

Environmental Engineering Chemical Process
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Lecture – 59
Applications of Ecell

Hello everyone, so again welcome back to the latest lecture session right. So, in the last session we were discussing the approaches relevant to using the redox potential right our reduction potential E_h right and we discussed relevant aspects and the analogies with respect to pE right and then we discuss the reaction feasibility right as and when would the E_h shall be positive right as in $E_{h1} > E_{h2}$ only an E_h shall be positive over the Δg than be negative right.

So, for that to occur again E_{h1} has to be $> E_{h2}$. Meaning that I believe what now reduction needs to occur at cell 1 right and oxidation will occur at cell 2 reduction at cell 1 meaning cathode right at cell 1 and anode at cell 2 for the Ecell to be positive and third the Δg to be negative for the reaction to be feasible and then we talked about the relevant aspect as an imposed potential. So, with respect to impose potential there are 2 aspects that we are going to look at I guess right.

So, let us say there is a reaction that is thermo dynamically favorable right. But you still want to promote such a thermodynamically favorable reaction you can again impose additional potential to promote this already favorable reaction and the second case is that say there is a reaction that is not thermodynamically favorable now right redox reaction that is not thermodynamically favorable.

So, but you want to you know get it through our you know make that you know your what do we say redox reaction that you want to go through that right. But that is not thermodynamically favorable right so what are you going to do now so you are going to impose and what is the external potential right. So, that this particular cell right now becomes feasible feasible enough for the electron transfer to take place without the potential great you know electron transfer.

But because of the impose of the external potential that you are going to apply replace you know that is going to go through that as in the redox process is going to go through. So, we are going

to cover that aspect now in this aspect though it is important to look at right say the terminology or Russian say the terminology I guess the science that are applied to this external voltage I guess.

And the reason being you know in your applied voltage right or the external voltage that you are a potential that you are applying pardon me. So, you have the positive terminal and the negative terminal. Depending upon to which electrode you connect your positive terminal right you are going to have what do you say promoting are not promoting your current redox process right. So, we are going to look at that right.

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$$E_{cell} = \frac{\Delta E_h^\circ - \frac{RT}{nF} \ln Q_{overall}}{1}$$

$$= E_h - E_{h_2}$$

$$\rightarrow E_{cell} = E_h - E_{h_2} - E_{applied}$$

+ve terminal being connected to cell 1 oxidation at cell ①
 -ve ⊖ Cell 2 reduction at cell ②

→

$E_{cell} = E_1 - E_2$

→

$E_{cell} = E_1 - E_2 - E_{app}$

$|E_{app}| > |E_1 - E_2|$

So, here we have the E_{cell} which is going to be $\Delta E_h^\circ - RT/nF \ln Q_{overall}$ of the overall reaction right. This is something that we have looked good in the past right in the previous session pardon me and that is also $= E_{h1} - E_{h2}$ now right so when you apply what is external potential or when we looked at the applied potential. So, E_{cell} is going to be written as $E_{h1} - E_{h2} - E_{applied}$.

Right but this particular standard form of using this particular negative term here would be contingent upon your positive terminal right being connected to cell 1 right and the negative 1 would then obviously be connected to cell 2 I guess right as in what does this mean. Negative would be connected to cell 2 right and positive be connected to cell 1 and then this would be

relevant to what we say symbols.

Or such that you need to use your with the applied voltage or potential and let us look at what it is but we are going to understand what this means what does this mean now when you are applying what do we say positive to what do we say positive terminal or connecting the positive terminal to the electrode at cell 1 that means you want to promote oxidation right at cell 1 right. And that would obviously mean you would want to then promote reduction at cell 2.

So, when you are trying to promote these conditions right this particular what do we say equation applies and this is the standard way to look at I guess. So, we are going to look at it in terms of the cells that we have looked at let us see so electrode chemicals are cell 1 and let us say this right and you are going to have your cell 2. And let us say this is the direction of your flow of electrons currently now right and what does this mean.

Now usually we have the cathode here right. So, cathode here but that would then be reductions that I need to reverse the flow of the electrons here and this is the anode here right anode here and this would be oxidation right and here I am going to arrest that here as in the direction of flow of the electrons. Let us say if the E_{cell} is positive as it is right yes so you are going to have $E_{\text{cell}} = E_1 - E_2$ eight and let us say this particular E_{cell} is positive here.

So, when it is positive you know that you will have reduction let us say at cell 1 that means the cathode and oxidation at cell 2 which is the anode here in this case let us see. And in this case obviously we did not have any external potential applied now. So, here we are now can going to consider in the second case let us say when we apply an external potential now. I am going to use the term or the symbol with respect to negative and apply similar to what we had here right.

So, that means my positive terminal now needs to be connected to cell 1 let us say let us see what that entails yes. So, I have my electrode 1 here or cell 1 and cell 2 right. And now I am going to put in my extended what do we say voltage here apply voltage here and this is positive and this is the negative terminal and that is the positive is connected to cell 1 and negative is connected to cell 2.

Let me write that as let us say cell 1 and cell 2 right so now you know what is going to be promoted now. All right so in general you know here the way you applied this particular terminal or the applied the voltage. You see that the electron flow from the negative terminal to the cell2 will be promoted and also electron flow from cell 1 to the positive terminal will be promoted and the electron flow would be within the applied battery.

Let us see if I can look at that let us see will be from+ to- and- 2+ outside here. Now what am I promoting I am promoting the flow of electrons from cell1 positive terminal and again electrons from negative terminal to cell 2. So, now they have this E applied right the magnitude of it let us say is greater than the magnitude of $E_1 - E_2$ right which in this case you know assuming that is going to be.

Now the electron flow is going to be reverse from this case right. In the earlier case we earlier had reduction at cell 1 but now you see here the way we have considered the relevant aspects and connected the terminals we are going to have promotion of oxidation at cell 1 and reduction at cell 2 right. So, now your particular cell1 is going to be your anode and your cell2 is going to be is going to be your cathode.

Right again and that is understandable here again so again here let us say if you connected in reverse and see if you for example connected your what you say now negative terminal to cell 1 and positive terminal to your cell 2 then this would have to be written as applied to how to be considered as negative. That is you know transforming this particular what do we see a variable to be overall positive I guess right.

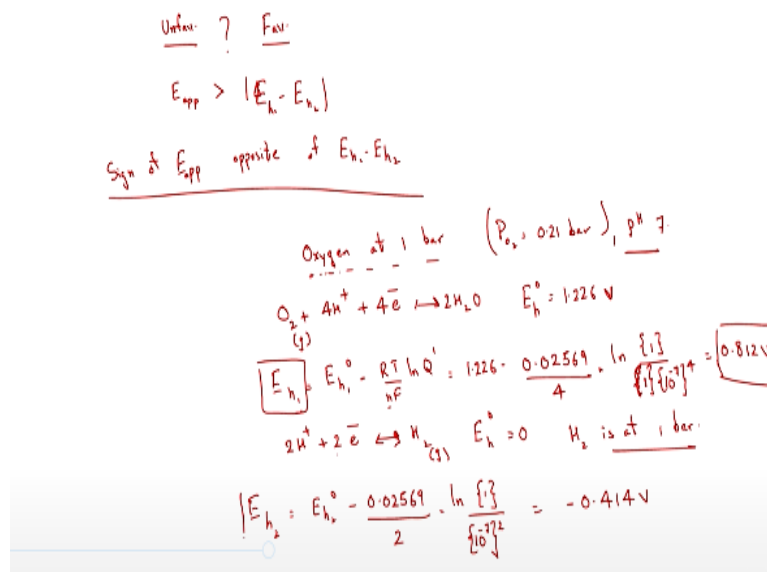
So, the sign of the symbol I guess is remarkably important and that is relevant to the negative symbol is relevant to the positive terminal being connected to cell 1. Right so that is something that you need to consider here. So, again well now look at the 2 aspects that we have considered or talked about earlier. As in let us say there is already a thermo dynamically favorable reaction let us say redox reaction and you want to further promote that.

So, what are you going to do now you are going to see to it that the E applied here is going to be negative here right. The E applied being negative what does that mean now that you are going to connect your negative terminal to your cell 1 and positive terminal 2 yourself in this particular example right. And let us say the second case that is a reaction is thermodynamically not favorable now.

So, we want to make that particular reaction thermodynamically favorable right. So, what are we going to do you are going to have an applied voltage or an external voltage right and how are you going to have the relevant what do you say variables or set ups that this equation is going to be right you are going to see to it that the E applied is positive. E applied is positive and magnitude with respect to the difference of Eh1 and Eh2 right.

Or it is going to be the difference what do we say have the opposite sign of delta Eh right and what do we see the sum of pardon me greater than sum of delta Eh right.

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So, let me just write it down so the second case as in the unfavorable reaction right similar to the example we just looked at and you want to make it favorable I guess. So, how do you do that you are going to see to it that you know your E applied let us say is first than in magnitude of your delta or let us write it as Eh1-Eh2 right it and also the symbol that the sign is going to be the opposite of opposite of you Eh1-Eh2 right.

And that is when I guess obviously you are going to promote a redox reaction that what we say not favorable and for that case obviously you need to apply higher external voltage and also look at obviously relevant connections and for that your E applied needs to be a different sign when compared to $E_{H1}-E_{H2}$ right. So, I guess now we are going to go over and look at a particular example right.

And look at let us say in which case would a particular what is a half reaction or set of 2 half reactions you know be favorable and let us say when you apply an external voltage of a certain what we say value how is that going to change right. So, let us look at that now so we will have oxygen at 1 bar let us say right keep in mind that usually the partial pressure of 0.21 bar and let us see the pH7 in this example we consider to be 7.

Let us say and the relevant half reaction we have with oxygen gashes $+4H^+$ I guess $+4$ electrons goes to $2H_2O$ and then the Eh potential nonstandard action potential is 1.226 volts let us say for this half reaction this is the data that I have and we are also going to look at the second electrode let us say where $2H^++2$ electrons right go to H_2 and obviously your reference of the standard hydrogen electrode right.

So, that is why obviously the reference that is obviously set as 1 $E_{H0}=0$ and for let us say for a certain set of conditions we are going to calculate the Eh value for both these cases and here to will consider that H_2 is at 1 bar I guess right and let us go ahead and calculate E_{H1} let us say. So, $E_{H1}=E_{H0}-$ again we now RT/nF natural logarithm of Q dash right $=E_{H0}$ is out here $1.226-RT/nF$ let us say here n is the number of electrons being transferred which is 4 right.

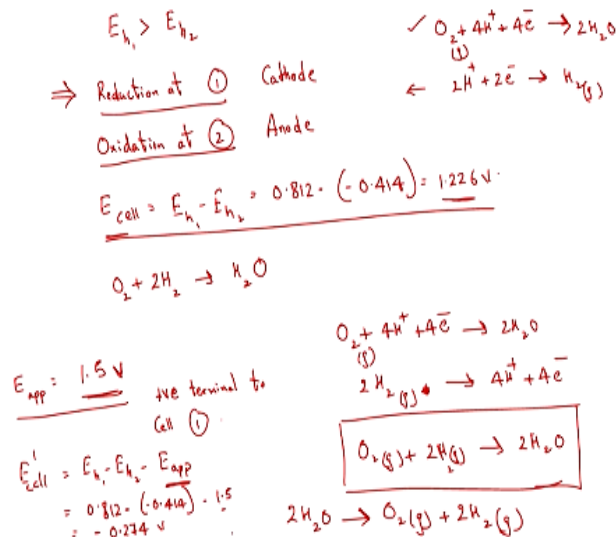
So, I guess the value of RT at 25 degree centigrade divided by the fact this constant is going to be $=0.02569/$ the number of electrons is $4*\text{natural logarithm of Q dash Q dash right}$. So, here you have activity of 1 out here right because water activity is 1/ activity of or the partial pressure of O_2 but in this example we are considering the case when the oxygen is that 1 bar let us say. So, the partial pressure of O_2 and that is 1.

So, I am going to take that to be 1 here right activity measured measured by partial pressure of O2 here. Because the pressure is at 1 that is going to be 1 here and H+ concentration is 10⁻⁷ right raised to the power of 4 right. So, that is why how we have Eh1 and that looks like turns out to be 0.812 volts right and similarly we are now going to calculate Eh2. So, Eh2 is going to be = Eh0 and again RT/nF.

And what is the value now 0.02569/ the number of electrons being transferred which in this case is 2 * natural logarithm of Q dash again so partial pressure of H2 the gas again. We assume that is going to be = 1 bar right so again it is 1 here/ activity of H+ H+ is again 10⁻⁷ it is going to be = 10⁻⁷ to the power of 2 raised to the power of 2 and looks like this value is going to be = 0.414 volts right.

So, here let us just summarize what we have you have Eh1 right and that = 0.812 volts and Eh2 is going to be = -0.414 volts right.

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So, here as we see Eh1 > Eh2 right so what does that imply now you are going to have reduction right reduction at electrode 1 right or which is now going to be equal to the cathode right and you are going to have oxidation. Oxidation at 2 or anode right now let us see what this the E cell is going to turn out to be. E cell is going to be = Eh1 - Eh2 right and the values being 0.812 and 0.812 - 0.414 right.

E cell is going to be $E_{\text{cell}} = E_{\text{h1}} - E_{\text{h2}}$ right and the values being 0.812 and 0.812-0.414 right and this is 1.226 volts right. Again E cell is positive right and that is positive and we saw now reduction at 1 and oxidation at 2 what does that mean by let us say the bands of reactions 2H_2 should go to H_2O right this is nothing but from bouncing this to off reactions. So, we have this going to as reduction as it is right and then this needs to be oxidation.

So, we need to swap this particular but half reaction and then multiplying it by 2 so that the number of Electron transfer is same or let me right that down here to support which $\text{O}_2 + 4\text{H}^{++} + 4\text{ electrons}$ right and the second I guess is 2H^{++} is 2 electrons goes to H_2 right and the gas is here and the gas is here right do we have the right equations I guess so. Now obviously if this proceeds as reduction this reaction will stay as it is.

If this proceeds at oxidation we need to swap it I guess right so and if you look at that overall reaction right what it is going to be $\text{O}_2 + 4\text{H}^{++} + 4\text{ electrons}$ goes to $2\text{H}_2\text{O}$ right and I am going to swap this and * it by 2 so 2H_2 again gas and gas right or go to $4\text{H}^{++} + 4\text{ electrons}$ and it is going to be nothing but O_2 gas + 2H_2 gas is going to or you can think of it as obviously oxygen oxidizing hydrogen or hydrogen reducing oxygen right.

One and the same and forming water right so that is what we end up having here right and this was the is the case that we see out there now right. So, now let us say were going to consider case say if we want to let us say promote the dissociation of water into hydrogen gas and oxygen let us right if I want to form hydrogen gas let us say. So, what do I do now I need to apply what do we say external voltage right I look at applied potential here.

That now needs to be greater than magnitude of 1.226 right and also it should also be in the opposite side. Now let us see what that is I guess right so here let us say we are going to have applied potential > 1.226 . Let us choose let us say 1.5 volts to be E applied right and now how do we apply this we want to see to that we promote oxidation at 1 right and what does that mean I am going to connect the positive terminal right.

Positive terminal to cell 1 right so then I can write the new E cell as $E_{\text{cell}} = E_{\text{h1}} - E_{\text{h2}} - E$

applied right and now that is again going to be equal to obviously 0.812-0.414 right right and what do we have that here – 1.5 right and so that is now going to be equal to -0.274 right. So, what do we see now volts so after applying this external what we see potential right we now have or we are going to favor the opposite reaction.

So, now we are going to have $2\text{H}_2\text{O}$ dissociating to form oxygen in the gases phase and hydrogen right again how would we go about that because we applied an external voltage that is greater in magnitude than ΔE_h I guess. Right which is 1.5 volts and I guess after applying this particular external voltage now the water is unstable and then it would now dissociate into the relevant to what we say compounds.

And obviously now at what we see cell 1 you are going to have now oxidation right meaning anode meaning cell 1 would act as an electrode 1 would be the anode and electrode 2 will now be the cathode right again just a minor or what do we say reworking based on the relevant applied potential I guess. So, now we will move on to the next aspect.

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ORP → Oxidation Reduction Potential

Ref. H^+

p_e, E_h

- ① Not specific to any redox couple.
- ② Not yet at eq.
- ③ ? No idea about speciation of various redox couples

It is going to be the ORP measurements I guess right. So, these are the oxidation reduction potential measurements right so here out there let us say you know you have commercial ORP meters now oxidation reduction potential ORP meters. So, what will they you know help you with let us see right so you again this will have a standard electrode standard hydrogen electrode

or told all the submerged calomel electrode or reference electrode code right.

And again it is going to measure the potential difference between the standard hydrogen electrode or the standard reference electrode. So, how is this ORP going to work you are going to have a reference electrode right your standard electrode and it is going to measure the potential difference versus non-reactive electrode let us say a platinum electrode let us say right and then let us say it is going to be able to give you the potential difference.

Between based upon the situation in the water right is it more reduced more oxidized or such and based on that you can approximate your what do we say Eh or pE solution now. So, in effect ORP the ORP meter will give you an idea about the Pe or the Eh solution right. So, in general it will help you understand now is it relatively more oxidized conditions that prevailed or relatively more reducing conditions that prevail in your particular solution.

And based upon that obviously you can you tailor that to your needs and right. But you know people think of ORP measurement as the (23:12) that will give you all the information that you need but there are obviously disadvantages and such generalizations just look at what they are now. So, keep in mind that ORP reading looks at the solution so it is not specific not specific let us say to any particular redox couple right.

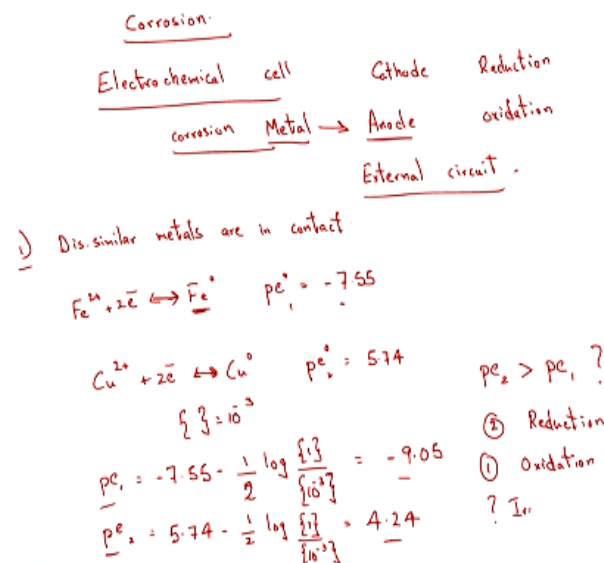
So, there can be multiple redox couples in the solution obviously right. So, the ORP meter or the measurement will not look at any particular what do we say redox couple it is going to be the cumulative right or the p that is existing in the solution now right. So, that is one particular aspect and again the key is that as you know redox disequilibrium usually what we is what predominates.

Say redox disequilibrium predominates what does that mean now let us say you are still you can still have a redox process that are going through and actually the p can change to right. You do not have your or the system is not at equilibrium so possible that your system is not at at equilibrium right so combined with us what is that we can glean or cannot glean now. So, while you can understand the solution currently has oxidizing conditions or reducing conditions.

Because the ORP reading is not specific to any couple and is also not what we say going to tell you the system is at equilibrium or not let us say or because you do not know that the kinetics can be slower right so what does it mean now it cannot give any idea about about the speciation a lot of various redox couples present in it present in the solution right. That this is an important aspect while the ORP will give you a generic idea.

It would obviously not provide you with the relevant information to be able to understand speciation of the relevant couples in the solution right. So, this is one other aspect and now we are now going to move on to another practical aspect with respect to redox process. So, this is with respect to corrosion that you would see out there right. So, corrosion again what is that now you can understand that they can in terms of an electro chemical cell right.

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So, we are going to look at that now right and we can understand it in terms of electro chemical cell right as in what do we have in an electro chemical cell obviously we have a cathode right where we have the reduction taking place we have an anode right where we have the oxidation taking place right and obviously what else do we need we need an external circuit external circuit bridging the gap.

Between bridging and acting as a bridge between the anode and the cathode right. We will see

external circuit now. So, in general you know when we talk about what do we say corrosion of metals. So, for example let us say your Fe iron in 0 valent iron let us say oxidizing Fe^{2+} let us say so, here anode is your metal let us or the surface of the metal is your anode right where the corrosion takes place yes.

And cathode obviously you know depends upon what is the electron acceptor out there right. So, were going to look at those aspects so again for corrosion to take place obviously you need your metal surface right which acts as the anode right where you have what we see the release of the electrons and oxidation and obviously you need a cathode which would accept or you know a place where surface where are or an electron acceptor I guess.

An electrode where we accept the electron or the relevant reactions there and then obviously you need an external circuit now. So, any of these three aspects if there means I guess obviously the corrosion would not go through. So, we are going to look at the what do we see a couple of ways to that corrosion goes through and then look at how we can control corrosion based on what we based on the knowledge that we have I guess.

So, in general there are 2 aspects again one would be with respect to when we have dissimilar metals being in contact. So, that is one aspect we are going to look at and obviously the other aspect is well let us say your metal is what do we say in contact with the usual electron acceptors out there and the most usual one obviously is your oxygen and that is the one we usually see out there.

But for industrial applications or such even when we have dissimilar metals that is a remarkably important issue. I mean dissimilar metals in contact with each other so were going to look at these 2 sets of examples I guess. The first set obviously is going to be the one when dissimilar metals are in contact right and so we are going to have an example here. So, it is going to be one with iron $\text{Fe}^{2+} + 2 \text{e}^{-}$ and Fe^0 .

And looks like value E^0 for this particular half reaction is $- 0.755$ and let that is also consider another half reaction dissimilar let us say copper $\text{Cu}^{2+} + 2 \text{e}^{-}$ right goes to Cu and this

particular P_0 is $=5.74$ right. So, again here we have the p_0 values for two half reactions and let us assume a case says when the Fe^{2+} and Ce^{2+} Cu^{2+} concentrations are equal to our activities are $=10^{-3}$ and work out the relevant p values.

And then compare them and see which metal will be oxidized or which metal will be corroded I guess right. So, let us look at so assuming that all the activities are $=10^{-3}$ so the Pe_1 right is going to be $=p_0 - 7.55 - 1/n$ right and log of what is activity of this particular what is a metal right pure metal so it is going to be 1 I say and $/10^{-3}$ right and that is going to be $=1/n$ as in n is 2 so that is going to be $=10^{-3} \cdot 1.5$ and that is $1.5 = -9.05$.

Right and then the Pe_2 is going to be $=5.74 - p_0 - 1/n$ again $1/2$ and times log of activity of 1 again required again C_0 pure metal right $/10^{-3}$ right again $1.5 \cdot 4.574 - 1.5 = 4.24$ right. So, from here you see that $p_2 > p_1$ right p_2 is greater than p_1 right so what does this mean now. So, it means that 2 will proceed as reduction and 1 as oxidation right. So, what does this mean now then the copper and iron are in contact with each other.

You know one is oxidation iron will corrode right because iron will corrode. So, obviously when you want to control such what do we say corrosion due to contact between 2 dissimilar matters let us say so what can you do now right. So you can have an insulation material between these 2 dissimilar metals. So, what are you trying to achieve there so this installation means you are cutting down on that external circuit right.

So, here we are when we are trying to control corrosion we look at the three aspects anode, cathode and the external circuit. So, when you have dissimilar metals in contact with each other you can have insulating material between each other as in you are preventing the contact between them and the transfer of electrons and thus there is not going to be any redox process going through.

Thus there is not going to be any corrosion of your particulate metal right. Or you can also have a sacrificial anode let me just finish that I guess.

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- a) Insul.
- b) sacr. anode
- c) E_{app} .

2) metal / soluble oxidant

$O_2, Cl_2, HOCl, CrO_2$

So, how can I control it 1 would be insulation against right insulating material and the other would be a sacrificial anode. So, you choose let us say another metal let us say who is so it is something like $p_2 > p_3$ let us say. You choose some metal and that will act as your sacrificial anode protecting your particular metal which is iron let us say that you want to see to it that does not corrode I guess right.

So, you are going to provide a sacrificial anode rather than iron acting as your or the metal surface of iron acting as your anode right so that is one particular case. Or you can also people do that rarely I guess in the industries anyway you can have an applied potential right. If you have the applied potential let us say you can see to it that the it is not thermodynamically favorable for this particular not thermodynamically favorable I guess.

So, this thermodynamically favorable reaction does not go through because you are applying an external potential I guess. So, this is one particular way to go about it so obviously we are also going to look at the second type of corrosion right. So, when you have a metal in contact with a soluble oxidant right. So, when you have the metal in contact with soluble oxidant such as that O_2 , chlorine. $HOCl$ right and CrO_2-4 right then again we can have corrosion.

So, obviously again we can look at what do we see the relevant p values calculating them and so on and go through. But obviously from your background you know the let us say O_2 is an

oxidizing agent it is an electron acceptor and again Cl_2 and HOCl here pardon me there again oxidizing agents. So, what does that mean now that their p value will be relatively high right compared to most p values of the relevant half reactions relevant to any other metals out there.

Let us say in that case obviously what would you observe now the p_1 being $> p_2$ right so you will have oxidation of your particular metal. So, how can you what do we say see to it that you control such type of corrosion now right. So, when you have this oxygen let us say dissolved in water let us say that is in contact with your particular metal now right. So, that is the reason why we paint it right again that is an insulating material we again paint it right.

So, that we are looking at you know cutting down that external circuit which allows for the transfer of electrons from one half reaction to the other right. So, that is the reason we paint metals that right or let us say you know you can also see to it that let us say obviously depending on the type of metal and initial layer of corrosion leads to formation of again metal oxides let us say.

And these metal oxides on the surface are again remarkably resistant to any other what do we say chemical process are transformation and they themselves act as an insulating layer let us see. Or lastly again you can promote formation of let us say an insulating there. In this case I believe we look at one particular example in our acid base relevant chemical process right as in we see to it that you know.

You have a layer of CaCO_3 let us say that would precipitate in your distribution network right. So, that would promote let us say not promote pardon me but we will see to it that you are what we say the distribution network or the pipeline let us say is not corroded why is it because you have a thin line of your precipitation on a metal plate. So, in such ways you can go ahead and what do we say control your relevant corrosion here.

Again two aspects more or less we are looking at cutting down or you know breaking that external circuit which acts as the connector for electrons from one half reaction to the other and that is again based on the relevant aspects we have looked at here right. So, again with that I

guess we are more or less done with today's session and we are going to wrap up the class in next session.

So, in the next session I guess we are going to look at the holistic approach right so thus far we have looked at equilibrium and kinetics and then looked at the major aspects as an acid base complex formation and precipitation inter solution. And again we looked at redox process and then as we went through the redox process we also looked at examples that you know gave us a holistic idea right.

As in what would the situation be if you looked at the theoretical aspect of just the redox process and then as we approach the true situation that we would expect out there in the nature as in redox in conjunction with precipitation and complex formation we saw how the system changes and why the relevant background is necessary in our particular chemical process right. And also throughout the class especially I guess with respect to let us say complex formation.

Or let us say precipitation we looked at let us say even in such simple aspects as coagulation and flocculation why such background is necessary as an easy charge neutralization that is relevant to your particular coagulation and flocculation or is it sweep precipitation or co precipitation right or sweep flocculation or co precipitation now. Again depending on that you need to choose your relevant coagulant right Fe^{2+} or Fe^{3+} and so on and so forth right.

So, in the next class we are going to look at it holistically again just a brief review of what we been up to and I guess then we will wrap up this course and that is it for today and thank you.