## Aqueous Corrosion and its Control Prof. V. S. Raja Department of Metallurgical Engineering and Materials Science Indian Institute of Technology, Bombay

# Lecture – 14 Forms of corrosion: Galvanic or dissimilar metal corrosion (Part-I)

And today we will be talking about an important aspect of corrosion that is called as galvanic corrosion or dissimilar metal corrosion.

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And the topic of the discussion is galvanic or dissimilar metal corrosion. Now, why you should be concerned with the galvanic corrosion? Why we should be worried about the dissimilar metal corrosion? If you look at the engineering components, in many cases consist of multiple metallurgy, multiple metals, they may use in combination like steel and stainless steel, or they may apply as a brass the steel, titanium may be with along with the stainless steels. And there are several reasons for that.

For example, if you consider a pipeline carrying water. And you want have a tap, where you want to take the water out, and you want to regulate it. We have seen when we talked about the galvanic corrosion that the materials requirement for a given application depending upon how critical it is, how critical the corrosion resistance is.

In this case, you take a pipeline, if there is a small amount of corrosion, there is a loss in thickness. And you are not going to see an apparent leak in the pipeline. But if there is a small amount of corrosion in the tap or in the valve, then what happens? The valve or the tap starts leaking, you may not able to control this.

So, while you select a steel for the pipeline, you cannot for obvious reasons choose steel for the tap and valve. Many of you know you would have seen various fittings right that they are made up of either stainless steel or made up of brasses, because stainless steels and brasses they corrode at a lower rate and so the leak is avoided. Now, they bring in similar problems at other places as well.

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I give you an industrial example ok. You know of this right. What is this unit called heat exchanger right. If you look at the heat exchanger, the shell what you see here is in this case made up of a carbon steel. Actually it is this is called an HP heater – high pressure heater in a thermal power plant.

The water is heated to high temperatures and so there is high pressure. So, this is made up of carbon steel. But you make the tubes with the stainless steel because the water in the tubes flow at very high rates and the carbon steel cannot withstand erosion corrosion. So, people go for a stainless steel.

Now, the tubes are stainless steels. Look at the tube sheets this is called a tube sheet ok, this is called a tube sheet right, and this is made up of a carbon steel. Similarly, if you look at the header, for example, this is header here right header this is inlet and this is outlet here. And this header, header is made up of carbon steels.

And these tubes, so what you see here they are impregnated into the sheets you can see this here. So, these are all tubes which are you know which are welded onto the tube sheet. So, you have a combination of carbon steel and a stainless steel being used.

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I give another illustration. You sometimes weld structures which is the stainless steel here, you weld this. The weldment the weld fusion zone we call it could have a different chemical composition as compared to the tube itself.

So, there are different chemistry, basically you can called this is metal 1, this is your weld fusion zone, and the tube we can call it as the another metal. They are coming in contact. Please look at they are coming in electrical contact, they are coming in electrical contact with each other.

The one on the top we see here slightly a different reason where the corrosion occurred here. This is a carbon steel, not a carbon steel it is alloy steel tube, it is a chrome moly steel tube used in boilers ok. Now, what has happened here was copper deposition in these locations.

The copper deposition has happened because the water carried corroded copper metals, corroded copper metal ions. And in fact, that copper ions came some of you might know that when you look at the thermal power plant there is also condenser, you have a steam, the steam goes to steam turbine, they does the work, the steam is getting converted into a water again by a condenser.

And condenser in this case was made up of cupronickel. And copper dissolved and that copper carried all through and got deposited over here. There are copper metal, and this steel they lead to what is called as galvanic corrosion. There are several reasons, the several places you see, the other obvious example that can happen is you sometimes coat steel with a nickel.

You have seen in car bumpers, you know you have seen in washroom fittings to make it looking very good for aesthetic reasons. If the coating is not proper, then you will see a galvanic corrosion between the nickel coating and the steel substrate. So, whenever you have two different metals coming in contact with each other, when I say contact I mean the electrical contact with each other, then it leads to what is called as the galvanic corrosion.

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Two dissimilar metals shorted electrically can lead to Galvanic Corrosion - Oris MM 713 L 14 Cell Mr0, NXL

So, two different metals, two dissimilar metals shorted electrically can lead to galvanic corrosion. This is the origin. The origin of galvanic corrosion comes like this. You know a very famous device most of us use in a very constructive manner where the galvanic

corrosion works and works for the benefit. What is that? Dry cell batteries, you know of dry cell battery right.

In the dry cell battery, take in dry cell battery, what is this made up of any of you, it is made up of a zinc sheet casing right, zinc casing. In the center you will see graphite, of course we will see a cap here right, we will see a cap, and that is a copper cap. The inside you may have something like ammonium chloride and you know and you also have manganese dioxide.

How does the current get generated here? It is getting generated because it is shorted now ok. When these two are shorted, when you short when you short these two right, when you short, the when you short graphite and zinc what happens it delivers a current, delivers a current and voltage.

Now, what is happening to zinc? Does zinc remain intact? How does the current come? The current comes because zinc dissolves and gives rise to electrons; the two electrons are used to reduce manganese dioxide to manganese oxide.

So, there is a voltage between difference between the zinc and this, zinc and this – this graphite electrode, but graphite electrode is not an electrochemical system by itself it is manganese dioxide and manganese Mn 4 plus and Mn 2 plus equilibrium here.

So, between these two, the current flows, and zinc is rendered as anode, and this is rendered as a cathode, and so the corrosion occurs. This is a well known example of the so called galvanic corrosion used very constructively. But this happens in the industries and that is not going to be good for us.

You have a carbon steel, and you have stainless steel, one of these two metals corrode and there is going to be what there is going to be damage to the component. So, there can be leak, or there can be you know it can happen. (Refer Slide Time: 13:38)



So, dissimilar metals can lead to the corrosion actually. Now, why it occurs? 1, we say that there are differing corrosion rates; and the differing potentials. So, if I have two metals, you know you take any environment ok, this is M 1, and this is M 2. I just put the environment, and then they short, and one is you know, so since they have two different potentials you know ok, and so that can lead to these things.

But even before it short it is possible that one will have a higher corrosion rate other will have lower corrosion rate. But if you look at closely, the corrosion rate differences are not the reason, you know, it is not the major reason. One is not the major reason; sometime it may not be reason at all. The second is the reason.

Now, so if you know these galvanic corrosion can occur when we have two different metals they come in contact with this, then we need to know two things. How do we predict which of the two will undergo corrosion at a higher rate, and if it undergoes at accelerated corrosion due to galvanic you know interaction, what is the corrosion rate of that ok. So, we need to know in this case ok, ok.

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6 Com vie Predict ?
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Can we predict galvanic corrosion, first question? Can we calculate, can we calculate galvanic corrosion? So, what is the basis for that, what will the basis for that? So, that we will see. This the third question that comes is what are the factors right?

If you know what are the factors the parameters that control galvanic corrosion, then it is possible for you to methods you know to devise methods of controlling corrosion, control galvanic corrosion. Of course, next is how do we evaluate at galvanic corrosion, how do you evaluate them?

So, let us now look into one after another, and see that we can have a clarity in all this, so that if you are doing a research or if you are developing a material, developing a processes or you are developing a monitoring technique for example, it is easy for you to do all these if you can understand all the five aspects of the galvanic corrosion.

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redicting galvanic corrosion pliential difference Electro motive force +0+1.498 MM 713 L 14 / Slide 07 +1.2 987 +0. +0.799 0.337 0.000 136 250 1.44

Let us take the first one. Can we predict corrosion? We all know the galvanic corrosion occurs primarily because of the potential difference. The potential difference is a reason. We are aware of calculating the equilibrium potentials right, you guys know about the potentials which is the thermodynamic property. In the standard state what you called that potential for the equilibrium? It is called as?

Student: (Refer Time: 19:34).

Standard potentials ok. So, the one readily available data in the literature is a standard potentials. And from the standard potentials, you can also calculate the equilibrium potentials provided you are given the e concentration or activity of species involved there.

For simplicity, if you take the standard potentials and put them in some order, either in the descending order of the standard potentials or in the ascending order of the standard potentials, you can list them by this right, and for different equilibria, and such a list such a series is called as electro motive force series ok. This is called as electro motive force, is not it, potentially it is a force, a driving force for the reaction to occur ok. This is called as electro motive force.

You can have you know atleast I mean you can have 100s of equilibrium not necessarily the equilibrium related to metal and metal ions, you can have between the you know its own species you know, for example, there are some organic molecules, there are even there are inorganic molecules.

Fe 2 plus, Fe 3 plus, any equilibrium can happen, not necessarily metal is involved there. So, you can have a an exhaustive list. But for us if you can look at you know the metals which are somewhat related to engineering applications, you just have a look at them, it is really somewhat interesting.

Look at some of them. For example, let say let us take the system like gold and the gold, and look at the standard potential of that, it has got here, volts right. When it says standard potential, it is implicit it is in relation to the standard hydrogen electrode. So, I do not really have to make mention about it, but all other cases you should make you mention in whose reference the potential is measured. You can also have you know just given few examples here ok. And you can also get it from the lots of published literature ok.

So, this gives you a driving force. Now, the electrode potential, or the standard electrode potential is given in the decreasing order from the highest we have here is a gold, and here lowest is the magnesium here ok. And somewhere you see here the hydrogen. And you know how to interpret this data right.

Suppose, any metal that is lying you know below this hydrogen you immerse it in the acid solution of standard state and in the iron standard state, then hydrogen is going to evolve, and all these above this metal you will not get hydrogen evolution taking place. So, corrosion will not takes place. So, you normally call this as noble right, and you call this as active generally that is how you talk about it.

And the nobility increases as you move from the top to the bottom. And you can compare any two the one just lies above is noble and the one below is considered as relatively active and relatively noble ok.

So, when we talk about all these, we talk about the relative values, not the absolute values right, if you take let say gold in gold chloride, and platinum in platinum chloride, you just couple them together, the platinum will be acting as a anode and the gold will act as a cathode. So, you can predict which of these will undergo corrosion.

What is the basis normally, we use a basis earlier called as  $E_{cell}$  is equal to  $E_{cathode}$  minus

Student: E.

 $E_{anode}$ , it has to be positive right. You recollect our discussion earlier right ok. So, it is possible to use you know this EMF series, and find out which of these metals which are shorted electrically can become anode and become a cathode based on the equilibrium potentials ok.

But can this be true? Can this happen in the real life situations? The real life situation do have a an equilibrium potential or you know standard potentials in the state where the metal is corroding? A steel is immersed in a water, zinc is immersed in water, it will establish a potential right. What is that potential called? When zinc immersed in water.

Student: Cathodic.

And it is what is the; what is the potential called?

Student: (Refer Time: 26:31).

That is simply called as a corrosion potential. So, it is going to establish a potential this is called as a corrosion potential, but what is the; what is the criteria for the metal to establish corrosion potential? How does that value is arrived there, how does the metal arrives at value? What is the basis for that, no?

When you when you take a steel, I mean let us take a iron and put it in acid. And after some time, it will attain a potential, which is steady state, slowly it becomes steady state. And you measure the potential and that is called a corrosion potential. Why does the metal reach that particular potential?

Student: (Refer Time: 27:27).

Yeah.

Student: (Refer Time: 27:29).

See that is a criteria for that. It has to satisfy the mixed potential theory. The rate of anodic reaction must be equal to rate of cathodic reaction, that is the place where the metal will stabilize, and the corrosion potential is stabilized; all other cases the potential will drift it will drift towards that actually that is a criteria for that ok.

So, in actual real life situations, the EMF series or the equilibrium potentials, they have very less relevance to predict the galvanic corrosion. So, what is the potential that is relevant actually?

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Corrusion Potential is relevant Equilibrium potential is melevan CDEEP pure IIT Bombay Alloye in Metab Galvanic Series graph MOSS Parine passive rickel > active

So, we look at what is called as corrosion potentials is relevant, and equilibrium potential is irrelevant. What drives them, what drives the current between let say zinc and iron immersed in any environment you know may be water, may be in acid, what drives actually?

What potential is that? It is the corrosion potential that drives the current between these two metals. Now, when you take corrosion potential, there is a problem. What is the problem? The corrosion potential is it unique to unique to a metal actually I take steel. Do you think the corrosion potentials are sealed to be same in all corrosive medium? Yeah.

### Student: No.

No. So, the corrosion potential of the metal will very much depend upon the environment, the temperature, the pressure, the concentration of the species nature of the species pH, the so many variation that you will get and you would probably must have a million of million data of  $E_{corr}$  values to compare. So, that is simply not possible in practice.

So, they developed a potential based on metals and alloys in pure seawater. Again pure seawater also questionable right. The composition of the seawater in Arabian Sea, may be

Bay of Bengal may be different ok. It was measured in US at Ann Arbor ok, it is deep inside the sea, so that the pollutants and all are not going to influence the corrosion potentials.

Again I do not know how many of you know even in a given environment, the corrosion potential is not going to be unique like you see in the case of equilibrium potentials. It can vary by few millivolts, 5 millivolts, 10 millivolts can really change the way you prepare the sample, sometime you prepared a very nice smooth samples, sometime mirror finish.

So, you are not going to have a unique  $E_{corr}$  value even a given environment even for a given metal alloy. So, you can only look at the relative performance, relative values of the corrosion potentials that is why we will see the Fontana books and many times they give you a relative positions and not the relative values.

You also see the ASM handbook the corrosion values are given as a band of values; you are not going to get the unique values. Why, it is kinetics, ok. Because of the kinetics, you are not going to have unique  $E_{corr}$  value, and so there is going to be a band of value you are going to have it.

So, what they have done is the pure seawater, and they list the corrosion potentials of that, and that is called as a galvanic series. I can just give some illustrations here ok. And if you see in the published literature, you will see lots of data, but let us give some important you know metals and alloys.

Platinum tops here, then you get the gold, then you get the graphite, titanium, ok, you have silver ok, you have say 18-8 moly stainless steel passive, and nickel passive, a copper nickel ok, you have copper zinc, and you have tin stainless steels which are active, cast iron, steel ok, aluminum alloys ok, have zinc. Before that I think you will get cadmium, you have aluminum, have zinc, magnesium, we are just moving from here like that.

So, you see some interesting behavior in the metals and alloys in galvanic series vis-a-vis the EMF series. There are some of them very obvious you can see that ok. I hope you will you could able to recollect some of them ok. I just put back here. You can have a look at this galvanic series, I am sorry the EMF series, you see how they are looking like this here ok. And titanium comes somewhere here, titanium comes titanium will come, in fact, the titanium will come even somewhere here actually ok. Titanium will come even below magnesium, is not it? How do you extract titanium? Use magnesium to extract titanium actually the Kroll's process, ok.

So, titanium come even below actually one of the most reactive material, is titanium. Compare this, and compare this, and what are the obvious differences, do you do you see right? What are the obvious differences you see in this? No differences?

Student: (Refer Time: 35:53).

What do you see?

Student: Alloy.

The first obvious difference you find is in the EMF series, you do not see any alloys you see only pure metals right. In the galvanic series you do see alloys and metals that is one major difference. What is the other difference?

Student: Water environment.

Of course, it is a sea water ok, of course, there is that is of course in a standard state or so it has to be its own ions that is of course, that is another implicit difference that you have. Anything more you see?

Student: Sir, very reactive in the electro motive force (Refer Time: 36:46)?

Yes, we see you know some of them which are reactive in the electro motive series, as I said titanium will be figuring somewhere here ok. The titanium is going go up. Even between platinum and gold the platinum acts relatively noble as compared to the gold actually, see there is a reversal taking place.

And even more important is the stainless steel exhibits the galvanic potentials at two locations the passive state and the active state. You know what the passive state is you know what the active state is right.

So, metal, when is passive, the potential is noble; when it is active the potential is relatively more negative potentials active potentials. You know the reason why it is right. Why does

it happen? When the metal spontaneously passivate, what happens to the  $E_{corr}$ , does it go up or come down, what happens? Anybody recollect that?

It goes up right you, if you look at the active passive trans passive polarization curve, you best recollect that the  $E_{corr}$  will lie at a very you know close to equilibrium potential if the alloy is not spontaneously passivating. If it is passivating? The potential will shift up.

So, obviously, that potential is noble compared to the metal exhibiting active potentials so. Stainless steel itself can form galvanic corrosion between themselves in the active state, in the passive state, you will see later that you know in act in a pit for example, it will act as a anode surrounding the pit, it will act as a cathode we will see that later ok.

I hope you are getting this point right. So you please do understand this. If you do not understand this you cannot predict galvanic corrosion in reality where what happens in the field ok. I hope you able to see the differences very clearly between these things so, practically we use the galvanic potentials.

Ideally if I am choosing an alloy somebody, somebody comes to you, and they ask you to select two different materials for application. What data do you seek? I need a steel and stainless steel or maybe somebody says I want to use titanium, and I want to use stainless steel I need to do together you know.

So, what data do you seek from, you say that use it or, what you do? So what is the environment you are looking at you know and that put and that environment you should get the corrosion potential that is what the right thing to do that. But if you do not have that data, now I have two tables. I have a table 1 which is a galvanic series, and the table 2 which is say EMF series, they are available readily for you. Which one do you use? I will use galvanic series because galvanic series is more reliable than the EMF series.

But do understand that there is no galvanic series which is applicable all through any environment. I give an example suppose in the rooftop you know you are going to use a you know two different metals. The galvanic series for that atmospheric corrosion is different from the galvanic series that you find in seawater, because some of them may passivate, something can happen ok.

So, it is important that you keep in mind that the galvanic series what you list here is seawater that should be used very cautiously only when you do not have the data corresponding to given application; otherwise you need to generate the data and that data can only be employed in selecting the materials material selection ok.



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Now, let us take the case of the galvanic corrosion what are the factors that affects the galvanic corrosion. We saw the potentials right. Now, what is that that governs the galvanic corrosion of the metals.

Let us take two distinct examples, a simple one and a complicated one, so that you can understand the electrochemical parameters that affect the galvanic corrosion rate of a metal. We have seen that when the galvanic potentials are different the one with the noble potential will act as a cathode, the one with the active potential will acts as a anode that you know that. But you do not know what rate at which the active metal will undergo corrosion.

So, how do you electro chemically you understand that? So, let us use the so called the Evans diagrams to understand this ok. Let us take the case of say iron and say platinum in let say 1 molar hydrochloric acid. How do I get this? Can you do? Now, I think you guys have mastered the kinetics and we discussed this for about 10 hours of lectures we discussed right. How do you do this? Anybody has a clue? You go apply mixed potential theory right.

So, first of all you apply mixed potential theory for platinum separately, mixed potential theory for steels I mean iron separately, you get the  $E_{corr}$  and  $i_{corr}$  for iron and platinum in that water without coupling them galvanically you know the corrosion rate. You put them together now.

Now, you rearrange all of them actually. Again mixed potential theory is applied what you do what do you say the total anodic reaction is equal to total cathodic reaction in overall system ok. You solve that equation, then you will get oh, which undergoes what or what rate it is happening at all taking place. So, simple galvanic theory ok, it can be involved by applying the Evans diagrams ok.

Suppose I take platinum, let us take platinum. I just take platinum here and you know in the case of let say take the platinum here now in the case. Now, what happens you go for standard states for simplicity let us go standard state, what is the equilibrium potential of platinum?

Student: 1.2.

This is 1.2. What is this platinum? 2 plus plus 2 electron gives you

Student: Platinum.

Platinum. Am I right?

$$Pt^{2+} + 2e \rightarrow Pt$$

And what about the other at equilibrium? Now, what happens in this case, will platinum corrode? Does platinum corrode? Platinum does not corrode at all. So, practically we do not use the dissolution or the platinum equilibrium when you talk about iron right.

Because you see here now when you put platinum and you in a acid and you shorted with a hydrogen, you will always have the hydrogen gas dissociating into H plus, and platinum will not dissolve ok. So, we do not normally use this. You have to see in the Fontana book; we do not see that this is there at all ok. And for iron, it is easier right. What is this cathodic reaction here? This is your exchange current density for what hydrogen on?

Student: (Refer Time: 47:34).

Iron, please understand that ok. So, this is your cathodic reaction, H plus plus electron gives you hydrogen like this.

$$H^+ + e \to \frac{1}{2}H_2$$

So, iron when iron corrodes, you have hydrogen evolution taking place. Now, let us put this together and see how the galvanic reaction occur between platinum and these things right.

So, this is platinum separately immersed in the acid, iron immersed in the acid separately. Now, if I am going to be together what happens? Now, let us look at this. This is iron and platinum shorted. This iron separate, platinum separate ok.

What are the equilibria you would have to be considered, there are only two equilibria to be considered. One is H plus is in equilibrium with hydrogen; iron is in equilibrium with Fe 2 plus. Am I right or not? Platinum 2 plus, platinum does not come into picture at all. Will it come? Does not come into picture right.

So, let us take the case of iron here. Let us take the case of iron right. This is your Fe 2, Fe going as Fe 2 plus plus 2 electrons.

$$Fe \rightarrow Fe^{2+} + 2e$$

Now, what is this called exchange current density for H plus and H on iron, please look at that ok. And this you want to put iron here you can draw this diagram for iron. This is see this is your exchange current density for Fe 2 plus Fe, and this is your  $E_{corr}$ ,  $i_{corr}$ .

Now, I want to represent now this is clear right, this is I am same thing I have written here only. Now, I want to now represent platinum in the solution. How do I represent now? What will happen on the platinum surface you put it an acid in a hydrogen, what equilibrium will be there in the surface of platinum.

Student: H plus H.

H plus H right. So, what is the how do you represent here? What will be the potential there? Will the potential of H plus H on platinum and iron will be different or same? The equilibrium potential for H plus H or iron and platinum, will it be same or different? Why

it will be different? How do you find out the equilibrium potential for H plus H. Come on quick. How do you find out the equilibrium potential? Can you find out or not, how do you find out?

Student: Number.

So, it is Nernst equation there is not it. Where has it come into picture by its platinum or an iron? The equilibrium potential does not depend upon iron or nickel whatever, it is talks about the partial pressure of hydrogen and the concentration of H plus ions that is not going to change. So, the equilibrium potential of that will remain the same, not going to change. This is the equilibrium potential of H plus and H right. But what is going to change on platinum?

Student: (Refer Time: 52:04).

Come on, I want to see you people talk, you guys no, come on. What is going to happen? Can you look at your handout anybody has the handout now, what is the exchange current density approximately for H plus H on platinum?

Student: 10 power.

10 power.

Student: Minus 3.

Minus 3 what amperes?

Student: Ampere per centimeter.

Centimeter square. For iron how much?

Student: Minus.

Minus 6.

Student: Minus 6.

So it is about 3 orders of magnitude higher for that. So, the exchange current density for that is going to come, come somewhere here. Am I right?

The Tafel slope remain the same. So, I write the Tafel slope here. This is the exchange current density  $i^{o}_{(H^+/H(Pt))}$ . Agreed or not agreed? So, this is on platinum. Now, what is the mixed potential theory? You sum up all the cathodic reactions and sum up all the anodic reaction.

Am I right or not? So, sum up this when I sum up this become so small. This is going to be your place where the mixed potential theory is applicable, and this is going to be is what this is your i<sub>corr</sub> of what of iron combined with platinum here. What happened to this one?

This is my equilibrium potential, sorry this is your  $E_{corr}$  of iron and when you short with platinum agreed ok. Agreed, not agreed? Now, if you agreed on it, now I am going to ask the question now to you, let us make the observations here.

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Now, you make let us look at the observations ok. They are in acid let say 1 molar HCl. Please notice they are not shorted now, just put it here. If you can closely observe the surface of iron, surface of platinum, what do you what will you see there, will you able to see anything or not? There will be?

Student: Bubble (Refer Time: 54:57).

What bubble, what bubbles it will be where there will be a bubble? Platinum? Where there will be a bubble?

### Student: Iron.

In iron right. In iron there will be gas bubbles what do you have what will be the gas the gas will be? Student: Hydrogen.

Hydrogen gas. I think you should have given simply one answer hydrogen gas that talks about you know you people are clear about it you know ok. So, you have a hydrogen evolution taking place on the on this.

Will there be hydrogen evolution on platinum? No, because platinum cannot get oxidized ok. So, there will be hydrogen evolution taking place. Now, what happens, I going to take it out and I am going to short this. You observe now what happens, where will the hydrogen evolve?

#### Student: Platinum.

Platinum right. Now, the hydrogen will not evolve, there will be less hydrogen evolution on iron, there will be more hydrogen evolved on the platinum right. So, the hydrogen evolution will start shifting from here to this what happens.

So, there will be more hydrogen evolution on iron compared to that on the platinum, the amount of hydrogen evolution on iron is less, but then the amount of hydrogen evolution on iron and platinum put together will be equal to the amount of iron corroding on iron surface. Can I say that actually am I making a sense?

#### Student: Yes sir.

The amount of hydrogen and evolved on platinum and iron, if you look at it ok, iron take this quantify which is which should be equal to the amount of iron that is getting corroded on the iron surfaces that is how the mixed potential theory is. What is mixed potential theory? The total amount of reduction is equal to the total amount oxidation takes place.

Now, in this case, if I measure the potential here using a voltmeter, what will happen to potential of when I shorten this, the potential of this, this will be same only, am I right, assuming that the conductivity is very very high conductivity here. When I put then this together, the potential will change. Now, what will happen to the potential of this system when short it?

When I do not short it, the platinum will exhibit a potential is equal to what potential equal to hydrogen equilibrium, whereas iron will exhibit a potential equal to corrosion potential right. Now, when I short this, what will happen to potential of these two? Go up, please look at your diagram only ok, what will happen to these potentials?

### Student: Increase.

It will increase right. The potential starts moving from here to this. I want you to look at the diagram. If you do not look at the diagram, analyze it, you cannot guess it, I think the moment you guess it you are finished. You have to look at the diagram. See what happens here is the potential start moving from here to this that is what happens mixed potential ok, it moves up here ok.

The potential moves from here to this, because this is a mixed potential theories you know because moves from here to this the hydrogen evolution on iron what happens now look at this the hydrogen evolution on iron is not decreasing. The amount of hydrogen evolution on platinum is more because now it is moved from this potential it is moved to this potential.

So, the hydrogen evolution on platinum is increasing because at when you just immerse platinum in the solution, this is the potential you are going to have it. And shorting the potential moves from here to this, but for the iron the potential moves from here to this, so that means, the hydrogen evolution on iron is decreasing, the hydrogen evolution on platinum is increasing from here to this. So, that is what will happen. I hope I think there will be an experiment in the lab I did not know how many of you already done it.

If you are not done it, you please do observe this, this particular test. I want you to observe it and see does it really happen or not happen at all ok. So, this is something you should be looking at actually ok. You, clear about?

Student: Diagram.

Yeah.

Student: Platinum (Refer Time: 59:12).

First means you are talking about this right ok.

Student: Also we know that platinum does not corrode.

Yes it does not corrode.

Student: By this, curves intersecting.

Which is it is intesecting in this point that is right; yes,.

Student: How we explain like with respect to this particular?

How do you explain this now? Suppose, I take a platinum right, I a more dip it in a sulfuric acid, and I shroud the sulfuric acid completely with the hydrogen let say 1 atmospheric hydrogen. So, what do you think will happen there? What do you think will happen what you can happen is of course you will establish the equilibrium actually ok, we will establish an equilibrium ok.

Will ok will this go to this one, it may not go here also. In fact, this will not go here ok. Suppose, assume that this guy is getting oxidized suppose you are getting oxidized right, there is must be reducing species to take. If I have platinum ions in this solution, what will happen to platinum ions, the platinum ions will get reduced.

So, you visualize the other situation I have platinum in the solution as platinum 2 plus, and I have 1 molar hydrochloric acid and I am also putting hydrogen in the system. I keep putting the hydrogen in the system what will happen now? Slowly platinum ions will get deposited as platinum metal will happen ok.

If on the other hand, there is no platinum ions in this solution what will happen, nothing will happen, the potential will remain here only because if hydrogen dissociates as H plus and electrons there must be some species should take electrons at all right. There is no species to take electrons at all that means nothing will happen there that is why platinum is considered as a reference electrode in this case.

What is the platinum actually? Platinum immersed in acid and shrouded with hydrogen. What is equilibrium there, the equilibrium is between H plus and H there is no oxidation no reduction take place, it goes both ways right that is why platinum in acid is considered as a reference electrode where there is no net oxidation no net reduction taking place. If you add some platinum ions obviously, all the platinum ions will slowly get reduced to platinum at all actually. So, question now, you are right you would not go here, it will remain here only ok.

Student: Sir, line is not applicable.

But, then the moment I am going to put platinum chloride, this line applicable is not it? If I put a platinum chloride, what is this one actually that is why I put here platinum 2 plus plus 2 electron gives you platinum, that means, the guy has got platinum ions here. Is no platinum ion, this guy will not even come at all actually here ok. You are right if you are going to use if you are going to read this title iron platinum in 1 M HCl probably, this fellow does not even figure here ok.

From that point of view it is correct. I just drawn this only to illustrate to you how the equilibrium will start shifting. If you do not have platinum ions, there will be no way you will get the hydrogen dissociation as H plus ok. It will dissociate again will reduce, there will be equilibrium establishing between platinum between the H plus and H on the platinum surface that becomes your reference electrode that is what happens at all actually.

Student: From the iron platinum couple system third diagram.

Yes.

Student: Dotted line represent according to the mixed potential theory the final outcome right.

What is this dotted line correspond to yeah it is good, what is this dotted line, what is this dotted line means?

Student: The sum of those (Refer Time: 63:13).

The sum of this: the hydrogen reduction reaction for this, iron reduction this iron reduction reaction occurs in the iron surface given by this kinetics. Hydrogen reduction reaction occurs in a platinum surface followed by this solid lines. So, what does it mean? If I hold; if I hold iron at that particular potential, the amount of hydrogen on iron is only this much, but on platinum it will be this much. But if I have both platinum and iron together, the total will be this much, is not it.

You just I know assume that I have a platinum and platinum, platinum and iron together, I shorted and I apply a common voltage, what will be the amount of hydrogen will takes place? This is on the iron and this is on the platinum the total will be for that particular potential that is the amount of thing that happens. Instead of your platinum I am going to put gold you look at the gold what is the value of gold actually there, exchange current density is given not given there?

Student: 10 to the (Refer Time: 64:23).

10 to the power minus 6 right. So, 10 to the power minus 6 is coming very close to this right, 10 to the power minus 6. Probably you will not get a huge difference in the hydrogen evolution reaction if it is a gold ok.

So, the line will shift towards this. So, the effect, in fact, we will see later the effect of galvanic interaction of gold and steel will be low as compared to the galvanic interaction between platinum and steel ok, because the exchange current density on gold is lower for hydrogen equilibria as compared to lot of platinum ok, so, that is what. We are now looking at what the kinetic parameters. So, what are the kinetic parameters that they are do not affect this now.

Now before we close, I want to look at this here. Look at what are the and look at this is the anodic Tafel slope of the active metal and a cathodic Tafel slope of the other one is ok. I think we will talk about this when we when you deal with two active metals. Here it is noble metal; here it is an active metal. So, we will see what happens when we have two active metals how they will change ok. And I think today I mean we can stop here provided you have any questions for clarification.

Student: Magnitude of water for the hydrogen evolution on platinum is that much that means in general we see that iron on iron there will be no hydrogen evolution when they (Refer Time: 66:08).

Virtually no hydrogen.

Student: Virtually.

But you cannot say no hydrogen.

Student: No hydrogen, virtually no hydrogen.

Virtually no hydrogen.

Student: Will it suppress that much the in that much that it suppresses all the hydrogen evolution?

That is because of that it is again we go back to same thing the Evans diagram only it talks about the relation between the potential and the current. You have a platinum here that is all. But what is the role of platinum? The role of platinum is to lift the potential from here to this otherwise the platinum is not talking to this steel at all anyway right.

Because it is lifting the potential here it is happening; otherwise any other metal will lift to that where value will happen. So, it is again the same Tafel equation is valid. You moved from here to here, you apply the Tafel equation you would still get the value ok. So, it is platinum or something else something else does not matter at all because as long as you know you follow the same Tafel line, this is the Tafel line at all ok. On the other hand, you move down the hydrogen evolution on iron will increase right

Student: Yes.

Ok, so that we will see later. When will you move down that you will see actually that will happen if you are going to take about a more active metal than iron the things will different, we will talk about it in the next class.