Indian Institute of Technology Kanpur

Present

NPTEL

NATIONAL PROGRAMME ON TECHNOLOGY ENHANCED LEARNING

Environmental Degradation of Materials

Module Lecture 09

Broad Subject: Pourbaix diagram, Kinetics of corrosion

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Till now we have talked about thermodynamics of metal dissolution or corrosion and in this way we have learned mixed potential. We have learned free energy change. We have learned this triangle where it's basically E0 then delG0 and K we have tried to connect these three parameters and these three parameters are connected to different three equations and from those equation we can be able to tell that whether a metal dissolution is thermodynamically possible or not. And in this way we have also seen what the origin of electric potential or a reduction potential if a reaction which is involving only metal dissolution or metal deposition then it would be and if let's say if a copper surface if copper surface in a copper sulfate solution copper sulfate solution, this is copper and so copper is depositing or copper is dissolving at some particular temperature and that time we have come across electrode potential and that electrode potential we have expressed in the form of reduction potential and then we have come to know what is the standard reduction potential and the standard reduction potential is nothing but the potential which is developed for the reduction reaction at the standard state and the activity of those ionic species should be one. That case we develop series considering all the reduction potential in the standard state at unit activities then we form a reduction potential series that gives us some idea that which would be active metal, which would be a noble metal, and then we have come across Pourbaix diagram, that Pourbaix diagram tells you the stability of different species at different pH and potential level and then we have also drawn a Pourbaix diagram for Nickel, Pourbaix diagram for aluminum and we have said that we have seen that there are different sections if this is my Pourbaix diagram for Nickel this is potential, this is pH that time my Pourbaix diagram for Nickel is this and then in point the area of different species this is Nickel. This is Ni++. This is NiOH whole two or NiO. Now from this we can also pinpoint which is the region for corrosion, which is the region for immunity, which is the region for passivity and this is also, this diagram this Pourbaix diagram is constructed on the basis of thermodynamic data either solubility data that means the solubility constant or the or the equilibrium constant for the reaction or the reduction potential as a function of pH or the activity of those species, ionic species, and that tells you the constant that gives you the construct – that helps you to construct Pourbaix diagram and we have also drawn it for aluminum but in most of the cases we come across iron. In case of iron also we can have a Pourbaix diagram and one important matter part one important issue with the Pourbaix diagram is this is considered involving H2O only. H2O let's say metal H2O system and where you can have oxygen which is dissolved in H2O.

So in this condition we can have a Pourbaix diagram. In case of iron also you can have a Pourbaix diagram in that case we can come across several equations. To mention few of those this is Fe+2+ 2e going to Fe, second reaction is Fe+3+e going to Fe+2. Third reaction is Fe+2+H2O going to Fe(OH) whole 2+2H+4, Fe+3+3 H2O going to Fe(OH) whole 3+3H, five, Fe+2+3H2O going to Fe(OH) whole 3+3H++1 electron. Then, 6, Fe+2H2O going to Fe(OH) whole 2+2H++2e. 7, Fe(OH) whole 2+H2O going to Fe(OH)whole 3+H+e like that you can have several such reactions involving the common product that form that is formed when iron reactions to H2O solution and H2O in the presence of oxygen. Now if this is the 7 reactions I am considering then I can also have a Pourbaix diagram for these reactions and that case a Pourbaix diagram for iron would look like this sort of Pourbaix diagram will come across, you will come across this sort of Pourbaix diagram where this zone would be Fe+2 sorry this is Fe this is Fe+2, this is Fe+3. This is Fe(OH) whole three and this zone would be – this would be a Fe(OH) whole two. Now on the right side this is pH extending. As the pH is increasing then right side also you can have complex ion formation then as you have seen in case of aluminum then at higher pH value also we can have again corrosion.

Now in this case this is basically reaction number one. This is reaction number two. This is this reaction this four – this fourth reaction is this one. This is fourth and then this is this reaction is third then this is seventh and this is six and five is this one.

So if you see reactions some of them are potential dependent, some of them are potential plus pH dependent and some of them are only pH dependent and accordingly you can have a horizontal line, you can have a vertical line like this number three which is only pH dependent so this would be horizontal vertical line with respect to pH axis this would be horizontal line because this is potential guided pH independent like that you can have such construction of iron in case of iron iron Pourbaix diagram. Now we know all those things and we can be able to tell that if the pH is this lets say my pH is this and the potential is this then I can say that this is in the immunity zone. If I am here so if I am here then I can tell that this is this is in corrosion zone because I am forming Fe+2 which is dissolving in the solution if I am sure I can tell that this is in passive condition because if you form a Fe(OH) whole 3 then it forms a layer on the iron surface and then further dissolution is hindered so that is the passive joke but can we tell anything about the rate? We cannot say anything about the rate of the reaction that what would be the rate at which iron plus 2 is forming from iron in H2O. We cannot tell that. So we only talk about thermodynamics but we cannot talk about kinetics about from this diagram so we need to get into the kinetic part so that would give me the convincing picture at what rate my corrosion corrosion of iron is taking place, corrosion of Nickel is taking place NH 2 a solution so now I will talk about the kinetic part of it. Kinetic of corrosion then if you combine then kinetic plus thermodynamics then the total picture will be depicted.

Now let me talk about kinetic. Kinetics of corrosion. Whenever you talk about the kinetic of corrosion then I should know what how we should predict the rate of corrosion. Without knowing the fundamentals of how the metal dissolution is taking place what are the processes at the interface of metal solution at the metal solution interface, what are the mass transfer reactions that are taking place, let us not bother about those things but still we can depict, we can measure the rate of corrosion by simple expressions. Now one expression would be without knowing anything about electrochemistry because we will be involving a little bit of electrochemistry without knowing the thermodynamics of corrosion but still we would be able to determine what is the rate of corrosion. Let's say a simple experiment I am doing I am having a beaker and now I put a small iron piece in the solution. Okay, let's say in HCl solution, deaerated HCL solution which is pure. Now in this solution after some time let's say I wait for one month then I will see that I'll take this metal out and measure the weight, [Indiscernible] [0:11:39] weight let's say when I dissolve when T equal to zero that means when I dissolve this, when I immerse this metal piece into the HCL solution that time weight was W1and after t equal to t which is let us say one month that time my weight is w2 then I can measure what is my loss in weight of the metal piece. So loss in weight would be equal to w2-w1. Now this is my loss. Now loss in weight now if I divide it by time this is time, so what is that though that means let's say loss in weight in gram okay and T is in month I can put month. So gram per month. That means that this much of weight loss is taking place per month. Okay. So that means some time factor is coming into picture and this is a rate of corrosion of metal piece, iron piece. Now this is a very simplistic approach and this is done actually in a experiment that we do immersion test, immersion test and then measure the weight loss and determine the rate of corrosion.

Now this sometime would be let's say the weight loss is very very small. Let's say weight loss is let's say a 0.001 milligram. Now with such a small weight loss per month if you would like to measure that weight loss there would be a possibility that you can have error in measurement. So we have to have some sort of convincing approach to determine the rate of corrosion. Okay and we should have some way to measure the corrosion in some universal rate, universal unit. Now what do you mean by let's say that there must be some universal way to measure the corrosion rate for example you are doing this experiment in seawater in a sea level and you are doing this experiment in dry condition okay so both the conditions you will have a different weight loss. If you have a different weight loss then you are using the same metal piece, same solution but the environment is different. The outside environment is different that case you will have you will experience a different weight loss but you are actually not specifying the condition, actually you are only specifying this gram per month. Then that should be a wrong measurement of corrosion. Okay. Corrosion rate. So we should have a proper measurement of corrosion rate and there we should also have a some sort of suitable unit for the corrosion rate. Now so this is a crude method. Now let us get into some much more scientific method to measure the corrosion. Now let's say for that we need to a little bit of electrochemistry and electrochemistry we have two laws for electrolysis. Before getting into the actual corrosion rate let us understand what are the laws of electrolysis that would give me some idea that how to express the corrosion rate in different units. Now laws of electrolysis one first law says that the amount of chemical change, the amount of chemical change occurring at any electrode either it can be dissolution or it can be deposition let's say in case of zinc, in case of voltaic cell in one electrode zinc electrode zinc is dissolving and on copper electrode copper is depositing on the copper surface. So in both the surface you are having two different chemical change one case it's dissolving one case it's depositing. So occurring at any electrode is strictly proportional to the quantity of electricity passed through the electrolyte, passed through the electrolyte. What does it mean? Let's say I am passing Q amount of charge that should be proportional to W. if the W is the either the amount of metal that is dissolving or amount of metal that is depositing on the metal surface. Now this is the case. Then W should be equal to ZQ. This is the first case and second case would be this one what it says it says that the quantity of electricity the second law says that the quantity of electricity, the quantity of electricity passed through the different electrolytes, let's say you are having voltaic cell this is zinc and you have connected it to the copper and this is a salt bridge and this is a zinc sulfate, this is copper sulfate solution and this is copper, this is zinc and you have sorted it and then you will see that current is passing from this end to this end and electron will pass from this end to this end and there will be if you connect this then the current since the current is flowing so you will have copper deposition and zinc dissolution. Now if you would like to find out what would be the amount of zinc that is dissolving and what would be the amount of copper that is depositing that can be related to a second law which says that if the same quantity of electricity let's say the same quantity I amount of current is passing from this end to this end then we will see that the quantity of electricity if same quantity, same quantity of electricity is passed through a different electrolytes this is one electrolyte, this is another electrolyte. If you are passing the same current through the different electrolyte then the amount that would be deposited or dissolving let's say here zinc is dissolving, here copper is depositing so that amount would be proportional that are basically all are chemically equivalent. Different amount of chemical changes produced are all chemically equivalent. It is passed through different electrolyte then the quantity of chemical change would be so this the quantity of the same quantity of electricity if that electricity is pass through this electrolyte as well as this electrolyte the amount that is dissolving that is zinc that is the dissolving a copper that is depositing those will be chemical equivalent produced are all would be chemically equivalent. So if the first law says this that amount of electricity would be proportional to the amount that is depositing or dissolving then the proportionality if you – the proportionality constant would be Z which is nothing but the electrochemical equivalent. This is basically the second law. This is the first law and this is the second law. And this chemical equivalent part is coming into this Z part, in Z section. Now Q is what? Q is nothing but I into T. I is current and T is the time for which you are passing that same current through these electrolytes then this should be ZIT. So now you have the amount that is depositing or dissolving you can quantify this if you know the time at full for which you were passing this current and if you know the current that is passing and if you know the chemical equivalent of either copper or zinc.

Let us understand this. Now Z is basically electrochemical equivalent. How do you find out Z? Let's say in case of silver, Ag. So Ag++e going to Ag so this is my reduction reaction and what what is my atomic weight of silver is 107.88 gram per mole. Now what would be my equivalent, atomic equivalent for this silver? So since one electron is involving so equivalent weight would be 107.88. If two electrons are involved then equivalent weight will be 107.88/2 but in case of silver one electron is involved. In case of copper, copper atomic weight is 63.55 so that case if you would like to find out what would be my equivalent weight for copper that case it would be the number of moles, number of weight of copper divided by the atomic weight of copper divided by the number of electrons that are involved. Let's say in case of copper, two electrons are involved so this would be copper and now that case the chemically equivalent weight would be weight of copper would be atomic weight of copper divided by 2 since we involve two electrons, and if for this reaction let's say M+n+ne=M then that case equivalent weight would be am/n. So here number of electrons those are involved for this reduction process is n so Ma is the atomic weight of M metal divided by n. That is the equivalent weight.

Now if I would like to now what would be my Z in case of silver, then if I pass one Faraday of electricity, one Faraday of electricity through this system. Let's say I am passing Q is 1 Faraday which is nothing but 96500 Coulomb per gram equivalent so that means 1 F if we pass then we will see that 1 gram equivalent silver will be deposited. So that means this 1 Faraday is equivalent to 107.88 which is nothing but this is my gram equivalent for silver. So this is gram is my final equation. This one Faraday would be equivalent to 107.88 gram. If you pass one Faraday of electricity then there would be a deposition of 107.88 gram. Now if you have this so then if we pass one Coulomb of electricity then the deposition would be if you divide this one by this then you would get 0.00118 gram. So Z is 0.00118 gram per Coulomb. So this is my Z and the relation is W equal to ZQ. So this is my total amount of electricity and this is my equivalent electrochemical equivalent. Now if you know then we have some idea that how much would be the deposition. Now in case of corrosion it's nothing but the dissolution. The same way you take it in case of dissolution so in case of dissolution the amount that would be dissolved would be W equal to ZQ.

Now I can express another equation which is nothing but let's say if I consider E is my gram equivalent, so E would be equal to Z into F because if what we have understood that one Faraday is equivalent to one gram equivalent so if I pass ZF amount of electricity this E is basically gram equivalent if I pass one Faraday of electricity so Z into F would be my equivalent weight of the system -- of the let's say in case of dissolution or in case of deposition. Now if two metals let us say in case of copper and silver, copper and zinc, copper this is my E for copper and this is E for zinc then E copper would be equal to Z copper into F which is nothing but Faraday. E zinc would be equivalent to Z zinc F. now the second law also says that if you pass the same current for the same time through this electrolyte as well as this electrolyte then this copper would be equivalent to E zinc. Now if you have this situation then E copper by Z copper would be equal to E zinc Z zinc and then you can say that E copper by E zinc would be equal to Z copper, E zinc by Z zinc, okay Z copper by Z zinc because if you take this, this side then this will be 1 Faraday if you take this side this will be 1 Faraday. So it would be E copper by Z copper would be equal to E zinc by Z zinc yes this is my relation. Now this is another important relations which also involves the second law that means this is following the gram when the same amount of equivalent species will be dissolving or depositing. Now from this law we can construct the rate laws, rate equations for corrosion. What is I? here the I, I is nothing but dq/dt the rate at which charge is flowing through the system either through the external wear or through the electrolyte. Now if you know this now what is 1 ampere current? 1 ampere current is nothing but flow of 6.2 into 10 to the power 18 electrons per second and if you consider the charge of electron one electron charge is basically nothing but 1.602 into 10 to the power minus 19 Coulomb, if you multiply this then you would get that this is coming out to be 1 ampere. Now if you know this now again we know if you let's say for this reaction M going to M+n+ne now I am considering with respect to dissolution if I consider with respect to dissolution then I have to consider oxidation reaction. So metal is going into metal ion. Now for this if I supply for this case if I supply Q amount of electricity, what would be the mole that would be electrolised or mole that would mole of metal ion that will come out into the solution or dissolve into the solution. So Q by nF would be this would be the number of moles which is considered in capital N, let me put it as small n this is my number of let me put in small dash, this is number of mole which will dissolve if you supply Q amount of electricity. So if you put this into this then I would be equal to $ instead of Q I put n dash nF and if by dt. This n dash is nothing but the number of moles. So I can separate it out dn-by dt and this n, small n is a constant because for this reaction this would be always n would be a fixed value F is also a constant so I just take nF outside. This n dash is nothing but the number of moles that is those are dissolving into the solution because of this oxidation reaction.

Now what is this? This is the rate at which number of moles is dissolving into the solution. So that means this is my rate of corrosion. So you can also mention it as – you can also term it now let me change let me remove this top part. So dn dash dt would be equal to I divided by nF. Now we can measure current easily with the help of an ammeter. So instead of Q I convert this rate of dissolution in the form of current. Now if you consider a dissolution from a metal surface, let's say this is my solution and in this I have inserted I have immersed a metal piece like this. Now where from dissolution will go through. Dissolution will occur from the surface. From the surface my metal dissolution will take place and that means the rate of an electrode reaction is often very complex because you have to consider several issues. Few issues will have just like for example what the way the metal ion is dissolving into the solution, the way what is the roughness of the surface, what is the double layer thickness or before considering the double layer thickness let's say metal dissolution the solution is solution is coming in contact with a metal surface and then you have charge transfer from metal surface to the electrolyte to the ions and then you can have the ionic distribution on the metal surface. Those are very complex issues okay but without considering those complex issues it's very simple that the metal dissolution is taking place from the surface. Let me stop here.

So this expression we are getting the number of moles dissolving in the solution per unit time is equal to the current that is passing through the electrolyte by nF for this reaction. Now whenever corrosion is taking place that is not taking place from the bulk. It is taking place from the surface. From the surface metal is dissolving. So it's a not an homogeneous reaction rather it's a heterogeneous reaction because you are involving a surface. From the surface it's taking place. So if you have let's say this is my one centimeter square surface and if you are having 10 centimeter square surface so the dissolution rate if you consider what would be the number of – what would be the weight that is getting dissolved, then in this case the weight dissolve would be more because you have larger surface area. So you know that this is my relation and now whenever you consider corrosion that means the corrosion is taking place from the surface and it's not the bulk phenomena, rather it's a surface phenomena and that means if you consider the surface and if it is heterogeneous reaction in order to normalize that data let's say you are considering for a surface of 1 centimeter square and if you are considering a surface of 10 centimeter square so then you have to understand what would be the rate per unit surface because if you consider 10 centimeter square there would be some irregularities and other things but or 1 centimeter square then you have to express the corrosion part in each area to normalize the data for these two cases. So if you have 1 centimeter square and if you have 10 centimeter square so for both the cases I know the reaction is taking place from the surface so I have to normalize the data, in order to normalize the data, then I have to divide this expression per unit area with the area so then I would get the expression in terms of if I divide it by area which is A here also I'd put A so then this expression would be number of moles dissolving in the solution per unit area per unit time. Now this is the left part. The right part would come I divided by nF and A if you consider this units you will see the same unit but now since I am having I which is the current the total current. Now in order to express the actual kinetic phenomena that is happening on the surface it's better to express current density rather current because the current density you will see later the current density is the actual expression for corrosion rate, actual kinetic parameter to determine the corrosion rate. So now this is the current density part here if you consider this part that is basically I by area which is nothing but I, the current density is termed as small i small i by nF. The A is getting into this i. So if it is ampere then this is ampere current density unit would be ampere per centimeter square or meter square whatever it may be. Now this is my finally I am getting d and n- Adt equal to now I am expressing in terms of current density my nF. Now let me take this part what is n dash, let's say the atomic weight for this is A is aM and the n number of electrons is involved to reduce Mn+ ion or other way around if it is oxidation reactions so ne number of electrons will be released. So if you know this what is n dash, n dash would be the number of moles would be equal to weight, let's say the amount if you say W gram of metal that has dissolved and if aM is basically the atomic number so number of moles that has dissolved would be equal to aM. So now instead of this let me put -- in instead of n dash let me put dW by Adt into aM. So aM for a particular metal is constant so this is I am taking out from this. So this is my the rate at which the mass is getting lost, our mass is getting dissolved in the solution would be equal to then i/nF so now let me consider dW which is the lost mass loss per unit area since it's a heterogeneous reaction or the surface reaction so I'm dividing it by Adt would be equal to iaM/nF. So this is my expression for corrosion.

Now let's say one gram is lost or dissolved, one gram dissolved area is one centimeter square and time is, this is area, this is mass loss, this is mass loss, this is area of the surface and time is let's say one second, this is time then unit for my corrosion rate would be one gram per centimeter square per second. So this is my unit for corrosion rate.

Now there are several units which can express the corrosion rate. One major unit is mdd which is nothing but – now this also you can express in the form of one gram per centimeter square par day or one gram per meter square per day. So when you express in the form of one gram per meter square per day that is the SI unit for expressing corrosion rate. Now if you there are other units one unit is basically one very common unit is mdd. mdd this this is a convention and mdd is nothing but the milligram per decimeter square per day so this is nothing but milligram per decimeter per day. Now one major criteria – one major information for if you would like to measure the corrosion in the form of mdd then you should understand that the corrosion is happening throughout the surface uniformly. We will come to know why I am using this terminology that this is expressed in the when there is a uniform corrosion throughout the surface. If there are localized corrosion if there is localized corrosion then you have to modify this expression. I'll come in a little while in a minute why you have to change this terminology.

Now if you know this if you know the weight loss, if you know the area, if you know the time then you can measure corrosion rate. Now at the same time if you would like to find out the correlation rate from this here you are not measuring what is the weight of electrode surface or what is the weight of electrode rather from current you can easily measure what is my corrosion rate because if you know the current, if you know the area of zinc electrode then you know the current density, you know the atomic weight of zinc, you know n in case of zinc the n is 2 and you know 1 Faraday, from this also you can express the corrosion rate in the form of mdd or 1 gram per meter square per day.

Let us have some example. Let's say in this case I know let's say in case of iron, pure iron, corroding in seawater and the current density is measured to be in case of iron this corroding in seawater so that case I miss the current density that is measured is 1.69 into 10 to the power -4 ampere per centimeter square. Now if we have this data you can easily determine what is the corrosion rate in the form of mdd.

Now mdd I have to express the corrosion rate in the form of mdd. I am just putting the value of Pi, iaM by nF in case of iron, aM equal to 55.85 gram per mole n equal to 2, F equal to 96500 Coulomb per gram equivalent and I know current also, this is nothing but 1.69 into 10 to the power -4 ampere per centimeter square. So if you put all those things into this equation you can get rate expression, corrosion rate expression in the form of mdd. This will be considered – this will be – I will check out this problem in the next lecture. Thank you.

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