Aqueous Corrosion and its Control

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Lecture – 02

Concepts/governing relation for predicting if a metal can corrode: Electrochemistry of corrosion

Can we predict if a metal corrodes? (Part-I)

Welcome to the 2nd lecture of this course Aqueous Corrosion and its Control. Before we proceed today’s topic I like to recollect what we discussed in the last class. We defined what the corrosion is; corrosion essentially means the interaction of the material with the chemical environment leading to loss of materials, loss of function and that is the way it should be defined.

We also looked at what are the implications of corrosion of engineering components. We saw that there is a huge loss for the nation in terms of a 3.5 to 4 GDP for any industrialized nation. And more importantly the consequences of corrosions are very severe; it can affect the safety of the people the environmental degradation can happen because of corrosion and in consequence of the pollution of the products with environment.

You can also affect the reliability of the components you can also affect the product quality. For example; manufacturing a pharmaceutical drugs. It is very important that these drugs are pure or you transfer water for drinking the water has to be pure. You can affect the products you can also affect the appearance of some of these you know components or maybe like you see the automobiles and so on.

So, this requires a concerted effort in order to control corrosion to large extent. We have seen in the last class also that thermodynamically the metals and alloys we deal with are unstable when they come in contact with environment.

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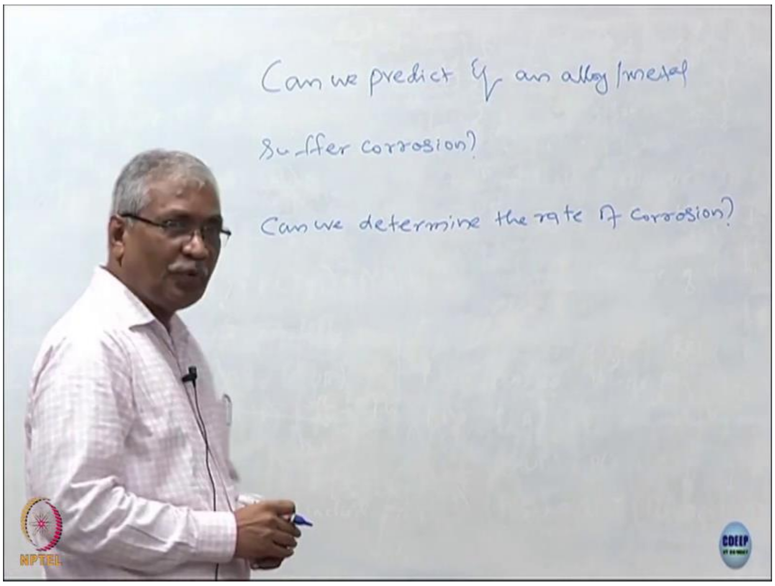

Can we predict if an alloy/metal
suffer corrosion?

Can we determine the rate of corrosion?

Now, the question comes to us is can we predict whether a metal can undergo corrosion or not. Can we predict if a metal can undergo corrosion if an alloy or a metal will suffer corrosion? Can you predict without doing an experiment can you predict? If we can so predict then can we really determine the rate of corrosion. These are the two fundamental question that we need to know we need to address before we address the actual corrosion problems.

Now, let us take the first one; can we predict if an alloy or metal can suffer corrosion in a given environment. Before we address this question we need to go a little deeper into what a corrosion means?.

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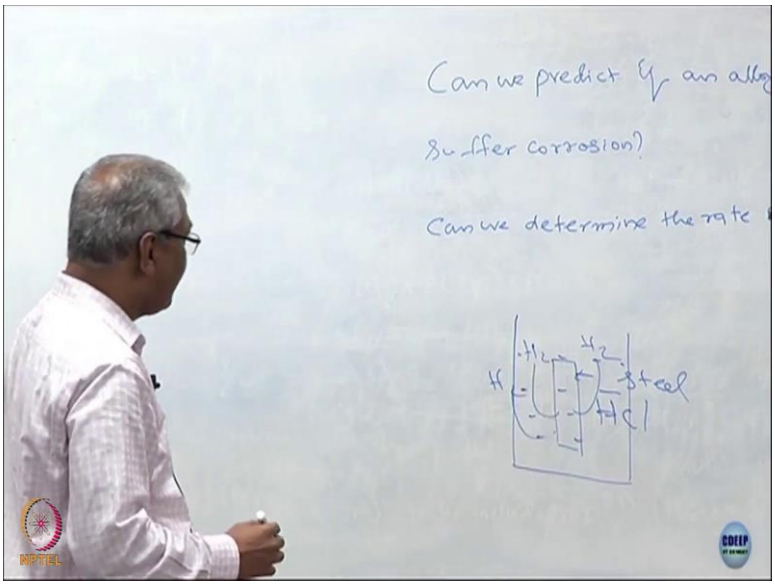

Say, take an illustration; if I take a beaker and I fill this with let us say hydrochloric acid. And I immerse let us say steel I must steel into this right immerse steel. The major constituent of the steel is what? Is iron right?

So, what do you think will happen here? What do you observe? Will that be corrosion in hydrochloric acid? Yes. So, what do you visually observe? You will observe with your eyes the evolution of hydrogen right then the gas. You may not know exactly it is hydrogen or not. You will see that the gas is being evolved on the metallic surface.

We have seen in the last class that the corrosion is oxidation of metal at the same time that has to be a reduction reaction right. The es so liberated during oxidation process need to be accepted by some species. So, there is an oxidation process it is reduction process. So, let us write this corrosion process in a chemical equation ok.

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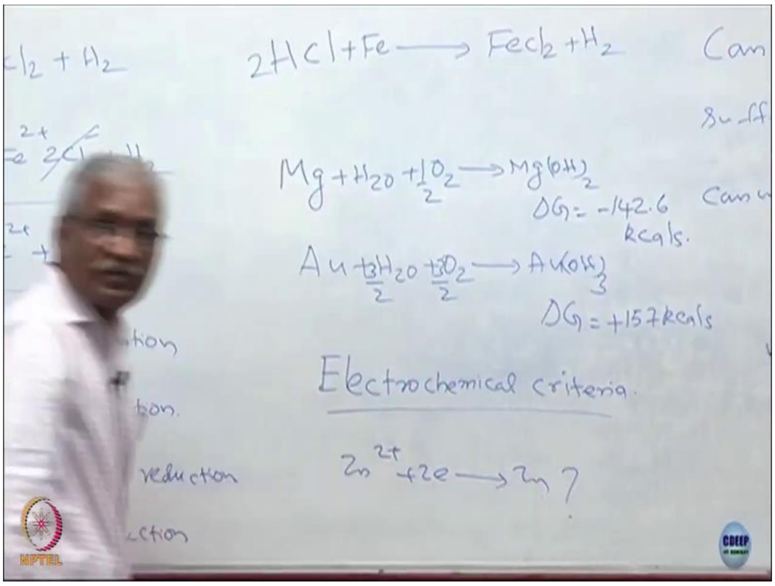

How do you write this? Hydrochloric acid you put let us say steel I simplify it as iron. And when they react with this what it forms? It forms $FeCl_2 + H_2$ right.

$$2HCL+Fe \longrightarrow FeCl_2 + H_2$$

So, this is a corrosion process the metal is getting oxidized and the hydrogen ions in the hydrochloric acid turns into hydrogen gas by reduction process.

Now, like that we can have several type of corrosion process. The iron can be immersed in sulfuric acid, the phosphoric acid. Can we really predict if the corrosion can occur with any chemical species? What is the first approach for you? It is a thermodynamic right, you look at the thermodynamics. What is the parameters you normally look at? Any of you?

Student: Free energy.

Your free energy change.

Student: Change.

Your free energy change for the reaction has to be negative; then that reaction becomes spontaneous. Please notice this is a spontaneous process the corrosion all along we refer to a spontaneous process we do not supply external energy for the corrosion to occur. See it is an external I mean it is an external agent, but a spontaneous process.

So, look at the change in the free energy for a reaction that will tell you if the reaction will be spontaneous or not. Can you give some examples the obvious example is;

$$Mg+H_20+1/2O_2 \longrightarrow Mg\ (OH)_2; \triangle G= -142.6\ Kcal$$

ok. And the free energy change for this reaction is the △G for this is -142.6 kilocals.

Now we can say that magnesium for sure will corrode what is exposed to water. I have introduced one more species here which is oxygen right. Water has dissolved oxygen present to the react and form magnesium hydroxide; it is a corrosion process.

The free energy change for that is negative so confidently you can say the reaction occurs. We also know of metals which are not undergoing corrosion when you immerse in water. The obvious example is what? Is a gold right? Gold does not undergo corrosion right.

So, you can write the equation for that gold immerse in water it consists of oxygen there, it forms $Au(OH)_3$ right. And you can balance the equation here, the free energy change if you calculate if this reaction has occurred is + 157 kilo cals.

$$Au + 3/2\ H_2O +3/2O_2 \longrightarrow Au(OH)_3\ ; \quad \triangle G=+157\ Kcal$$

What does it mean? If this reaction has to occur you need to supply this energy, over here you derive energy, energy is comes out of the system. So, this reaction is non spontaneous and so you can conclude that it is possible to predict based on the free energy concept whether the reaction will occur or not.

But think of a corrosion process like you have a steel tank holding sulfuric acid, you want to know corrosion occurs or not, or think of a case where the pipeline is buried in the soil now there are two types of corrosion. Corrosion occurs because of the soil interaction, the corrosion occurs because some product goes through the pipeline it could be a petrochemical product, could be a water.

How do you really predict? Can we really go on determine the free energy change for all this corrosion processes? It is not very easy ok. So, although the fundamentally the free energy change is easy to use easy to understand. In practice it is not very easy to determine this actually. So, this cannot be used with comforts in predicting whether the metal will undergo corrosion or not.

So, we need to go for a different criteria and that criteria is going to be what is called as electrochemical criteria ok. Now we need to understand before we get into defining the criteria we need to understand what is an electrochemical reaction ok. So, that is important to understand.

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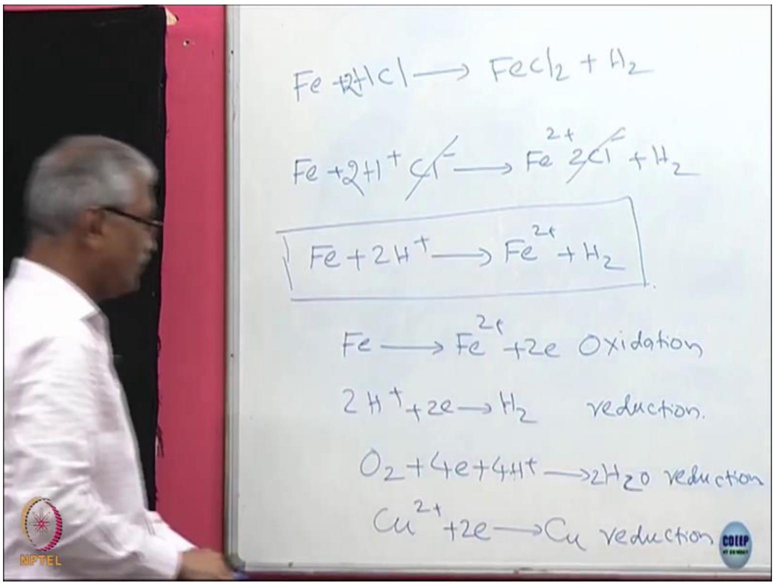

$Fe + 2HCl \longrightarrow FeCl_2 + H_2$

$Fe + 2H^+ \cancel{Cl^-} \longrightarrow Fe^{2+} \cancel{2Cl^-} + H_2$

$\boxed{Fe + 2H^+ \longrightarrow Fe^{2+} + H_2}$

$Fe \longrightarrow Fe^{2+} + 2e$ Oxidation

$2H^+ + 2e \longrightarrow H_2$ reduction.

$O_2 + 4e + 4H^+ \longrightarrow 2H_2O$ reduction

$Cu^{2+} + 2e \longrightarrow Cu$ reduction

Let us go back to this equation here ok. Look at this equation; iron I write again iron reacts with hydrochloric acid and forms $FeCl_2 + H_2$

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

Do not worry too much about the chemistry I think we will try to minimize as much as we can ok, but you have any doubt any time you are free to you know ask questions I will clarify that ok. But some amount of chemistry is very important in order to understand the corrosion process.

Let us take this reaction now look at closely; your iron it is in the metallic state. The hydrochloric acid is in what form? You have an ionic form $2H^+ Cl^-$. And you have ferric chloride is in the ionic form $Fe^{2+}2Cl^-$ and it is in the molecular form.

$$Fe + 2H^+Cl^- \longrightarrow Fe^{2+}2Cl^- + H_2$$

With this you can understand very clearly how the charges are getting a transfer ok.

So, what is common here? And I think I need to change this please change this reaction here I think there is a mistake over here also I think you need to change that ok please change that its not properly balanced. So, it should be 2 here right. Now what happens you can strike this, you can strike this what remains iron interacts with $2H^+$ and giving rise to what and giving rise to Fe^{2+} + H_2. So, this is the actual corrosion process occurring on the metal. You call this electrochemical reaction because the charges are transferred.

Let me write it again to make it clear what happens; iron goes into solution as Fe^{2+} and you have $2e^-$

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

And then these es interact with hydrogen ions and form hydrogen molecules.

$$2H^+ + 2e^- \longrightarrow H_2$$

Now it is clear the corrosion process consists of what? Consists of an oxidation and it consists of a reduction process.

We saw this pictorially in the last class; that iron gets oxidize as Fe^{2+} releases $2e^-$ then these $2e^-$ accepted by H^+ and this so release, releases hydrogen. So, you have one oxidation and at least one reduction process I can make it more complicated how do I make it more complicated? Assume that the hydrochloric acid as dissolved oxygen right.

Student: Yes sir.

Can oxygen dissolved in water? It can similarly the oxygen can dissolve in this. So, you can have one more reaction what is the reaction it could be?

$O_2 + 4e^- + 4H^+$ and it leads to water . $O_2 + 4e^- + 4H^+ \longrightarrow H_2O$

So, you can have one more reduction reaction.

So, the same es provided by iron can go to H^+, can go to O_2 here, H^+ and it can form water. So, you can have many reduction reactions. You can add if you want for example, I have a copper ion in the solution Cu^{2+} can combine with $2e^-$ you can form copper.

$Cu^{2+} + 2e^- \longrightarrow Cu$

So, there can be another reduction reaction. So, you can make it more and more complex ok.

In fact, in practice the corrosion processes are always complex it is not that simple many reaction can really occur. It looks very difficult now can we really predict the metal corrode or not? That is the task. So, that we will see that how you can simplify this and you can write a simple equation to show that; yes it is possible this reaction can occur.

For example, I have put $Cu^{2+} + 2e^-$ gives Cu as reduction. Can I write like can I write say $Zn^{2+} + 2e^-$ giving as Zn and iron corrodes. Can I write like that, is it possible you? You can ask questions. It may not be possible so that is what we are going to look at in the subsequent lecture ok. So, how do we really predict these reactions occur or not ok. So, far any of you have any questions ok. So, it is clear now.

So, let us go to the next step of our you know our understanding towards how do you predict if corrosion occurs.

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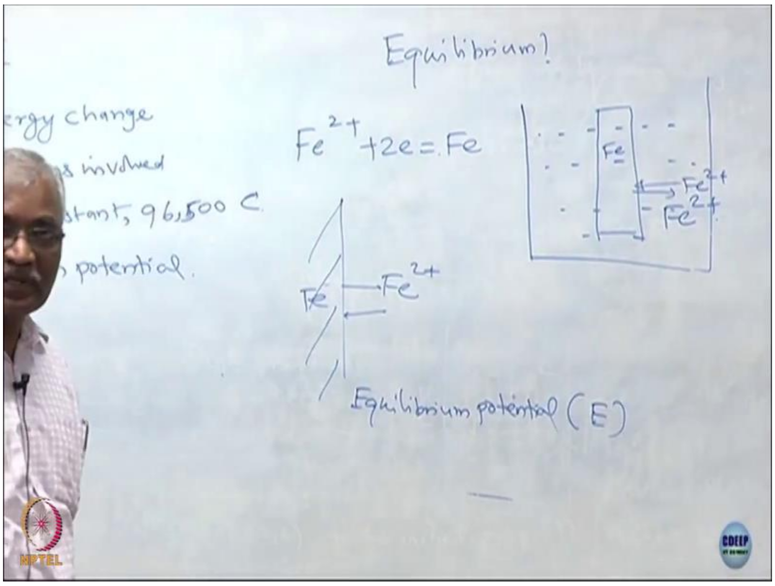

You are aware of what is called as equilibrium. You aware of this right.

Student: Yes.

What I mean here is a thermodynamic equilibrium where the rate of the forward reaction is equal to the rate of backward reaction.

Now, if you deviate from the equilibrium, what happens? Either the forward reaction is faster than the backward reaction or the backward reaction will be faster than the forward reaction. So, let us use that concept let us first of all define what an equilibrium is? What an electrochemical equilibrium is? Why you are defining electrochemical equilibrium? Because we consider the corrosion is in electrochemical process.

So, first let us define what is an electrochemical equilibrium. Let me go to the iron dissolution in sulfuric acid. Let us look at the equilibrium of iron in the solution if I take a beaker and I take in this a solution consisting of Fe^{2+} ions right. And then I immerse a pure Fe in this; this nothing else Fe^{2+}, irons are in the solution iron is immersed in the solution.

So, what is expected would happen? What is expect would happen is that iron will go into solution as Fe^{2+} will happen now? The Fe^{2+} will again go back as iron that is in equilibrium ok. If the rate of this forward reaction and the backward reactions are equal; then we say it is under equilibrium condition.

Now, I write this equilibrium here $Fe^{2+} + 2e = Fe$. Please notice this is an equilibrium sign Fe^{2+} is in equilibrium with Fe; this rate of reaction forwards the rate of reaction backward and both are equal. When this happens at this interface the interface between what? The interface between the iron on the solution you establish a potential right.

So, I define it as I have metal surface here and I have Fe^{2+} ions they go and go back and between these two interfaces between these two solutions ok. A potential is being established and that potential is called as equilibrium potentials that is called as an equilibrium potential.

I can have two ways of looking at it; I can look at from thermodynamic point of view what is the free energy change for this equilibrium to exist? Delta G and at the same time I can also define this process in terms of equilibrium potentials. I define as E and there exist a relation between two; what are the two? The free energy change and the in-equilibrium potential remains two right that exists a relation between these two. What is this relation famous relation? Most of you would have studied long ago right.

Student: (Refer Time: 24:07).

10th or 11.

Student: (Refer Time: 24:08)

We call famous Nernst.

Student: (Refer Time: 24:12).

Equation right the Nernst equation is known for us and one second. So, we know the Nernst equation. What is Nernst equation?

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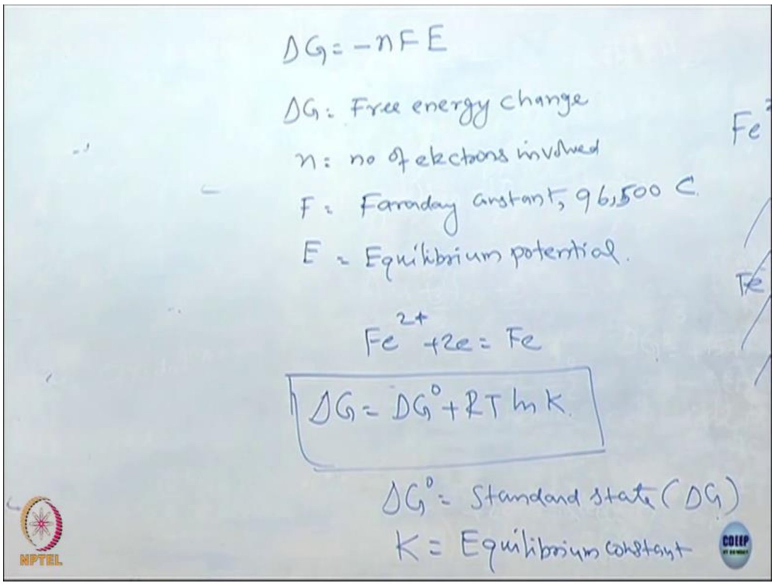

$\Delta G = -nFE$

ΔG : Free energy change

n : no of electrons involved

F : Faraday constant, 96,500 C

E = Equilibrium potential

$Fe^{2+} + 2e = Fe$

$$\boxed{\Delta G = \Delta G^0 + RT \ln K}$$

ΔG^0 : Standard state (ΔG)

K = Equilibrium constant

$\triangle G=nFE$

$\triangle$G is the free energy change for the reaction n is what? The number of es involved in what? Involved in oxidation and reduction process and F is Faraday constant. And it is what is the value? Any of you?

Student: 96500 C.

and E is the please notice I write this as equilibrium potentials. I write this mass equilibrium potentials; potential that defines the equilibrium state.

We are not talking about corrosion; what is corrosion? It is a spontaneous reaction of oxidation and corrosion I mean oxidation reduction process over here. No, we are talking about they are just in the equilibrium. Does iron corrode here? Does it corrode? Does not corrode at all you wait for 1 day or 1 year the rate of oxidation of iron is equal to the rate of reduction of iron nothing happen.

So, we are now only defining the equilibrium state ok. So, you have

$$\triangle G=nFE$$

Now I have a reaction, I have an equilibrium for example, I have something like Fe^{2+} + $2e^{-}$ gives you Fe. If I need to know the free energy change for that and related to the potentials I have

$$\triangle G= \triangle G^0 +RT\ln K$$

right. We people are aware of this equation. What is delta $\triangle G^0$ here?

Student: (Refer Time: 27:29).

At the standard state ok. So, is it is the standard state ok. A standard state G is equal to the free energy change. So, the free energy change can be related to the $\triangle G^0+RT\ln K$, what is K here? Any of you? K is equal to the equilibrium constant, it is called an equilibrium constant. What is equilibrium constant? Can somebody, can you can you tell from here how do you expand this?

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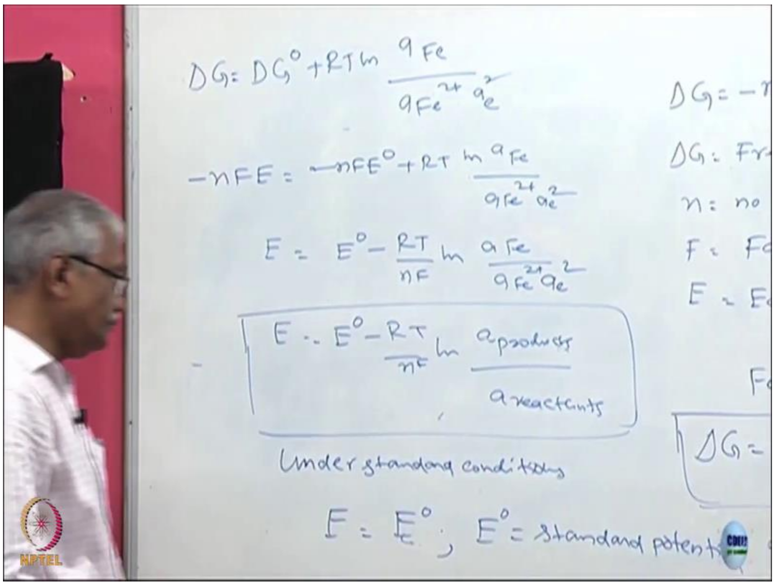

How would you expand this for this equation above equation

$\triangle G = \triangle G^0 + \quad RT \ln (a_{Fe}/a_{Fe2+} * a_{e-2})$

What happened the activity of iron upon the activity of Fe $^{2+}$, activity of e here right talk about it right.

Now, let us substitute $G =- n\triangle FE$;

you have - nFE = $nFE^0 + RT\ln(a_{Fe}/a_{Fe2+} * a_{e-2})$

And I can rearrange, $E = E^0 - RT\ln(a_{Fe}/a_{Fe2+} * a_{e-2})$. Sorry, you know activity of (Refer Time: 30:26) ok.

You can generalize this one right? How do I generalize this? I can generalize this as

$E = E^0$ - RTln(activity of the products/activity of the reactants). I can apply the standard state here what is the standard state? Where the activity of the product is equal to activity of the reactants and they are unity right.

So, under standard state standard conditions I would put that way. What is the standard conditions? Actually any of you? Standard state is slightly different from standard condition ok. The standard state is purely thermodynamic concept, the standard condition means it also talks about temperatures right. In a standard state it can be any temperature, in a standard conditions we defined the temperature is what temperature is 25 degree Celsius ok. In any case the activity of product is equal to reactants it becomes unity.

What happens? E is equal to E^o and what is E^0? Is equal to standard potentials; $E^0$is called standard potential. Are you followed? So, whether it is E^0 or E both represent the equilibrium conditions. I again emphasize it is equilibrium conditions you are not gone to corrosion yet.

I define the equilibrium condition and allow the equilibrium condition to deviate, then what happens? The corrosion occurs my first task is to define the equilibrium condition where in these species involved in corrosion are well defined

Student: Yes sir.

Are defined.

What are these species which we are considering in the case of iron in hydrochloric acid? The equilibrium condition of Fe in Fe^{2+}, H with H^+; we are looking at 2 equilibrium conditions. So, my task is to first understand how do I define, what parameter do I use to define this equilibrium and then use that to predict if the corrosion will occur or not ok. So, that is the way we are moving now.

So, we are now gone into the electrochemical criteria of defining equilibrium from a thermodynamic criteria. For equilibrium to exist in thermodynamic criteria $\triangle G=0$ right. In this case the equilibrium a condition for that is E^0, I mean E here. So, we can able to translate the free energy change into a potential here; that potential we called as electrochemical potentials or called as the equilibrium potential now ok. So, this is the first task for us any of you have any questions on here ok.

I will ask this question to you; suppose I would like to know let us look at imagine a thought process thought experiment right. I want to know the equilibrium potential of zinc in zinc ions ok. I want to measure it maybe in the lab actually. So, what do you mean by zinc is equilibrium with zinc ions; what do you mean by that? Physically what it means? What do you mean by equilibrium right; when I say zinc or in equilibrium with zinc ions how we visualize it?

Student: Present(Refer Time: 35:08).

So I have a solution where I have zinc ions are present. I just simply dip zinc into it establishes in equilibrium and you measure that potential and that potential is called equilibrium potentials. You call a standard potential once the concentration or the activity of zinc ions are consider as unity ok; so this what I mean. So, you can have in extent this for almost all kinds of the equilibrium systems. It could be for hydrogen again hydrogen what you do you have H and H^+.

How do I define the equilibrium condition for hydrogen and hydrogen ions?

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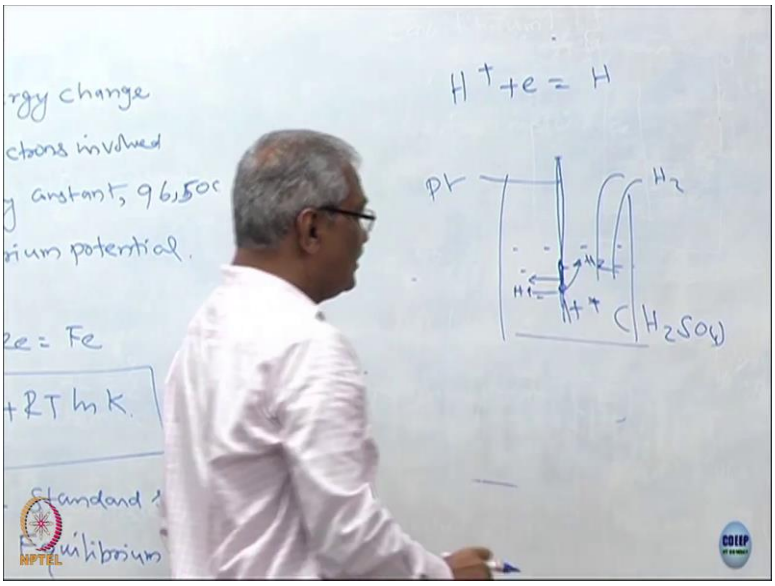

Let us say H^+ is in equilibrium with H here there is no metallic right. How do I establish? I would take a small beaker, I would take H^+ ions; what is H^+ ions here? It is let us say sulfuric acid ok. And I showed this with the hydrogen gas bubble this and I put a platinum electrode here right. This is my a platinum electrode I can also keep any noble metal I can have you know maybe rhodium I can have ok. And I can have gold for example, and I put it.

Now, how do I establish equilibrium? Over here metal surface the hydrogen will get oxidized as H^+, the es are released right this H^+ will again get reduced here and goes as hydrogen gas. So, you need a metallic connector in order that the exchange is taking place. So, how do I determine the equilibrium potential for various systems? That is our next task.

How do I determine this I would say I have taken copper I am going to dip copper in copper sulfate solution of 0.1 molar concentration. I am going to immerse it let say in 0.001 molar concentration of copper sulphate. Will the potential shown by the copper in both the solution the same or it will be different? It will be?

Student: Same.

Be same or different? Will be different. What is the basis?

Student: (Refer Time: 38:12).

Because it is this Nernst equation. So use the Nernst equation to determine the equilibrium potential for any electrochemical systems. So, that is the first step that you should understand right. So, the first step is to calculate the equilibrium potential.

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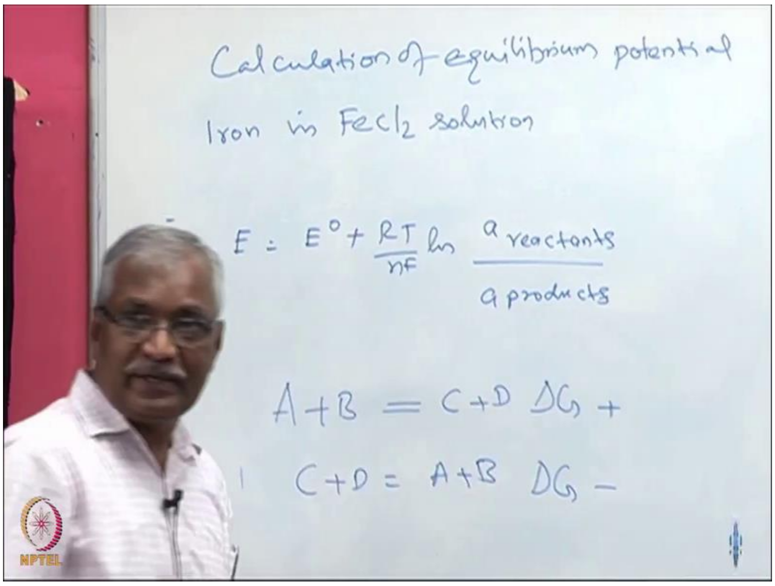

Calculation of equilibrium potential

Iron in $FeCl_2$ solution

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{reactants}}{a_{products}}$$

$A + B = C + D \quad \Delta G +$

$C + D = A + B \quad \Delta G -$

Let us take let us say iron in say ferric chloride solution ok. That is the say calculation of equilibrium potentials; iron in ferric chloride solution; will you do that. We use the Nernst equation ok; $E = E^0$ + RTln(activity of the reactant/activity of the product)..

I can change also write I can just change this. This is always a conclusion about the calculation of the potentials because we try to convert the thermodynamic parameter into electrochemical parameters.

Let us go here A + B this gives you C + D or C + D gives you A + B, ok. The free energy is change for that is let us say; let us say + the free energy change for that is considered as negative here right. This is what generally you do here. And we have some issues when you comes to electrochemical potentials.

So, I need to clarify this. So, that you do not make any mistake in determining the electrochemical potentials. Let us take this value here E^0; what is E^0?

Student: (Refer Time: 41:05).

Standard potentials ok.

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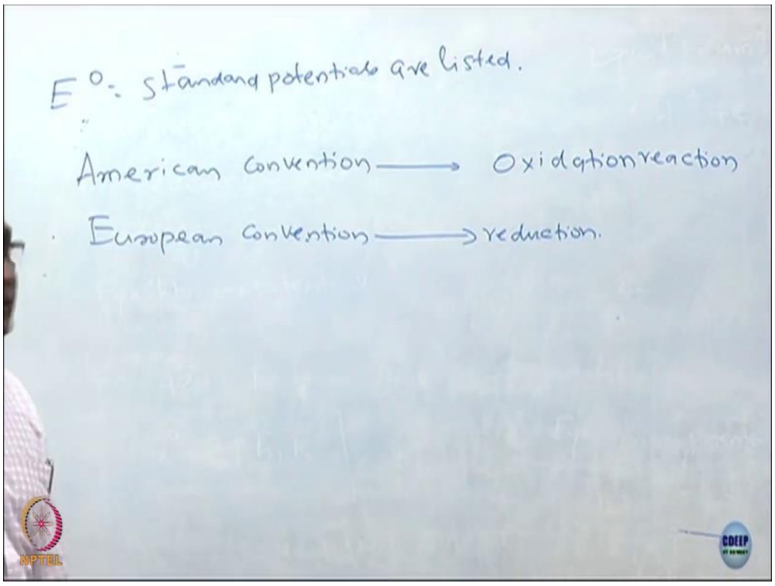

E^0:- standard potentials are listed.

American Convention ⟶ Oxidation reaction

European Convention ⟶ reduction.

The standard potentials are listed are listed ok. There used to be two conventions earlier one is called as American Convention other was called as European Convention ok. In American Convention they used to define the potential based on in oxidation reaction, here they used to based on a reduction reaction.

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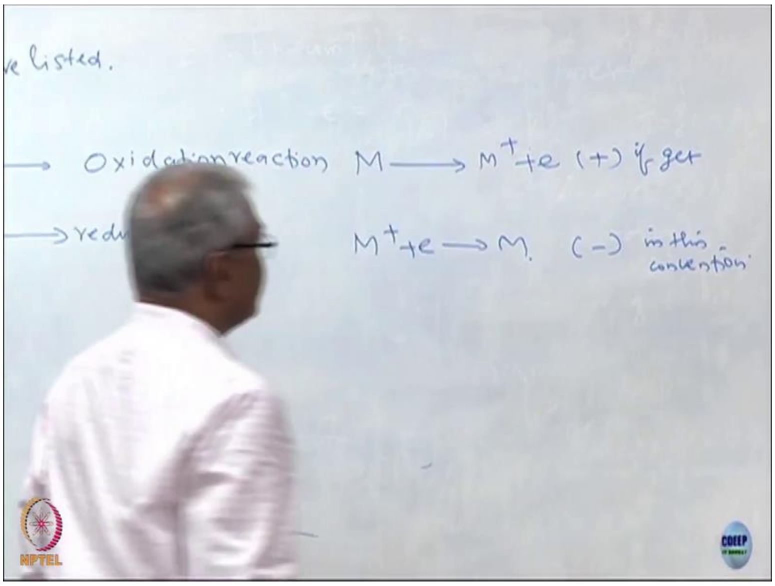

For example, I have a metal M represent this as $M^+ + e^-$. And European Convention they look at it differently $M^+ + e^-$ gives you as M right. If you use a Nernst equation for this the Nernst equation for this literally use it ok; you will get one sign here you get the another sign here. Numerically the value is going to be same it not going to change, but the sign is going to be different.

For example, if you get here positive if you get it at here it becomes a negative automatically it becomes negative; negative in this convention. So, that is a problem in actually defining what the equilibrium potential is; you take the old books and if you take the old Fontana book, you would write as standard oxidation potentials or some other people write as standard reduction potentials. That clarity is very important without which you are likely to make mistake in really predicting if the metal will corrode or not ok.

Now, let us me try to explain this why you should not look at either American Convention or European Convention both are wrong, this is not correct ok. What is say so?

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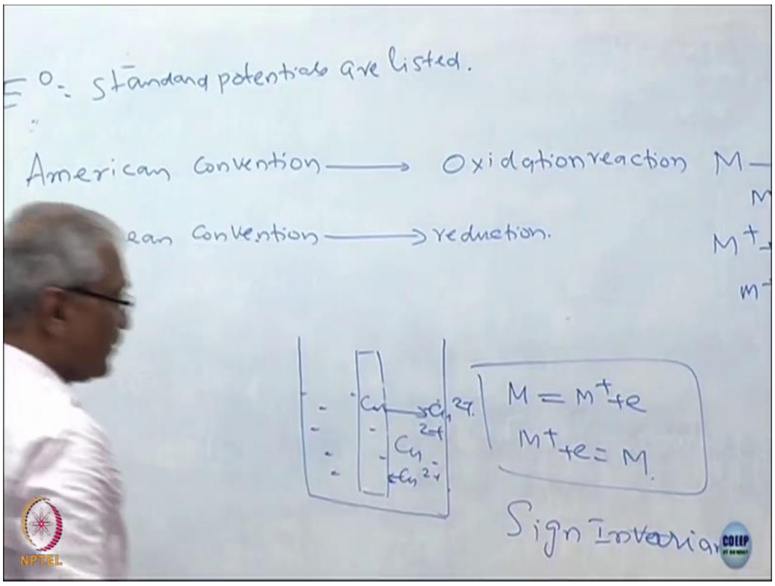

Let us take an equilibrium any equilibrium you can take you want. Let us say copper; I immersed copper in Cu^{2+} ions solution right. What is happening here? That be equilibrium right.

So, what is equilibrium here? The equilibrium is that Cu goes as Cu^{2+} and Cu^{2+} return back and gets deposited. The oxidation reaction reduction reaction both of them occurring on the same surface, unless the rate of oxidation equal to rate of reduction you do not call it as a equilibrium process ok.

So, we are now talking about equilibrium potential please look at this. The potential established between the metal on the solution is equal to; what is it called? If I measure a potential that exists by in the metal as a solution what is that potential called? That is called as a equilibrium potential now. So, the potential so measured is equal to equilibrium potential.

Now, let us take these two conventions right. Let us take an American Convention we call a standard oxidation potential, but also means the equilibrium potential right. We call a standard reduction potential this is also called equilibrium potentials, either way you use ok it is written like this written like this. In fact, the better way of writing here would be M is going to be $M^+ + e^-$ here $M^+ + e^-$ is equal to M here. I just reversed this equation.

But please notice if I write this way or this way; that means, I can write either as M going as M^+ + e^- or I can write as M^+ + e is M. In both the ways I represent the equilibrium; whatever way I represent this is the picture, just look at this is the picture is same or different?

Student: Same.

Same. So, you cannot have a potential for this different from this because both are describing the same manner, look at it now. So, it is not the equation you written in a different manner, but actually equilibrium means the metal is in equilibrium with the ions. No matter how you write it in the lab you do an experiment it represent a transfer of copper ions to solution and so and the copper ions from the solution to the metal.

So, it is not depend upon this does not depend upon this; so it is independent. So, that means, the sign invariant actually is called sign invariant ok. So, it is a sign invariant. So, the electrochemical potential is sign invariant. So, first and foremost you need to understand that electrochemical potential is sign invariant.

It does not depend upon American Convention it does not depend upon European Convention, you do not call as standard oxidation potential, you do not call as standard reduction potentials, you simply call as standard potentials; which implies it is standard equilibrium potentials. The same is true for equilibrium potential you do not call equilibrium oxidation potentials, you do not call equilibrium reduction potential it is simply it is in equilibrium potentials. So, that is what is important.

So, I have so far try to explain to you what is mean by electrochemical equilibrium I suppose right. The electrochemical equilibrium exists at the solid solution interface. There is an exchange of ions or charges between the solution on the metal interface ok. And you doing so it establishes a potential we call them as equilibrium potentials.

If this activity of the ions in the solution is considered as unity; it becomes a standard potentials. I did not so far mention about this here for a pure solid the activity is always considered as a?

Student: One.

Student: Unity.

One actually suppose you take a copper alloy this is not one actually ok. So, it is generally this is considered as unity here when I talk about pure metal pure solids; be it platinum, be it nickel, be it iron, in the pure form the activity is assumed to be to be equal to one. So, far any of you have any questions about what is mean by electrochemical equilibrium. Can I proceed?

Student: Yes.

Further.

Student: Sir, (Refer Time: 50:12) How do we use Nernst equation?

So, now, the question comes is ok, if I am going to use Nernst equation how I going to use Nernst equation for example, that is what the question is right. So, how I because the Nernst equation if you see here reactants and products.

Depends upon how do you write it right? I can write on the left side oxidized product right side is reduction product or I can write left side as reduced product right reduced as species as a reactants and you have oxidized one as a product right. So, you have this problem. So, that problem I think we should need to resolve otherwise you do not know how to calculate actually right.

But the point you need to be clear about is it is not oxidation it is not reduction it is simply equilibrium. So, that is what I think you should be first be aware of it actually ok. How to do that? I will come to the next step as to how you really calculate this these are these values.

So, calculation of equilibrium potentials ok.

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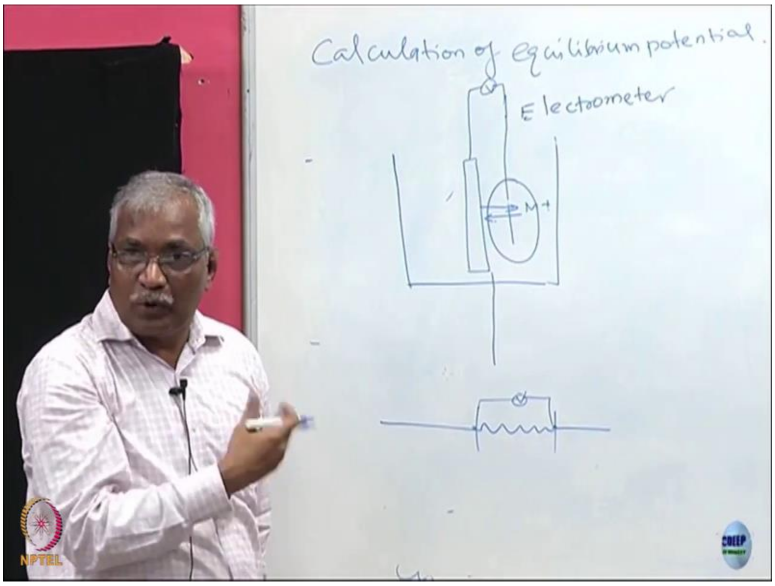

First the basis; the basis is it establishes a potential here right. So, there is a potential existing between the metal and the solution. I need to measure this I need to measure this.

So, how do I measure this potential? How do I measure this potential? Measuring potential you know suppose I have a resistor how to measure the potential between these two point? I connect to voltmeter and I make a contact here I contact here I measure this; to measure the potential across a distance to different locations I need one more reference actually. So, potential is always measured with respect to the other one right.

If I have to measure the potential here I need to insert another probe this things right. I use a probe, I can use a voltmeter, I can use what more precisely we call as electrometer right. What is the difference between a simply saying voltmeter and electrometer? Electrometer does not allow the current to pass through you know when you measure the voltage. Or you can use in a high impedance voltmeter right.

When you use a high impedance voltmeter what happens? Does not allow the current to pass through you will understand this concept when you talk about polarization later stage. At this point of time it is enough to understand that you need to measure the potential using an electrometer or an I impedance voltmeter ok

Suppose I put a probe here I measure it what do you think will happen? When I put here I am going to get a another interface here right. I am going to have an equilibrium between this one and the solution. So, there is going to be a potential develop automatically right. So, you are going to develop another potential here right. There is going to be another potential developed by the probe.

So, you will essentially measure only the potential difference; you will never able to measure the absolute value of this potential because no matter what you do you need to have one more probe to measure and that establishes a potential that is a problem; that means, is ok. Absolute potentials cannot be measured you can measure only the relative potentials.

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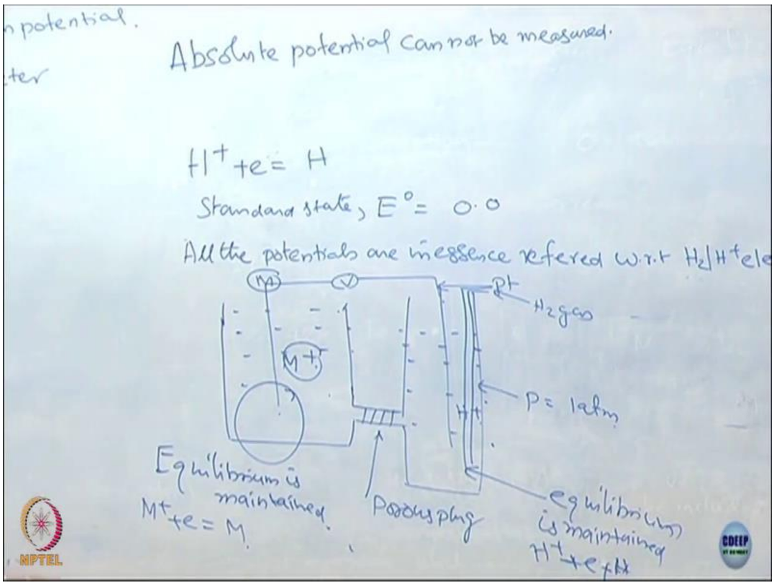

Absolute potential can not be measured.

$H^+ + e = H$

Standard state, $E^\circ = 0.0$

All the potentials are in essence refered w.r.t H_2/H^+ ele

So, what you do in this case you use the equilibrium $H^+ + e^-$ giving rise to hydrogen in the standard state ok the E^0 is considered as 0. So, you are assuming the equilibrium of H^+ and hydrogen is equal to 0 right. So, when I use an hydrogen electrode here I measure the potential and that potential is called as a simply the electrode potentials. So, that means, ok.

So, all the potentials are in essence referred with respect to hydrogen, H^+ electrode ok. So, this is the most important thing you should keep in mind; I again repeat you cannot really measure absolute potential electrochemical potential of any systems it is referred in the reference of, hydrogen because it is assumed to be 0 in the standard state ok.

Now, let us come back to this the measurement of potential here; how do you do that? Plug I use that say it some metal M is in equilibrium with the M^+ metal M is equilibrium with M^+. And here what happens I have a platinum wire I have H^+ and bubble hydrogen gas.

What is the pressure here? P equal to 1 atmosphere and I measure this voltage using an electrometer. When I measure this voltage with respect to electrometer; what did what it does? It does not allow the current to flow through this please notice if I have a potential one and the potential two I just electrically short; what happens?.

Current will start flowing that is not going to happen here you we do not allow the current to flow; that means, equilibrium is maintained; equilibrium is maintained ok. And here also the equilibrium is maintained. What is the equilibrium here? It is nothing, but $M^+ + e^-$ gives you M. What is the equilibrium here? $H^+ + e^-$ gives you hydrogen ok. The equilibrium is maintained now I am going to measure the voltage.

And that voltage is we called as the equilibrium voltage or equilibrium potential; you agree. Can I call this is as an equilibrium potential? As long as the current does not flow as long as the equilibrium is maintained here the equilibrium is maintained over here. And the voltmeter is just measuring the potential of this equilibrium with respect to this equilibrium. I have made this equilibrium as value the potential of this is equal to 0 and so whatever value you have measured here is called as the equilibrium potential.

Did I make it clear to you? Did I make clear or anybody has any questions?

Student: How do we get the equilibrium potential of the metal since there is no kind of flow to the voltmeter?

See one of the ways ideally you know how do you measure the potential using a potentiometer. Anybody remember the potentiometers by null deflection method anybody did your experiments right. I want to measure potential between the point one and point two I do a null deflection method. So, that I keep on adjusting external.

Student: Resistance.

Resistance voltage. And when the when the you know the current does not flow so potential measured between these two right is actual potential right. So, I apply external voltage actually so that current is not going to flow. So, what we do in this case is that it is external. So, potentiometer is essentially the balancing time right you balance it with external equal amount of voltage I do that.

So, what I do? I ensure that the potential applied externally is almost equal to these two value so that the current does not flow between these two you know normally we use a galvanometer right. And keep on pressing it and find out at one point of time there no deflection takes place the potential measured is equal to the potential between these two points.

So, when we say that I have potential one, and have potential two, I use an electrometer; that means, the electrometer is supposed to be not allowing any current to flow through that; at that point of time you measure the potential between these two. And that potential is equal to the actual potential of the system. Otherwise when the current flows you will see later there is something called polarization you will not able to measure the actual values.

So, what I refer here is; you need to measure potential when they are under equilibrium conditions. The current flows they are no more under equilibrium condition you are not going to measure the actual value ok. So, that is what it is. So, we are measuring the potential under equilibrium condition and so it is called as an equilibrium potential. What I am trying to say this potential is not only calculated using the Nernst equations, this potential can also be measured in the lab you can go to the lab you can measure it.

I think we will do some experiments in the in the lab to measure the potential of copper copper sulphate solution and see that the measured value is almost equal to what you calculate. So, it is possible to calculate and also possible to measure. The question is; what you calculated and, what you measure has to be same ok, so that is the point we are going to come to this. Am I clear in this actually ok.

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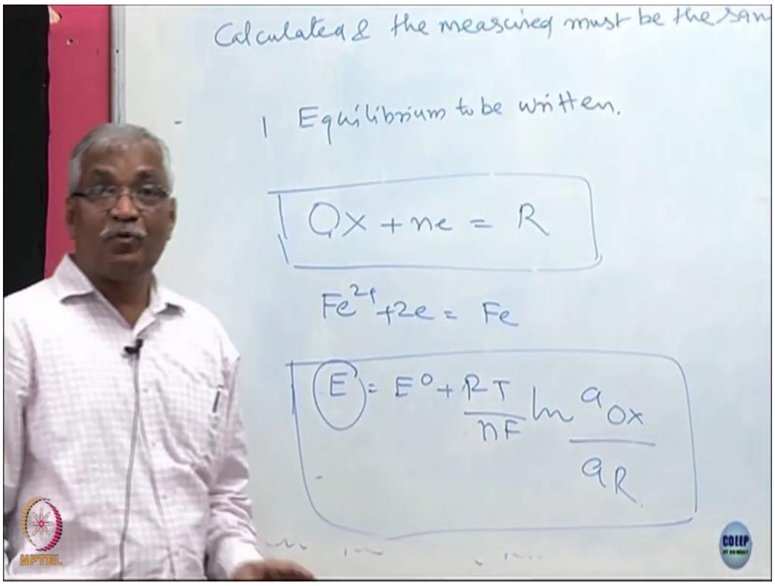

Calculated & the measured must be the sam

1 Equilibrium to be written.

$$\boxed{Ox + ne = R}$$

$$Fe^{2+} + 2e = Fe$$

$$\boxed{E = E^{0} + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{R}}}$$

So, how do I calculate the potential? Now the calculated potentials and the measured must be the same ok. It cannot be different in these two. So, it becomes same if you write the equilibrium to be written the equilibrium to be written as follows. Always write oxidized species on the left hand side and reduced species on the right side; this is the first thing we should start with. You may have an equilibrium; what all the species under equilibrium here; this is oxidized species, reduced species ok

Suppose an example you want I will say Fe^{2+} + $2e^{-}$ gives you Fe. This is reduced species this is oxidized species right like that ok. Then you write the Nernst equation right Nernst equation E = to E^{0} + (RT/nF) ln (activity of the oxidant/the activity of reactants). Please write always like this then you will not have any problem. Whatsoever, in actually calculating the value which is equal to or which will be equal to the measured value.

So, no matter what you know reaction we deal with the equilibrium should be always written as oxidant on the as a reactant and reductant as the product you should do that you should do this. So, when you do this and you will not have any problem in terms of the obtaining these values of this.

Please notice now E is a function of what the standard potential the activity of the oxidant, the activity of the reductant actually. Of course, these are not going to be changing right for a given reaction; n is constant, T is a given temperatures, R is a gas constant, F is a Faraday right. So, they are not going to change so the E can be changed by changing this the activity by changing the activity of the reactants.

For all practical purposes in our course we will consider the concentration equals to the activity.

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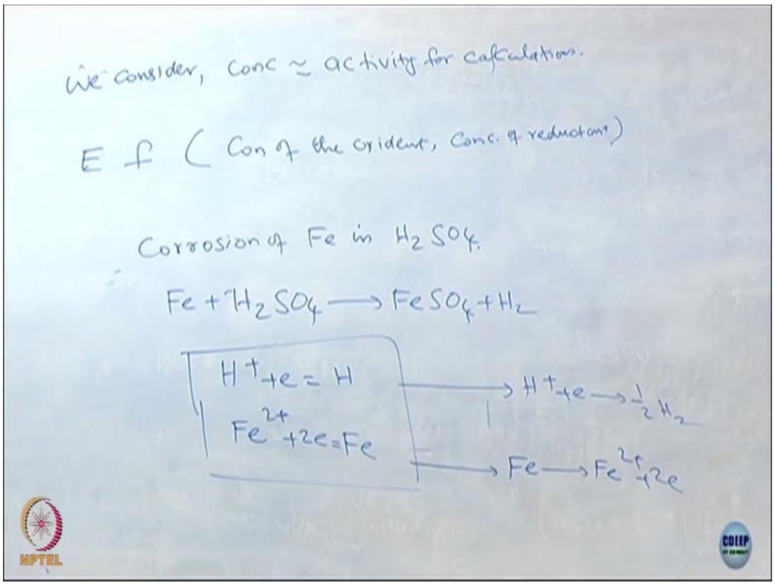

We consider, Conc $\simeq$ activity for calculations.

E f (Con of the oxident, Conc. of reductant)

Corrosion of Fe in H_2SO_4.

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

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

$Fe^{2+} + 2e = Fe \longrightarrow Fe \longrightarrow Fe^{2+} + 2e$

So we consider, consider concentration is equal to activity for calculations ok. So, you do not have to worry about what the activity is. Actually what is the relation between activity and concentration? Any of you know?

Student: (Refer Time: 69:42) activity.

So concentration multiplied by.

Student: Activity.

Activity coefficient is equal to activity right ok. So, they so, but you do not worry we normally considered the activity coefficient are equal to unity it is not true ok, but you for all some practical purposes you simplify that actually ok. So, we considered the concentration equal to activity and use this equation to measure this. Please notice E let us look at E here; when will the E go up?

Student: (Refer Time: 70:27).

When will the E go up? When the activity of oxidants increases? When will the E will reduce? When the activity of reductant changing. So, you can change these values please understand; that means, E is a function of I would use a term now concentration of the oxidant and the concentration of reductant ok. So, if both of them can change these values.

So, the first exercise for you is to learn to calculate the equilibrium potentials. Let me go to the next step ok; I will explain and then leave it for you to think over until we meet next. Let us have this corrosion of let us say iron in let say sulfuric acid.

I want to predict if the corrosion occurs or not in sulfuric acid. How do you predict? Let us go back to the corrosion reaction iron it is immersed in H_2SO_4. Sorry, I think it is (Refer Time: 72:42) excuse me iron immersed in a H_2SO_4; it is give rise to what? Ife(SO_4)+ H_2

here.

Now, you know in this case is going to corrode. I just only want to give you know how you can prove that the iron will corrode in sulfuric acid. Before corrosion occurs there will be 2 equilibria right. What are the equilibria I will have one equilibria will be $H^+ + e^-$ gives you H_2 the other equilibria will be Fe^{2+} + 2e gives you Fe. These are the 2 equilibria that will be existing right.

If iron has to corrode what should happen? So, what should happen is this equilibrium now what happen should happen is? Iron should go as $Fe^{2+} + 2e^-$ s and this should go as H^+ ok, you know about it.

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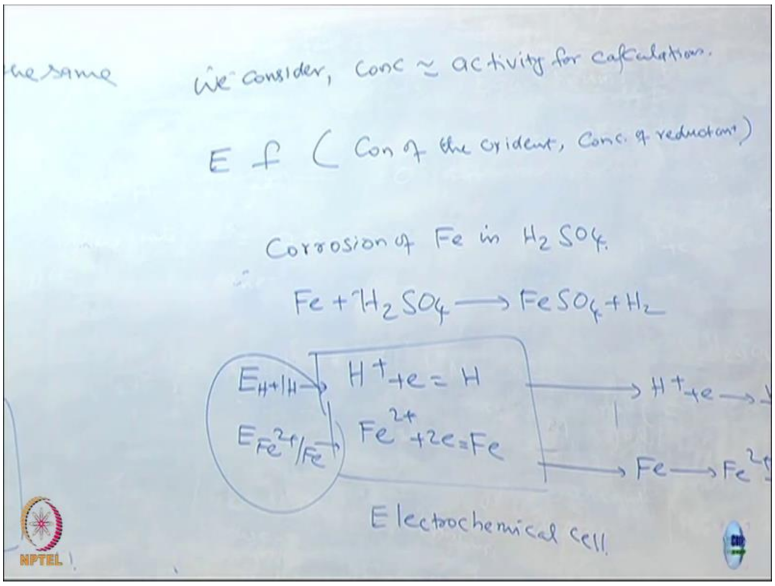

he same

We consider, conc ≈ activity for calculations.

E f (Con of the oxident, Conc. of reductant)

Corrosion of Fe in H_2SO_4

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

$E_{H^+/H} \rightarrow$ $H^+ + e = H$ $\longrightarrow H^+ + e \rightarrow$

$E_{Fe^{2+}/Fe} \rightarrow$ $Fe^{2+} + 2e = Fe$ $\longrightarrow Fe \longrightarrow Fe^{2}$

Electrochemical cell

And you also know that this equilibrium has one potential; this potential is referred as H^+, H is 1 potential for this. And this has got what E_{Fe}^{2+} /Fe as have a potential.

So, this equilibrium is not defined in terms of the two electrochemical potentials E you know E $_{H+/H}$ and E $_{Fe2+/Fe}$. And with reaction occurs like that what will happen to this? It forms a cell it forms in electrochemical cell it forms electrochemical cell right. The electrode 1 the electrode 2 you form a cell now it forms a cell.

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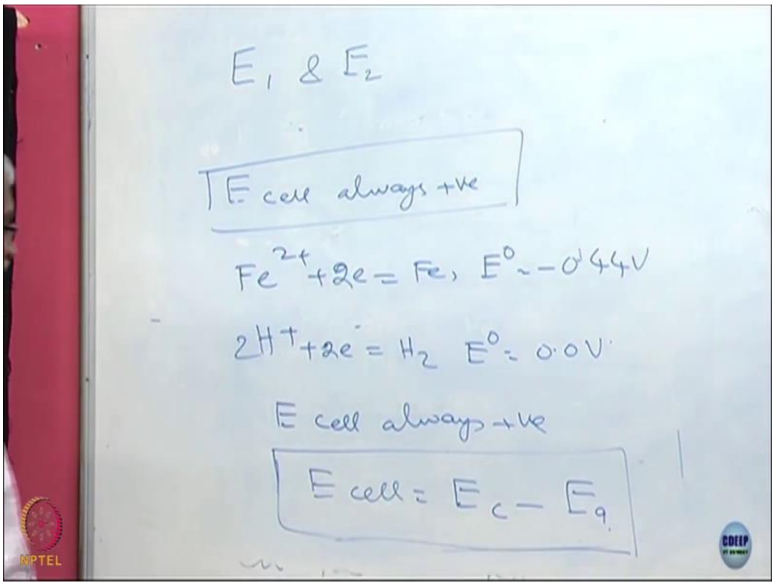

E_1 & E_2

$\boxed{E \text{ cell always +ve}}$

$Fe^{2+} + 2e = Fe, \; E^0 = -0.44V$

$2H^+ + 2e = H_2 \; E^0 = 0.0V$

E cell always +ve

$\boxed{E\,cell = E_c - E_a}$

So, I have E, E_1 and E_2 ok. And you have a E cell is always positive no matter what happens right. You have electrode 1 electrode 2 I connect them you will get a positive potential right. Irrespective of what the value of E_1 is and E_2 is as long as they are different you will join them together the E cell will always be positive. It can never be negative at all ok.

Now, the question is can this can this occur, can this occur? Now let us give some value for this ok. And now I assume that I assume now iron in equilibria with a Fe^{2+} in equilibrium with iron in the standard condition which is equal to E^0 is - 0.444 volts. Suppose I assume this and I also have an equilibrium potential for hydrogen and E^0 =0.0 volt.

Please look at this let us look at this and the E cell will always be positive and the E cell is equal to, what is how do you define E cell? Any of you remember? Is equal to $E_{cathode}$ - E_{anode}, $E_{cell} = E_{cathode} - E_{anode}$. If the corrosion to occur if the corrosion to occur this reaction has to be this is cathode or anode?

Student: Cathode.

Cathode this has to be anode. For the sake of argument for the argument sake you assume that this is the cathode and this is the anode right. For sake of argument assume this is the anode and this is the cathode.

What does it mean? That iron will not corrode in the sulfuric acid am I right or not I assume that iron will not corrode in sulfuric acid. What is wrong in my assumption? I assume because I do not know if I know I do not have to predict right I do not know. So, I assume that iron is not going to corrode in sulfuric acid. Then you make a calculation see what happens to E_{cell}?

Student: (Refer Time: 79:19).

We do not talk about delta G now here.

Student: E_{cell} (Refer Time: 79:24).

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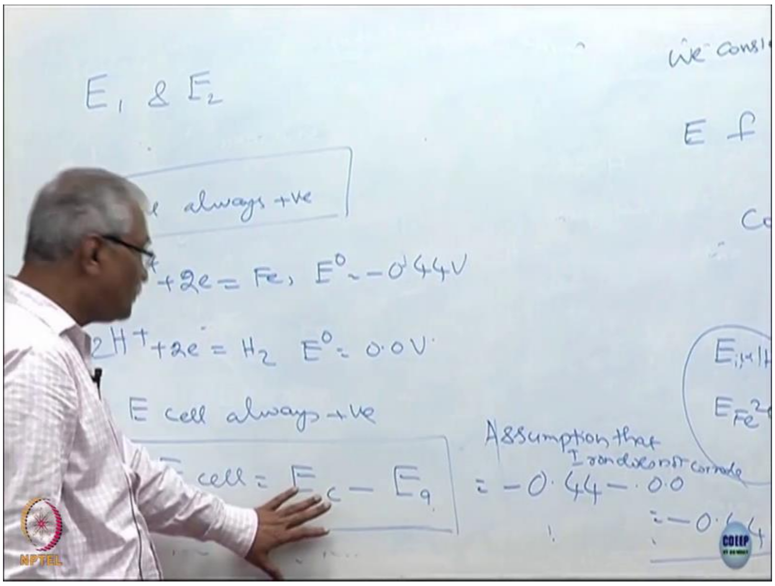

You look at the E_{cell} now what happens right. What E_{cell} now? E_{cell} in this case is equal to -0.44 minus of 0.0 is equal to -0.44 volt. So, I assumed; what the assumption here? The assumption that iron does not corrode assumption that iron does not corrode leads to E_{cell} which is - 0.44; which means I assumed it wrongly. Then I correct myself and I will say yes iron is anode it is a cathode and get the answers.

What is the advantage of this? The advantage of that is that I do not have any assumption I do not assume in oxidation potentials, I do not assume to be reduction potentials, I do not assume anything. I am free to assume wrongly and try to calculate I can get corrected ok. So, you will never go wrong if you are going to understand what is equilibrium? What is equilibrium potentials? What is the cell voltage? And accordingly apply these concepts. You can clearly predict that a metal can corrode or metal will not corrode ok.

So, no assumption whatsoever is involved in all of these processes. So, that is why it is important that it will be systematic in our own understanding of the electrochemical concept. I think we have come you know close to the end of the session. I think we will continue this tomorrow it is very important.

What I want you to read understand during the intervening period is please go through all this note first of all. Understand what is electrochemical equilibrium. How do I define this electrochemical equilibrium using the Nernst equation. How do I calculate the equilibrium potential using the Nernst equation. What is the relation between the E cell and the corrosion?.

So, we did not cover much but these are the basic things that will come to you again when I talk about oh will the metal corrode or not. If I know that zinc is corroding why should I calculate it right. People assume let us assume oxidation and so corrode and express it is not going to happen.

So, no assumption should be involved and you should go purely based on the fundamental understanding of the electrochemical processes. I do hope that when you come next time you have read once. We will have more discussion on this and.

Thanks.