrosion, you have tri corrosion, so aqueous means it's aqua means water so the corrosion involves H<sub>2</sub>O, okay, that is basically aqueous corrosion.

Now we have also seen that, in the core structure also we have seen that there are microstructure related forms, environmental related forms, stress-related forms, even in geometry also tries to affect the corrosion, so let us have a small brief on the forms of corrosion, let's say in your application, in actual situation you can have a material now after some time, after some time let's say one year you were seeing that the material, if it is exposed to the environment you will see that the material has lost some of the material from the outer surface, okay, this the hatch part is already lost or dissolved or eroded due to some reason. Now you see that the most of the case in all the sections if you take a section you will see that the loss of material is happening uniformly throughout the cross section. Now this is, you can call it as

uniform degradation, uniform degradation or if it is corrosion than uniform corrosion. Then you can also have let say you are having one material M1, another material M2, okay, then if you expose this material, this combination of this two material if you exposed it to a solution, okay, then you can have depending on the electrochemical characteristics of M1 and M2 in that solution either M1 can dissolve preferentially or M2 can dissolve preferentially, now that is basically happening because of this coupling of these two different materials and this is termed as galvanic corrosion.

Okay, now you have another thing let say you have a material you have a stainless steel, SS steel, now you have a rubber band, you have a rubber band, now you put that rubber band in acid media you will see that after some time this will be into two hubs, it will be broken into two hubs, it will be broken into two hubs, now you will see why this is happening, because if you see carefully the rubber band is making a crevice in this region, and now corrosion is very aggravated, very much aggravated or the rate of corrosion is very fast compared to the other surface very fast in this junk, so in this junk preferentially the corrosion will occur or the material loss will occur and then finally you have, and the rubber band also is exerting some pressure than because of this two combination it can go break into two pieces because you are having a corrosion, preferential corrosion that means a sort of corrosion is extending into the material and then you have the stress, you have also the stress factor associated with a rubber band stretching, so now you can have a breaking of this material into two hubs, this is due to crevice formation we can call it as crevice corrosion.

Now you can also have let say if you take a brass, if you take a brass, copper 30% zinc alloy, this alloy if you expose it to by potable water what you will see that after some time let say one year or so you will see that the surface is coming reddish in color, this reddishness, this is reddish, red color is coming, this red color is coming because of the print you will see, if you if you study that the top surface you will see that a copper is depositing on the surface. Now if you carefully again observe you will see that in this region, in this region the zinc percentage goes down and copper percentage goes up if you compare the concentration 70:30, that mean 70% copper and 30% zinc and so copper 30%, from 70% it can go to 90%, from 30% zinc it can go down to 10%, so that means you see preferentially zinc is coming out and copper is staying back, this is a sort of dealloying in initially you have mixed copper and zinc to form an alloy, now you are exposing into a solution or aqueous media, now because of this effect zinc is coming out and copper is staying back so it's a sort of preferential dissolution of zinc from the alloy, that's why it is called dealloying or dezincification.

So just I'm giving a briefing of what are the forms that are available, okay, then you can also have PT, now PT you have a stainless steel okay also let us not consider the stainless steel example, let us stick a mild steel, if you take it, if you etch it in nital solution 5% nital solution for a longer period, for a longer period if you etch it, you will see that in addition to the grain boundary you will see up there are some etch pits, there are some black regions on the grain, in the region of grain so that black regions are basically nothing but etch pits and these etch pits are forming because of a sort of corrosion called pitting corrosion. Fine, now you have, that means in some region the dissolution rate was very fast, but other regions there is a sort of uniform corrosion, so if you see this in cross sectional, if you take a cross section now if you see let say you have cut this portion you have sliced it out, okay, now if you check it then you

can see that this region this if you see from this direction you will see the crack has, this pit has moved like this, so that means you have no, almost no corrosion on this regions or uniform corrosion but the attack is very severe in this localized region, this is called pits, okay, and its associated with the pitting corrosion.

Now you can have also stress corrosion, that the stress part I will come later, but let us see what would be the effect of velocity. Now the velocity part I have discussed in the last lecture, so if you have a pipe and then you are having a flow of fluid or the water, now if you have a sharp corner, or sharp bend in the pipeline then you can have a sort of corrosion which is the combined action of impinging force for because of water which is mixed with dirt material and that is associated with, that is basically nothing but erosion corrosion.

Now you can also have cavitation, cavitation also I have told a little bit, now you have a flat surface, you have a water bubble if it breaks then it exerts a lot of pressure on the material, so this material locally it will get deformed, if it gets deformed that means the outside the surrounding region is not deformed, the deformed region is high energy region, and high energy region is always susceptible for corrosion attack, so this is called cavitation, because of bubble formation and it's breaking. Now you can also have fretting, for example the valuing one example is that is the railway material let say this is a rail, and this is fastened with one fastened with the people, okay. Now if you see that when rail is coming it's getting heated up, now when rail, one train is coming it's getting heated up and it's expanding, when train is moving out that means it again cools down it again contracts, and this contraction and expansion at locally is happening so that local portion is having a fitting action, a very small alternate of alternate movement of these regions, so that force and it's also under pressure, okay, under pressure and then this pressure as well as this fitting action this alternate motion it gives rise to a sort of wear, okay.

And now if you have, when it, this friction is happening that friction leads to high temperature, heat locally the heat is increasing and it's also in the environment you have oxygen so if you have oxygen if the local temperature increases, if the material in this region can get oxidized and this oxide was very brittle in nature so oxide if you have a fitting action so oxide will move out so it will expose a fresh material. Now fresh material again would get oxidized and that oxidation would lead to again the breaking of that oxide scale and then again fresh material is exposing, so this is happening continuously, so you are having continuous loss of material, so it's called fretting corrosion. Fretting corrosion, now you have also action of stress, one is stress corrosion, stress corrosion let's say one material, one component is under static tensile stress, static tensile stress, statics tensile stress now this stress in the normal component, in the design component if it, it should be designed, the design stress should be lower than the yield stress of this material.

Now it's lower than the yield stress of the material so we cannot expect that the material would deform, because the lower stress I have already calculated on the basis of designs stress. Now in this condition if you have a corrosive environment, that corrosive environment would lead to corrosion so let say in this region some corrosion is happening, and this is under root, okay. Now gradually you will see the cross section is going down, cross section is going down gradually the cross section is thickening, it is thinning down, now if it is thinning down, now

this is depending on the because on the basis of say design stress you have calculated much load it can carry, now the load is fixed, load is fixed but gradually we will see since the cross section is lowering down or the decreasing so you are going to increase the stress at this region, okay if you increase the stress once it goes it can go beyond the fracture stress and that fracture stress then it can break, so it's a sort of static tensile stress you are having and because of corrosion action you are having a failure of that material in the form of fracture, so this is called a kind of stress corrosion cracking and stress corrosion cracking all as involved statics tensile stress, this is stress corrosion cracking.

Now that means it involves stress as well as corrosion. Now you can have corrosion fatigue, let say a material which is on that material you have alternate stress, compressive, tensile compressive strength side, that is a cyclic stress is given to that material, now that material if it is associated with the corrosion then this tense this fatigue factor as well as corrosion factor both can lead to a corrosion fatigue or a material failure. Now you can also have hydrogen induced cracking, now last class or last lecture also I have said that hydrogen can lead to embrittlement in the material, if it in brittles the material that means it becomes very brittle in nature, so there is a possibility the material can fail by cracking, so these are the forms which are associated with the micro structures. Important factor is micro structures, second is environment, third is stress, fine, these are the components, major components, then you can also have associated with this composition, then you can have since this stress is acting as a mechanical action, now we have again seeing that there could be a soft factor there could be soft issues for example you can have design, you can have design related things, that is another important factor, there are several factors like this, okay, those will guide what sort of form it is.

Now this part I am taking, I am just briefing because this part will be taken care of by Dr. Chaudhary who is from IIT Roorkee, okay, so I am just briefing this, just to give some example that what are the examples of forms of corrosion.

Now coming to the thermodynamics part, let us see what we have seen in the last lecture. In the last lecture we have started corrosion, now when we define corrosion we have introduced few key words, one is loss of material, loss of materials, second one is, now in this case you can also have loss of performance, let say you don't have any direct loss of materials, but still you can have loss of performance let say you are wearing some, let say silver ornaments, silver ornaments if you find that some after some time with the use it becomes little dark in color, it becomes dark in color because the silver ornament is meant for ascetics, okay, if it becomes dark then it will not show, it will not be beautiful to wear that dark silver wear, silver ornaments so that means what is that darkness? Because silver sulphide is forming, this is also a kind of corrosion, but that one is not, we are not getting any loss of material rather we are losing the surface appearance or the aesthetic part is becoming the silver is becoming dull in nature, so that is loss of performance is another important factor.

Now you can also have loss of properties. Loss of properties, because of either loss of materials or it can be mechanical, let say you are having stress corrosion cracking this is a kind of mechanical factor, okay mechanical issues or let's say the material is failing without giving any signal that is a mechanical failure or then you can have chemical effect okay, that is loss of

properties the chemical properties will get lost, there will be loss in chemical properties, there can be loss in electrical properties, fine so that means this is a loss of materials.

Now another key word was, second key word was engineering material, so corrosion is a loss of materials as well as degradation in useful properties of an engineering material because we are not bothering about anything which is not in practical use, so the material should be in practical use at the same time we should see that what sort of corrosion is happening and then we should plan accordingly that what sort of protection mechanism we can think of, but before that we should understand what sort of material is this, this should be engineering material. Now the most important part associated with corrosion is there is one more key word which is nothing but electrochemical, electrochemical reaction with environment. Now this is a very important part, this loss of material or rather loss of engineering material is happening because of electrochemical reaction with its environment.

Now, so now let me concentrate on this part, let us understand what do you mean by electrochemical reaction? Last lecture I have just shown one example that iron corrosion, iron going to  $Fe^{++}$ ,  $+2e$  and this two electron is getting consumed by this reaction, this reaction and this one, and this one we are combining and forming  $Fe(OH)_2$ . Now that time we have seen that any this process it involves exchange of electrons. Exchange of electrons between what this iron is leaving two electrons and giving rise to iron ion,  $Fe^{++}$  ion, then these two ion will get consumed by this reaction form  $OH^-$  ion, so it's a kind of transmitter of electron from one place to another, this thing can happen on our material surface. Here it's happening on iron surface, iron surface that means what is happening, iron is going as  $Fe^{++}$ , so now it's leaving two electron, this two electron is coming here, okay, now this two electron is combining with oxygen  $H_2 + 4e$  going to  $OH^-$ , so that means in order to get four electron you have to have  $2Fe^{++}$  formation another  $2e$  so combination of these two process it gives rise to four electrons, this four electrons will be comes in by this reaction. Now we have also seen that this is called anodic reaction, this is called cathodic reaction. Now that means any process which involves transfer of electrons as well as that electron if somebody is leaving some electron that electron should be consumed because the charge cannot remain as it is, there must be a charge balance.

Now, if you see I have also said in the last lecture that oxidation reaction with  $M$ , it can also form  $MO$ , this is also a sort of corrosion, but I will come to that, why it can be considered as corrosion if we understand what is the electro chemical nature of corrosion, that means from this it's very clear that there should be one or two anodic reaction and one or two multiple cathodic reactions depending on the situation, actual situation but there should be balance in charges, so no charge will should remain free.

Now if you consider some examples, let us see some examples this is one example, let us see one more example, let's say you know, solution in a beaker you have  $HCl$  which is deaerated, deaerated means it doesn't contain any dissolved oxygen and it is also very, very pure, very pure means it doesn't contain any other species except  $HCl$ . In  $HCl$  sometime can be contaminated with  $Fe^{3+}$ ,  $Fe^{+3}$  this ion can be there in a  $HCl$ , so this is a sort of impurity in this medium, so we don't have this in this. Now I have put a zinc rod here, if you put a zinc rod you will see that you take out that zinc rod after some time you will see that zinc has put it, because there would be weight loss in a zinc, and if you check this media you will see that there is a  $Zn^{++}$  ion,

initially there was no ion of  $Zn^{++}$ , but now you will see there is a  $Zn^{++}$  ion after some time, what is happening now, let us investigate this part, now if you blow it up the small region here, let me blow it up, this region I have blown it up, now here since zinc is coming out, so zinc is coming out  $Zn^{++}$ , now from zinc it is forming, now if you form  $Zn^{++}$  there should be two extra electrons that is released by zinc atom, so that two electron will stay in the metal, now these two electrons are extra so it has to be consumed, who will consume that? Now at the same time another observation you can see that when you put zinc in this HCL media you will see that there are some bubble formation on this surface and then this bubble will grow and then it will come out as in the form of gas, if you analyze this gas you will see that this is nothing but  $H_2$  hydrogen gas. Now that is hydrogen gas is forming, how would you expect hydrogen gas formation? Now what is the source of hydrogen here? The source of hydrogen here is HCL if you break it you will find that there are two things  $H^+$  and chlorine ion. Now, since hydrogen is forming, that means must be  $H^+$  ion is the source of hydrogen, so  $H^+$  if you would like to go to hydrogen how would you form  $2H^+$  ion can combine two electron go to H molecule, so this molecule will move up.

So now you see that means this electron, who is consuming that two electron? It is consumed by hydrogen ion, so now this electron is coming here and then hydrogen ion, two hydrogen ion they are combining these two electron forming  $H_2$ . Now you see what are those two reactions which involve electron? One is zinc which is forming zinc ion leaving two electron, and another one is two hydrogen ions are combining this two electron forming  $H_2$  ion, now you see which one is electron accepting reaction, electron accepting reaction is this an electron which is being left out by metal ion that is, this is here you are basically leaving two electron from the zinc atom, so this is, what is this process, this process is nothing but anodic, this process is cathodic. Now what is the thumb rule? Okay, the thumb rule is or how do you judge which process is anodic and which process is cathodic, if some process takes electron or combines electron that is called cathodic, if something which leaves electron that reaction is called anodic.

Now this is cathodic, this is anodic, so here this is anodic, this is cathodic, now the process on the surface where this process occurs, cathodic reaction occurs that is called cathode. And this process where it occurs that is called anode. Now there would be confusion, I am coming to that – let say you have one cell, galvanic cell where you have zinc rod and copper rod, this is zinc rod, copper rod, you have a separator through which ions can transfer, but mass cannot transfer, now you connect this to, what will you see and here it is zinc sulfate solution, and here it is copper sulfate solution. Now if you see, if you put ammeter here you will say that current is flowing, now current will flow from this to this direction. Fine, now if current is flowing in this direction and also you will see some changes here you will see that copper is depositing here and zinc is corroding in this region, so zinc is coming out as  $Zn^{++}$  and copper deposition, and what is the source of copper, from which deposit can take place? That is the  $Cu^{++}$  ion, so  $Cu^{++}$  it combines two electron, it has to combine two electrons in order to have deposition, so it goes to Cu that -- on this and zinc can from its forming from zinc metal so zinc metal is gradually coming to the solution, by that way it leaves electron, and it leaves electron, so this electron who will consume? This process will consume, okay, so if this process consumes that electron what is the, where the cathodic reaction is taking place? This surface cathodic reaction is taking place, so this is cathode, and this is anode, this is perfectly fine.

Now let me see what happens if you have a system where you have two electrode, okay, now you are electrolyzing  $\text{H}_2\text{O}$ , when you electrolyze  $\text{H}_2\text{O}$ , what you do, you send electrical energy and then you are getting chemical reaction, the chemical reaction in one case you will form  $\text{H}_2$ , and one case you will form  $\text{O}_2$ . Which surface do you think you will get  $\text{H}_2$ , this is  $\text{H}_2\text{O}$ , and if  $\text{H}_2\text{O}$  that means oxygen should come from this,  $\text{H}_2\text{O}$  will break down in the form of  $\text{H}^+$   $\text{OH}^-$ . Now  $\text{H}^+$  has to combine with one electron from hydrogen atom and then again it should combine with another hydrogen atom which is though, so which is basically coming from the electron acceptance reaction so then combines it and then forms hydrogen molecule. Now if it forms hydrogen molecule that means  $\text{H}^+$  plus electron hydrogen another reaction going to  $\text{H}_2$ , so combined  $\text{H}_2$  now this is a cathodic process.

Now you are supplying current, which side do you think, now if you see the polarity, this side is connected to a negative terminal if you think this is a negative terminal so current will flow from which side to what site? So current will flow always we know that from positive to negative terminal. Now if you want to see which direction electron is flowing? Electron flows opposite to the current flow, so that means the electron will flow from this end to this end. So which one is cathode here, now your cathodic reaction, this electron is coming here, so this electron will be taken care of by this reaction and this is the cathodic reaction, so this electrode is cathode. Now if this electrode is cathode the other reaction will occur there and there oxygen will generate.

Now here this is negative terminal, because it's connected with a negative terminal, here it is positive terminal because it is connected with positive terminal, now you see here the cathode is negative terminal and anode is, the other side is anode, anode is positive terminal. Now come back to again here, here which one is negative terminal? Negative terminal should be that part which has excess electron. Where we have excess electron? Here you have excess electron, so this must be negative terminal. Now at this negative terminal what process is taking place? You are having anodic reaction, fine, here the negative terminal you are having cathodic reaction, here you are having anodic reaction, so if you go by the sign of that electrode then you are lost, better you should, what should be the cathode or anode, here it's anode, anode it becomes negative, here anode it becomes positive, here cathode becomes positive, here it becomes negative, so if you see from this negative or positive sign then you are lost, rather you should see which side this electron acceptance reaction is taking place and which side electron giving a reaction is taking place. Always this is convention, wherever you find electron accepting reaction that will always be cathode, irrespective of the sign, whether it's a negative or positive it doesn't matter, if electron accepting reaction is taking place on some surface, this is cathode.

Now you have, this is one and another process where electron is left out that is anode. Now here in case of galvanic cell, this is anode, this is cathode, because here we have positive, where you have cathodic reaction, here you have negative reaction, or we had here anodic reaction but the sign is negative here, here it is positive, and this is cathode here, this is anode here, cathodic reaction is taking place here, this is cathode, though its sign is negative, this is anode, though its sign is positive, so go by that means this confusion always be there, it's better that you go by this convention.

Now if you come to this, so you have one region, one region you have zinc, I just remove this let me again draw it, zinc is going out,  $Zn^{++}$ , if zinc goes out what happens here? You have a loss of material, so you have a dead, now this electron is coming here combining with hydrogen, okay, so this is the cathode here, this is the anode here, because here anodic reaction is taking place, here cathodic reaction is taking place. Now if you combine this what would be the product? The same way, what the way we have done it for iron case,  $Zn^{++}$  is going into solution, solution and in the solution you have which is left out, chlorine is not taking part in the reaction, so chlorine is left out, so zinc combined with chlorine, two chlorine it will form  $ZnCl_2$ , so this is my product. And which is another product? Because hydrogen is also coming out  $H_2$ , fine, so if you want to see the complete reaction, the complete reaction becomes, now we have from this reaction is pretty clear that there is charge balance, but there is one more balanced reaction is taking place, this is nothing but the mass balance.

So we have two major balance, one is charge balance, one is mass balance, this two things should be there and what is the electrochemical nature? There should be one or more anodic reaction, there should be one or more cathodic reaction, but finally the total charge would be, should be zero. So in case of zinc in deaerated pure HCL medium, there are one cathodic reaction, there is one cathodic reaction, and there is one anodic reaction. Now let us see one more example, where you will see there would be one anodic reaction, but there would be two cathodic reactions. Let say you have a beaker, you have HCL again, dilute HCL and in that you have not done any deaeration, so it has dissolve oxygen. If you have dissolve oxygen, but at the same time it doesn't have any impurity in it, impurity means there is no  $Fe^{+3}$  ion in the solution.

Now again you add one zinc rod, if you insert zinc rod, now again you will observe that zinc is corroding, but if you see let say the same concentration of HCL you have taken and the same time period you have spent in two case, one case it's zinc rod, zinc rod in deaerated HCL, pure HCL and pure but here you have oxygen and pure, you will see the same thing here you will also see weight loss. Now weight loss means zinc is corroding, and zinc corrosion means, zinc is going to  $Zn^{++}$  and on this way it leaves two electrons. Now again, you blow it up this small portion, now here you have one case this portion zinc is going out and leaving two electron these two electron go somewhere on the other side if anodic reaction is taking place that means zinc iron is forming, if anodic reaction is taking place in some place so cathodic reaction has to occur on this zinc surface, just to take care of this two extra electron which is getting generated. Now who will consume that? There are now two sources, one source is  $H^+$  which can consume electron, there is one more source as you have seen in case of iron, oxygen in the presence of  $H_2O$  it can also consume electron and giving rise to  $OH^-$ , it giving rise to  $4OH^-$ , so this is one cathodic reaction, this is another cathodic reaction, that means this is one, this is two, and what is the anodic reaction here, this is only one anodic reaction, so one anodic reaction, two cathodic reactions, so this electron when it comes out from this region, these electrons will be consumed by this two reactions,  $H^+$  as well as  $O_2$ .

Now if you have this, how many electrons do you need for this? There should be charged balance, how many electrons do you need for these two reactions? You need four electron and you need one electron, so simultaneously in order to balance that extra charge here you are consuming more electrons so electron must come from this source, from this anodic reaction, so



more and more zinc ion should come into the solution leaving two electrons more and more electron and so that, that electron will be sufficient to take care of these two reactions, in order to maintain charge balance. Now there also would be mass balance, okay. Now if you see that there are two reaction like this so that  $H^+$  plus electron going to H, now if you combine two things so  $H_2$  can form or  $O_2 + H_2O$ , this reaction also can occur, so that means here you have to have more and more electron supply to this region, because these two reaction consume more number of electrons and here in one atom if you consider, then it releases two electron so it has to release more and more zinc, more and more electron and on this way you can have more and more zinc dissolution.

So now you see, now if you keep it for the same time duration, let's say one month also you have kept it, this one also one month, you will see the difference in the situation would be here the loss of material will be large, would be more, here the loss of material will be less, so here the corrosion is less, here the corrosion is more, fine, because, because we have more number of cathodic reactions and anodic reaction is one, okay, for the time being you consider in this manner, you will see the greater detail of weight when you come to the mixed potential theory. Now for the time being you see there are more number of cathodic reaction, there is one anodic reaction, so anodic reaction should occur more and more, so to take care of this extra electron that is getting consumed by these two cathodic reactions.

Now further let me add  $Fe^{+3}$  into this system, that means now you have HCL oxygen and then another ion  $Fe^{+3}$ , now  $Fe^{+3}$  has the tendency to accept electron, so  $Fe^{+3}$ , this  $Fe^{+3}$  can also consume electron, one electron it can consume and form  $Fe^{+2}$ , so what is this? This is also electron accepting reaction, so this is also cathodic reaction. Now you have three cathodic reaction, you have three cathodic reaction and one anodic reaction, what would you expect, what would be the corrosion rate in this case? Corrosion rate would be more in this case, if you have oxygen if you have impurity, so gradually you see in this case the corrosion would be less, in this the case where you have only oxygen that case you have little more and if you combine, if you have one more species  $Fe^{+3}$  then again you have further increase in corrosion rate or dissolution rate, and that means you see, why you think that there is increase in corrosion rate as you go from this to  $HCL + O_2$  and then  $HCL + O_2 + Fe^{+3}$ , because there has to be charge balance, now that charge balance is basically leading to more and more corrosion in the zinc, in order to supply that greater number of electrons that are needed for cathodic reaction to take place. Fine, so that means you have to have the charge balance and you have to have electron accepting and electron giving our reactions.

Now there are other examples also but you will come to know those example gradually, I will come to those examples one by one, but now let me go ahead with the fundamental aspects of it that is the, before that let me also say the basic, important basic principles of corrosion, let me point out, one is mass balance, second is charge balance, fine, then third is you have ions going to solution, this is nothing but corrosion and this is nothing but anodic reaction. Fine, now these three are very important part of electrochemical natures of this corrosion. Now if you consider what are the components of this section, you have to have metal surface, fine this metal surface can be divided into two section, one is cathode, another one is anode, here you see this section where anodic reaction is taking place that is anode, this section where cathodic reaction is taking place this your is cathode, so you have cathode and anode.

Now second thing is you have to have a medium where ion can go, so what is that medium? Here the medium is HCL and this is nothing but the electrolyte, okay, so you need cathode anode in electrolyte, fine. Now this, as well as when you have this you have two different reaction, one is cathodic reaction and anodic reaction. Now in case of cathodic reaction you have  $M^+ + e$  going to M. Now let us understand this reaction on the basis of oxidant and reductant. If you would like to understand this let us consider this reaction, what is hydrogen? Hydrogen is a reducing agent, okay. If hydrogen is reducing agent that means it reduces something and on the way it gets oxidized, okay, so if it reduces that means hydrogen would reduce something and it would get oxidized, now consider get oxidized, that oxidized part, if hydrogen is oxidized that means it has to leave electron, if it leaves electron so this is oxidant, this is reducing agent, because reducing agent will get oxidized, so it will leave electron, if it leaves electron what species would form  $H^+$ , so  $H^+$  is what? This is oxidant or oxidizing agent, fine, that means this is reducing agent, this is oxidizing agent or oxidant or this is called a reductant. Now in common sense you will see that this is expressed as red, an oxidant is expressed as ox, fine so if you consider this reaction you can write it as  $ox + e$  going to red.

Now cathodic reaction, this reaction is taking place, this is ox, this is red, and what reaction here it is taking place? This is ox, this is red. Now if you combine this two, what would happen? Those two electron will get cancelled and then you will have, you will have, sorry, let me put a different name here in N,  $N^+$ , so if you combine then  $M^+$  plus N giving rise to  $N^+$  plus M, this is the complete reaction. Now this is what? This is ox, this is what? This is red. Let me give this as red 2, this is red 1 and this is ox 1, this is ox 2, so this is ox 1, this is red 2, it is ox 2, this is red 1. Now what is happening here? You are having one reaction where ox is going to red that means oxidant is going to reductant, this process is called reduction. This process is called reduction that means every cathodic process is the reduction process. And if reduction, reductant goes to oxidant that is called oxidation, every anodic process is a oxidation process.

So now you have a reduction process, you have oxidation process if you combine reduction + oxidation, if you take this part only, if you take this part only then it goes to redox, so if you combine cathodic anodic reaction, actually you are giving rise to, it will actually, what is happening? One case reduction, one case oxidation, and then if you combine the first, this underlined part is the redox reaction. So in case of electrochemical reaction you have metal surface, anode, cathode, you have electrolyte, at the same time you have redox reaction, this is very, very crucial thing, you must be having reduction reaction and that should be coupled with an oxidation reaction and then combinely you have to have a redox reaction. So these are the important components of electrochemical reactions.

Now coming to one issue that I have not given any, I have said that oxidation is also a corrosion process, okay. Let us understand that part before I go to the actual thermodynamic consideration of corrosion. In case of oxidation, what is happening? You are having M metal, it combines with half of oxygen going to MO, if you see the oxidation number in this case, this is 2-, this is 2+. Now let me have two sections, one case I have the zinc process, zinc corrosion in HCL, so  $Zn^{++} + 2E$ , zinc, now this two electron it's combined by  $H^+$  plus E,  $H_2$  and this is oxidation, this is reduction, so combinely it is basically a redox reaction.

What is the anode? This portion is anode, on the metal surface, this portion is cathode because here cathodic reaction or reduction reaction is taking place here oxidation reaction or anodic reaction is taking place. So now you have all the four components, you have electrolyte here which is nothing but HCL, you have metal surface which is cathode, this part is cathode. Now all the four components you have, electrolyte, cathode, anode and redox.

Now let us see here why that we have all those processes or not, all those components or not. Now metal surface, this is metal surface, let's say we have oxide layer, now you have MO, you have oxygen here, you know this is gas, this is oxide, this is metal. Now you have two distinct interfaces, one is metal oxide interface, which is this part and another one is oxide gas interface which is this part. Now as I have mentioned there could be diffusion of oxygen ion from outer surface to inner surface or metal ion can diffuse out, so if, and from this if MO is the oxide that means there must be metal ion formation metal ++,  $M^{++}$  and there could be oxygen ion formation which is oxygen 2-, how would you form oxygen 2- from oxygen? That is you have to add two electrons then only it can go to  $O^{2-}$ , also here you have to, from metal you have to take out two electrons then form (audio gap 0:55:18 to 0:55:29) process would occur at these interfaces, at the same place, which is metal oxide interface. So if this process is happening here, this process is happening here, what is this process? This process is nothing but oxidation or anodic reaction, and on what surface anodic reaction occurs? On anodic surface, so here which one is anode? Anode is this, this surface is anode. Now which surface this reaction would occur? This reaction would occur because here you have access of oxygen, so this reaction must occur on metal oxide, oxide gas interface. So if, what is this reaction? This is electron accepting reaction that means this is a cathodic reaction or this is a reduction reaction. Fine, so reduction reaction is happening at this interface, so what would be this? This would be cathode, fine.

Now let us compare with this, you have anode here -- you have cathodic reaction on this surface you have anodic reaction on this surface, you have electrolyte here, fine. Now we know we have come to know that this surface is anode, and on this surface this reaction is taking place anodic reaction and this surface is cathode, this reaction is taking place. But how would this reaction get two electron, that was initially oxygen is in zero state, fine, so there must be some source of electron, the source of electron is, and this has to pass through this medium, okay, and this medium electron can flow, so this medium is acting as a conductor, but now if you have these two processes so electron is coming from this to this, and then it is consuming, this oxygen is consuming two electron forming oxygen 2 minus ion.

Now which surface do you think it would grow, the oxygen, if you constantly supplying oxygen then constantly this surface would keep on growing, keep on growing. Now which surface would grow? It would be decided by where this metal ion is combining with oxygen ion and forming this, okay. Now oxygen ion is diffusing through the oxide layer to this surface, it comes to this surface then it finds  $M^{+}$  ion, so then immediately it will combine with this so oxide will, layer growth will take place on the surface.

Now instead of that if metal ion comes from this to this, so through this metal oxide layer then metal ion is coming here it again finds oxygen -2 and combines there it forms MO. So metal ion it diffuses out then metal oxide forms on this surface, if oxygen ion diffuses in then metal oxide form, oxide form on this surface.

Now here which is the electrolyte? HCL, and what is the function of electrolyte? It supplies the charges or the ions. Ions goes into electrolyte or ions, ions are coming from the electrolyte to the electrode surface, here if you think that oxide is going on this surface metal ion is passing through this metal oxide layer and coming here, so what is that function of metal oxide? It's nothing but electrolyte, so metal oxide is acting as electrolyte. So this is electrolyte, fine. Now if this is electrolyte so you have all the four components, this is anode, this is cathode, this is electrolyte, and you anodic reaction or oxidation reaction, you have reduction reaction or cathodic reaction, if you combine this two and it forms redox reactions. Fine, so if you compare this two thing this is aqueous corrosion, this is high temperature oxidation, both are having the similar components, and similar electrochemical redox reactions is happening. So this is also a form of corrosion. Thank you.

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