Corrosion - Part I

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Lecture - 07
Electrochemical Nature of Corrosion of its Thermodynamics

Hello everyone. Let us begin 7th lecture. And in our 7th lecture, we will now start looking at Electrochemical Nature of Corrosion and its Thermodynamics.

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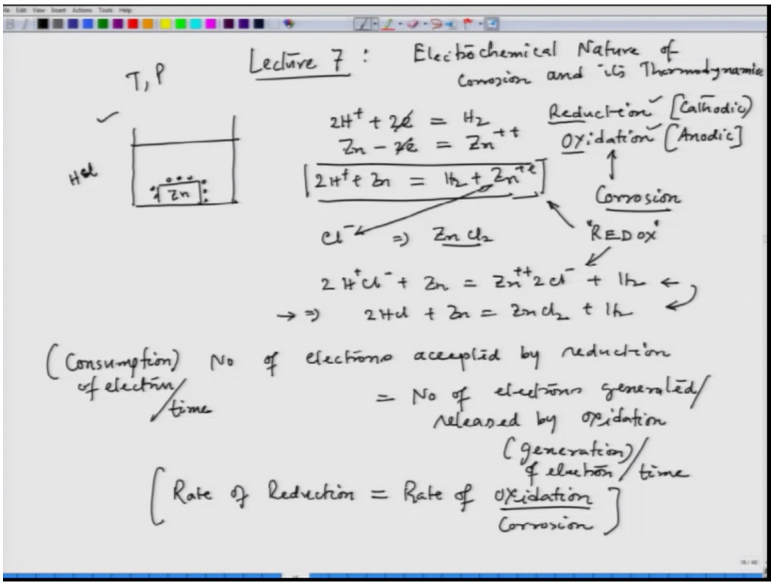

So, lecture 7 Electrochemical Corrosion and, its Thermodynamics. Now, when we talk about this electrochemical nature, we will bring in the examples what we have already discussed in our earlier lectures. The example is if we have a zinc plate dipped in dilute HCl solution and this is a zinc plate let us say.

Now, once we putting that zinc plate, we see that the bubbles are forming on top of zinc surface. And these bubbles are nothing, but hydrogen gas. Now, if we analyze this particular reaction because these bubbles are forming, because of some reaction then will see that one reaction is this one this is anodic reaction or we call it oxidation.

Now, two electrons are released by zinc atom and it goes to zinc iron. Now, electrons cannot remain free. It has to be balanced by some mechanism, because the total amount of charge is constant in this universe. So, we call it charge conservation. So, these electrons will be accepted by some other reaction. The other reaction is nothing, but H plus 2 e it goes to H 2. Now this is reduction reaction and we also call it cathodic and this is anodic. Now if we combine them, then we will see that 2 H plus plus Zn 2 electron this two are cancelling each other so; that means, we are maintaining charge balance and then, also we are also maintaining the conservation of charge concept. So, that becomes H 2 plus Zn plus plus.

Now, this is the complete reaction. Now as we have understood before that when some metal iron metal atom converts to metal iron. So, it goes into the solution and that one we call it corrosion. This is nothing, but corrosion. So, oxidation is nothing but corrosion. Now, in this case interestingly this is the complete reaction; this is the complete reaction, or if we consider another species that is present in the solution which is chlorine iron.

Now, that chlorine iron will react with zinc plus plus, so it will form zinc chloride. So, the complete reaction, we can also write in this form 2 H Cl plus Zn equal to Zn plus 2 Cl minus plus H 2. So, this is another way to write a cell reaction. So, here I am sorry that we missed 1 plus sign here and finally, from this we can write this reaction.

Now, this is the complete cell reaction and in order to have this complete cell reaction, we have to have two reactions; one is reduction, another one is oxidation. They are running parallelly. Now, interestingly if we see in the reduction if we take only the red part and in the oxidation if you take only the OX part, if we connect them; then it becomes REDOX and when we have REDOX reaction, then only we have these complete reactions.

So, for the complete cell reaction which is nothing, but the REDOX reaction, it has got one reduction reaction and one oxidation reaction. And when we have this REDOX reaction, we have the corrosion of zinc in the form of zinc plus plus iron. And this REDOX reaction is important in the sense that only oxidation cannot take place or only reduction cannot take place see. If there is one reduction reaction, there must be one oxidation reaction, at least from this particular example it is very clear.

And then only we have complete cell reaction. And interestingly in the REDOX reaction, we have the number of electrons accepted by reduction is equal to number of electrons generated or released by oxidation reaction. This is very important aspect and that, we maintains the charge balance and also the charge conservation

Now, this also reflects a kind of rate thing in rate kind of aspect; rate means per unit time. Now, if we have this particular reduction reaction happening at a different rate, than the second oxidation reaction, then there will be cumulative charge conservation charge consumption cumulative charge consumption. This is nothing, but the consumption and this is generation. So, what I am considering that if we have more amount of the number of reactions of this first reaction which is reduction reaction, happening at a much higher rate compared to the second reaction which is oxidation.

That means at any given time we have more amount of electron consumptions than the generation. so, which will not maintain this charge conservation.

So, in order to maintain charge conservation so, consumption of electrons per unit time should be equal to generation of electron per unit time. So, the rate of reduction should be equal to rate of oxidation and since oxidation is nothing, but corrosion; so, it becomes rate of corrosion this is extremely important concept. The rate of reduction is equal to rate of oxidation or corrosion. .

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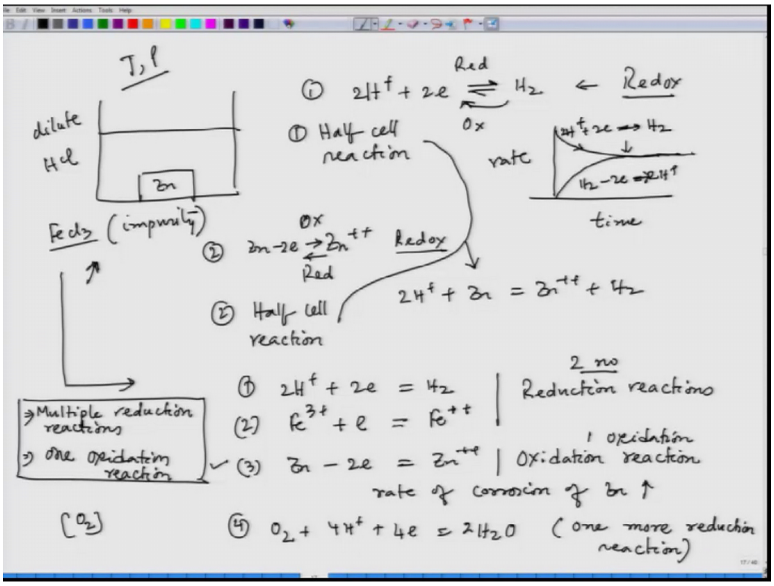

Now, if we go to see some other considerations. For example, in this situation the example, what we have considered in the previous case, you have zinc and same HCl solution dilute. And in this if we have let us say, if we have little bit of FeCl 3, a small content it is considered as impurity, then the situation would be different.

Now, before considering this situation as we have seen that if the previous case, if this particular condition; if it is happening at a particular temperature and pressure, if I we maintain the temperature and pressure and if we make it a close system. So, this reaction this particular reaction would reach to equilibrium. Now, when it reaches equilibrium then this reaction it also reaches equilibrium.

So, now if we consider this particular reaction the forward reaction is nothing, but the reduction reaction. So, this is reduction now if we remove this part so, then it becomes only red. And interestingly reverse reaction is nothing, but oxidation and if we remove this part, then also this becomes a REDOX reaction. So, combinedly it becomes another REDOX reaction.

Now, in the beginning of course, hydrogen gas generation would be very fast rate. Now, if we consider the rate criteria, time, rate in the beginning, we have huge amount of hydrogen ions in the systems. So, the rate at which hydrogen gas will be generated will be very fast in the beginning and as we have a time lapses, then the rate will decrease and it will be like this. It will flatten out; that means, thus it reach a steady state

Now, when this particular thing is H plus plus 2 equal to H 2; now once we have a generation of hydrogen the reverse reaction would start happening. So, the reverse reaction would take place, now that initially it was almost no hydrogen gas. So, it will start with a 0 and then it will also merge with this particular rate. So, this is H 2 minus 2 equal to 2 H plus.

So, this is the point where it reaches equilibrium. So, the rate of forward reaction is exactly same as the rate of backward reaction. Similar situation can arise zinc plus plus zinc can go to zinc plus plus here the forward reaction is OX and the backward reaction is red reduction. So, this is also a REDOX and it also reaches equilibrium when the system reaches equilibrium.

Now, interestingly for this complete cell reaction 2 H plus plus Zn equal to Zn plus plus plus H 2, it is combination of this reaction and this reaction these two reactions are electrochemical in nature, because it involves electron acceptance or electron release and they are called half cell reaction; so, this is half cell. This is one half cell this is second half cell, which combines and then forms a complete cell reaction.

Now, coming to these example when we have dilute HCl and we have little bit of FeCl 3. In the previous case we have one reduction on one oxidation. Now interestingly in this case, there will be one additional reduction reaction. Now, let us see what is that additional reduction reaction, first in this case first reaction would be definitely 2 H plus plus 2 e equal to 2 this is of the same has what was considered before.

Second reduction reaction which is Fe 3 plus accepts one electron and it goes to Fe plus plus Fe 2 plus this is also a reduction reaction. So, these are two reduction reaction and there would be only one oxidation reaction which is zinc plus plus. This is oxidation reaction.

Now, as we have mentioned that there should be rate of reduction reaction should be equal to the rate of oxidation reaction. Now, here we have two reduction reactions, so you need more electron supply for those two reduction reactions. So, where from this extra electron would come to take care of two reduction reactions; it has to come from this reaction. So, the generation of or release of electron from zinc atom would increase, or at the same time the rate of which zinc would release electron would also increase, it means that the rate of zinc dissolution would also increase and finally, it suggest that the corrosion rate of zinc increases.

So, we have a system where we have multiple number of reduction reactions. So, here two reduction reactions 2 number and 1 oxidation and that would increase the rate of corrosion. And exactly that is observed when you have zinc in a in the solution of dilute HCl, where you have little bit of FeCl 2 Cl 3 impurity and of course, temperature and time temperature and pressure both are same both are maintained same.

Now in this case, we can also have a consideration of dissolve oxygen. Now, if it is containing dissolve oxygen dissolve oxygen would also allow another reduction reaction. So, this reduction reaction for this case since its acidic medium; so, then the reduction reaction involving oxygen would be this would be the reduction reaction and this is a very strong reduction reaction. So, we are having one more reduction reaction.

Now, in this system we have three reduction reactions and one oxidation reaction. So, in order to maintain the electron supply for three reduction reactions, the number of atoms of zinc going into solution by releasing electron for the reduction reactions would also increase per unit time. So, the rate of oxidation or the rate of corrosion of zinc would further increase. So, as we see these three examples that in a system, we can have one reduction and one oxidation or there could be multiple reduction reactions and one oxidation.

But the total number of electrons supplied by the oxidation reaction would also increase because we have to maintain three reduction reactions, but at the end we have to maintain the total rate of reduction should be equal to total rate of oxidation. So, these particular concepts will be clear and it will be continuatively understood when we talk about mix potential theory. So, this is consideration where we have one reduction multiple reduction reactions and one oxidation reactions.

We can have a situation. so this particular thing we are having if we try to see a situation so, multiple reduction reactions and one oxidation reaction all three examples. .

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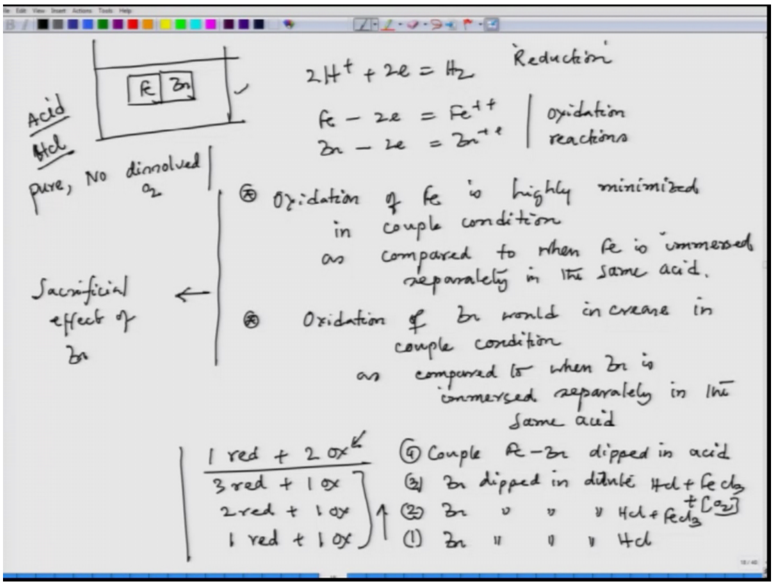

Now, we have example like where we have one reduction reaction, but there could be multiple oxidation reaction. The classic example is if we have iron and zinc, this couple this galvanic couple is placed in acid. Let us say HCl acid the situation would be like there would be two reduction two, one oxidation reaction and if this acid HCl is pure as well as no dissolved oxygen. So, then we do not have any other reduction reaction except hydrogen reduction. So, this reduction reaction would take place, and two oxidation reactions are Fe, zinc; these 2 oxidation reactions.

Now, interestingly when we have individual individually iron is dipped in HCl or zinc is dipped in HCl, their corrosion rates are considerably high. But once we have this situation a galvanic couple of iron and zinc are dipped in that couple is dipped in HCl, then we have both this oxidation reactions going on and one reduction reaction. But interestingly that time our observation after sometime if you check it out that couple and try to analyze, we will see oxidation of iron is minimized in couple condition has compared to when iron is immersed separately in the same acid.

But at the same time, if we see the zinc, oxidation of zinc would highly increase rather in couple condition as compared to when zinc is immersed separately in the same acid. So, what we are saying qualitatively, but when we talk about mix potential theory, we will also quantify that how much would be the reduction of iron reduction of rate of oxidation of iron or how much would be the increase of oxidation of zinc. Here the reduction means I would say when how much would be the alluring or decreasing the oxidation rate of iron and how much would be the increase in oxidation of zinc, when we have a couple and that one is dipped in HCl solution and this is the very concept of sacrificial effect of zinc.

And here also REDOX reactions are taking place. Here, REDOX reaction if we consider REDOX reaction. In this case, we have 2 OX 1 red, but in our earlier situations this is 2 OX and 1 red or I would consider since we are talking about REDOXnot OX red. So, we can put it as 1 red 2 OX, this is the example couple of iron and zinc dipped in acid.

And in the previous situation all three examples, this is example 4th example three was zinc dipped in dilute HCl containing FeCl 3 and dissolve oxygen where we have three red plus 1 OX 2 zinc dipped in dilute HCl plus FeCl 3, we have two red reaction reduction and 1 OX reduction reaction and finally, in the first case where zinc dipped in dilute HCl; we have 1 reduction and 1 OX. So, like that there could be number of oxidation reactions and there could be number of reduction reactions in a particular cell. But finally we have to make sure that we have to see that the rate of total reduction should be equal to the rate of total oxidation. And because of that total rate of reduction and total rate of oxidations are same in order to maintain charge conservation. So, in this three cases, we have increase in zinc dissolution, as we go upward we have more and more zinc dissolution. But in this case, we have a sacrificial effect of zinc iron dissolution decreases or minimized and zinc corrosion increases and that is the very concept of sacrificial anode nature of zinc on iron surface. So, let us stop here we will continue our discussion on electrochemical nature of corrosion.

Thank you.