Environment Engineering: Chemical Processes

Prof.Dr. Bhanu Prakash Vellanki
Department of Civil Engineering
Indian Institute of Technology – Roorkee

Module No # 12
Lecture No # 58
Introduction to Electrochemical Cell (E cell)

Hello again so welcome back to our latest lecture session first again a couple of minutes to understand and we have been up to into last session right. So in the last session we looked at what do we say a couple of minor what do we say derivations where we try to understand the system let us say and relate PE in terms of let us say the molar GIBBS energy of electrons for the particular redox couple and again to be able to relate that to the redox potential right.

So we were able to do that and then we went ahead and looked at I guess two half reactions at the standard states and non-standard states and try to understand that let us say and then in terms of both the PE values or looking at molar GIBBS energy of the electrons in each of those redox couples to be able to understand let us say in which particular direction would the what do we say reaction proceed as in which half reaction would proceed as reduction and which one would have to be oxidation and the redox process to go through right.

So in that context obviously we looked at the case that electron obviously who want to travel from higher energy state to lower energy state right so obviously I guess once this electro transfer during these electrons transfer from higher energy state to lower energy state so what are we going to observe we are going to obviously observe release in energy right.

So obviously what we are driving at here is that in this or during these what do we say transfer of electron right and because the electron is worse that higher energy state compared to its just destination where it is lower energy state you are going to have release in energy meaning when these redox process goes through let us say right you are going to have or release and energy and we can calculate that too.

So let us see again look at the example that we had earlier so this was the example at non-standard conditions right non standards the nonstandard conditions where at PH7 and that the activities of HOCL and CL- respectively 10 power -4 and -3 but for the couple oh SO42- H2S it is 10 power -3 and then we understood the system and saw that because the energy of the electron.

Let us say or the molar GIBBS energy of the electrons in the couple or which respect to couple SO42- and H2S is higher than the 1 with HOCL and CL- are the 1 in equilibrium with HOCL and CL- we know that the reaction of the electron would like to move from these couple to here right or these couple meaning that these particular one will go through as reductions right it is going to accept the electron obviously and this is going to go through as oxidation because it is going to release or donate the electrons right.

So here as you see again there is going to be an energy release and calculate that so delta G of that particular reaction is going to be equal to what now right it is going to be equal to – 120.48 which is final state right – 20.96 right and that is I guess is approximately = 141.4 and the units as return here where 2 joules per mole right per mole right so wherever there is electron transfer I mean electron transfer or 1 mole of what do we say electron transfer here form the couple SO42- and H2SL and CL- 141.4 kilo joules will be released during that particular redox process right.

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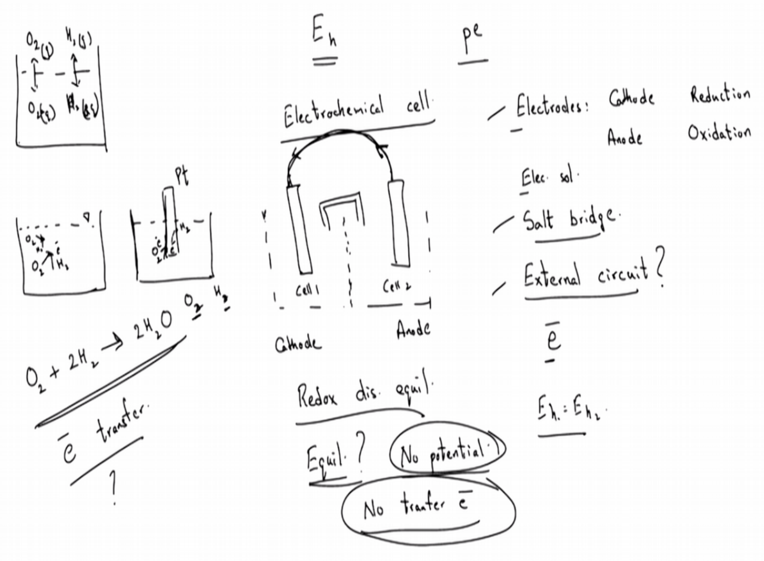

So I guess that help the system in slightly a better manner too right so we will now move to the EH approach right. So until now we have discussed the aspects related to PE and so on right so we were now going to look at the EH approach I guess so this is relevant to our electro chemical cell AH approach or redox let us say right electro chemical cell and let us look at what sum of these components are right.

So you will have the electrodes right and electrodes are cathode where you have the reduction taking place and anode that which you have the oxidation occurring I guess right and the you will have also have your electro solutions right and then more importantly you will also have these salt bridge or guess. Let us see the relevance of these with in short time salt bridge pardon me right electro chemical cell.

So let us look into visualize what up to here so let us here we have our cell and our electro here cathode and anode let us say we have semi permeable brain or if it is not that semi permeable we need a salt bridge and discuss again why we need that and let us say this is the cathode here at cell 1 and this is the anode here right cathode is where the reduction is occurring right so the electron transfer will be from the anode where the oxidation is occurring where is in the electrons or being released right.

And through the conductor right and we also need to have the external circuit that is something I miss writing up here I am going to have the external circuit right an why do we need these external circuit because you need a conductor for the electrons from one electrode to other right. So here this is the external circuit and obviously without these external circuit you will not have what do we say the electrons is being connected from one cell to the other.

And the other redox reaction will go through right so now let us just try to understand the relevant of all these what do we say aspects that we looked at electrodes the solutions salt bridge and external circuit I guess right. So electrodes I guess there are two kinds as in the reactive and non-reactive have in these electrodes that take part in the half reactions let us say or involved in half reactions.

So about time you will have loss of these electrodes let us say non-reactive similar to let us say the platinum electrodes let us say or non-reactive and I guess they just act as say the media not media I guess the surface at which the relevant half reactions occurs now right. So again we have reactive and non-reactive to what we say electrodes now. So again we have cathode and anode right the surface of which are which they themselves are involved in half reaction here.

So the anode you have the anodes the oxidation are released at the cathode we have the reduction electrons are gained. So anode and cathode but do the electrons go from here to there now. So that the reason why we need to know the what is it now external circuit I guess right so you need the external circuit and obviously without the external circuit you will not have the redox process go through right.

So that is the key aspect and again just because the electrons are being transferred now does that mean that redox process is going through or any other issues we need to consider now. The issue is that you know now it is going to be a charge imbalance now right. So the electrons are being transferred right so there is going to be net what do we say increase is in the negative charge in your let us say the solution in the cathode I guess right and then what is going to happen now again that will what do we say dissolute the redox process from going through.

So for that I guess obviously for the charge balance occur we are going to have to look at the salt bridge or have a semi permeable membrane let us say right. When let us say where it would allow the what do we say transport or the relevant salts or cations and anions or anions let us say such that there is a balance respect to the charge now right. Again there are different cells as in different kinds of cells as in both the electrons or in same solution or electrodes in different cells or solutions pardon me and so on different configuration.

But major aspects are the need for the two electrodes the external circuits and the salt bridge I guess right. So these are the aspects again one aspect here is you know what is the relevant of these what do we say electrodes or the cells or such let us say so let us look at one particular example right we are going to consider case let us say where we have water in equilibrium with water not water pardon me the atmosphere.

So we have oxygen and hydrogen in gaseous phase and let us say they are going to be now that equilibrium or in equilibrium with your water so we are going have O2 in aqueous phase and O2 in and H2 in the aqueous phase right pardon me right. We have O2 with equilibrium with the aqueous phase and again EH2 in gaseous phase in equilibrium with the H2 in the aqueous phase gaseous and aqueous phase in equilibrium again now we have we know relevant half reaction right and if we look at over all half reaction we know that $O_2 + 2H_2$ can lead to formation of your and H_2O right.

So this is one reaction that can occur though right let us look at what are the condition required for the that too occur now as we know this reaction occurs only when there is an electron transfer now right and for that to occur what needs to occur your O_2 molecule right needs to collate with the H_2 right the aqueous forms of both the O_2 and H_2 need to collide for the electron transfer to take place again let us say O_2 and H_2 right.

So this can obviously some times what do we say create issues not some time I guess what we say create issues with kinetics let us say instead of that let us say if I have an electrode let us say platinum electrode let us say right how will that assistance further in this particular reaction now as in the relevant half reaction with the oxygen let us say can occur here and the relevant electron let us say can be transported to the oxygen molecule from here while the relevant half reaction right with respect to the H^+ and can occur out here.

And the electrons can transfer here through the conduction let us say or obviously the electrode whereas act the conductor for the electron transfer. As in now we do not know the electron H_2 molecules let us say O_2 aqueous form or O_2 H_2 let us say to collide or they need be any fusion now.

So the reaction or half reactions can occur at different places of the surface of the platinum electrode and the electron transfer can take place from the site of what do we say the H_2 related half reaction to the side of the O_2 related half reaction now right. So this when obviously now promote to the relevant what do we say overall reaction this is just by one example.

So obviously though if we get you know look at such particular cases though we cannot let us say constructively utilize this flow of electrons from one what do we say redox couple to the other though. Let us say if you have your battery or such what do we trying to do we are trying to constructing constructively utilize the what do we say current or let say flow of the electrons let us say right.

So to be able to do that obviously you are going to have let us say two electrodes let us say right two electrodes right again cell 1 and cell 2 let us say and you have electrode one here and electrode two here and now we have separation of two what do we say half reactions which of the half reactions are occurring at just the on the same electrodes right.

We are now going to have only one half reaction at one electrode another half reaction at another what do we say electrode and you are going to have the transfer of these particular electrons here form one cell to other which depending upon the relevant redox process and relevant energy that would be released let us say right you can utilize accordingly constructively now right.

So here again the aspect that we need to look at is what drives the reaction now the redox process or the transfer of electrons. Again keep in mind that everything is you know in nature out there the reaction involved out their see to it that energy of the system decreases now right. So in that case again what is it about now so thee reaction only go through when there is redox dis equilibrium right only when there is redox disequilibrium right where let us say the electrons dis equilibrium and they try to approach each other right and when there is equilibrium now there is no more potential now right.

So there is no more potential now yes there is no more potential and thus no more what do we say transfer of electrons. So obviously let us say for your electron transfer to occur or obviously the system needs to be at redox disequilibrium one and the tow cells reach equilibrium let us say right you are not obviously going to have any for the transfer of electrons let us look at the previous slide to help listed this.

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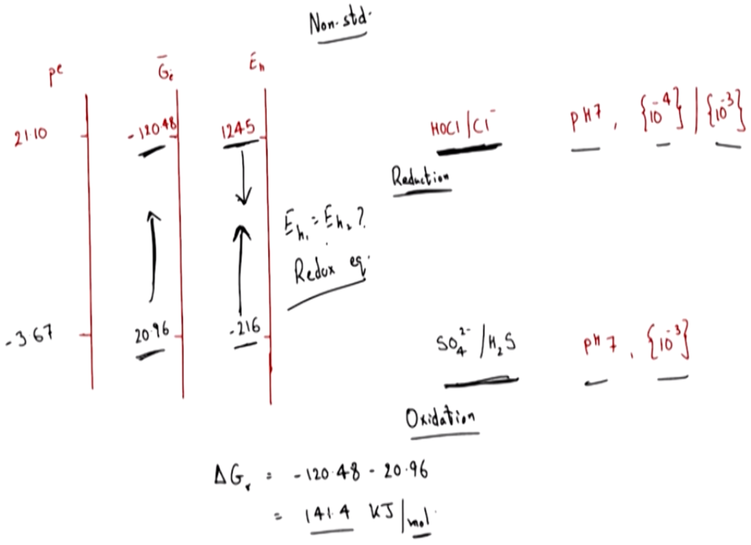

So here let us say you have what do we say EH here right redox potential for what do we say one cell redox potential for cell two now so how is it going to go through now that both the potentials or they travel in such a directions that both the potentials are going to be equal now right. So one the EH one is going to decrease and EH2 is going to increase and once these EH1 = EH2 what do we have now we have redox equilibrium right.

So once again when we have that EH1 = EH2 right we have equilibrium and then no more potential and no more transfer of the relevant electrons right so again this is the whole aspect that we need to keep in mind again as in one example we consider is your battery right. So what do you mean by when back to as exhausted or useless now right it mean that you know the redox equilibrium has been reached right and you have then there is no further potential driving the you know transfer of the electrons I guess.

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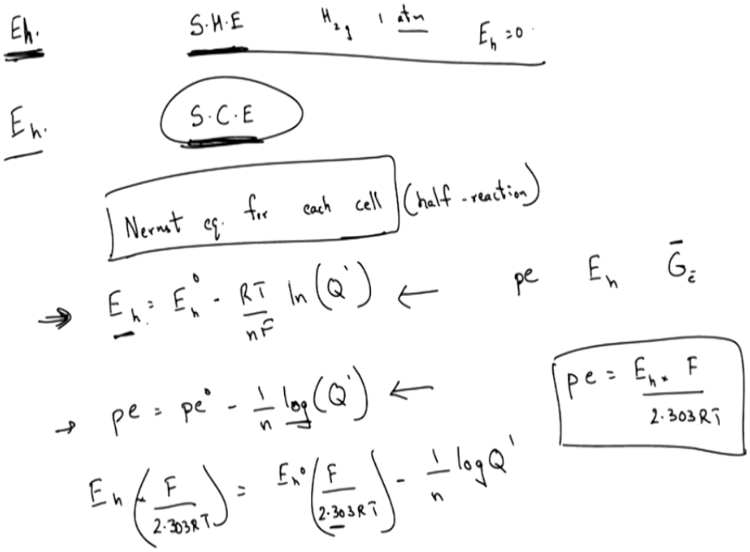

E_h. S.H.E H_{2g} 1 atm $E_h = 0$

E_h. S.C.E

Nernst eq. for each cell (half-reaction)

pe E_h $\bar{G}_i$

$$\Rightarrow E_h = E_h^0 - \frac{RT}{nF} \ln(Q') \leftarrow$$

$$\rightarrow pe = pe^0 - \frac{1}{n} \log(Q') \leftarrow$$

$$\boxed{pe = \frac{E_h \cdot F}{2.303RT}}$$

$$E_h\left(\frac{F}{2.303RT}\right) = E_h^0\left(\frac{F}{2.303RT}\right) - \frac{1}{n}\log Q'$$

So now we are going to move to the relevant aspects now so let us again moving on I guess right so particular aspect which was discussing here is to be able to calculate or measure EH I guess right electro redox potential how do I do that people look at the standard hydrogen electrode let us say right. You know I guess hydrogen gas at 1 ATM pressure and the relevant half reaction let us say and in reference to this standard hydrogen electrode you try to measure the potential of this particular redox potential of your particular cell or the half reaction.

So based on that you can calculate the relevant EH of your particular cell now usually you know carrying these or you know standard hydrogen electrode maintain that may be relatively different so even if you do not have the reference of standard hydrogen electrode which we set to be let say EH to be 0 let us say right. That is the reference here let us say similar to your mean sea level now right.

The standard hydrogen electrode let us say but let us say let us say if you most people might have used your PH meter right what is that measuring now right. It is measuring again the potential there right again if you are measuring the potential you need two electrodes right so one electrode would be these standard calomel electrode right where you have I believe HECL2 the solid right you know do not take my word on that we have the standard calomel electrode now.

So you know you have with in the PH meter you standard calomel electrode and let us say the other electrode would be let us say in your solution let us say where you have let us say semi permeable membrane we have H+ would tend to what do we say B is observed on the surface of the membrane let us say or this semi permeas membrane and then you are going to again measure what is that now the potential difference between this standard calomel electrode right and the half reaction at the other platinum electrode.

So when you dip your PH meter in your solution what are we measuring again you are measuring the potential difference there right. So again you are measuring the potential difference and calibrating that at phase 3, 7 and 11 and so on right and you are telling the system that the PH mirror that this potential difference is equivalent to 3 such potential difference is equal to 7 and so on. So that is how you end up measuring your what do we say you PH I guess right.

So again and just a illustration I guess of where we come across this particular concept so again when we dip your electrode what do we say PH probe into your solution in effect you are measuring the potential difference between two half reactions there right anyway standard calomel electrode but or standard hydrogen electrode so reference electrode should be able to measure your redox potential of your particular half reaction I guess right.

So moving on though we come to standard equation which is the (()) (17:28) equation for each cell okay or for each half reaction I guess and this is something that people might understand once settle down EH = EH naught – RT / NF natural logarithm of Q dash. So I guess once you write this down you should immediately be able to see the analogy with respect to PE = PE naught right - / N and being the number of electrons being transferred natural logarithm of Q dash right.

And again earlier we looked at the relationships between PE EH and molal GIBBS energy of the electrons in the last session I gave right. So again looking at the same principle or even manipulating the again this I guess or if I manipulate the first equation these as EH into F / this value will be 2.303 RT let us say will be equal to again EH naught into F/2.303 RT – 1/N log should not be natural logarithm here the natural logarithm here right.

Log Q dash that is the reason why we have the 2.303 value here the PE 1 will with respect to logarithm but not the logarithm to base 10 not logarithm to base 10 that was not logarithm to the base C it was minor error their so here again we looking at this what can you understand here I guess right we can understand that PE value is nothing but = EH into F / 2.303 RT right this is again something similar to what we looked at or derived in our previous sessions here right.

So again you see that you see the relevant analogies right and from there we can understand that the system again and this particular equation is called the nerviest equation for the each cell here right and here these are the redox potential that people will use or look at here right.

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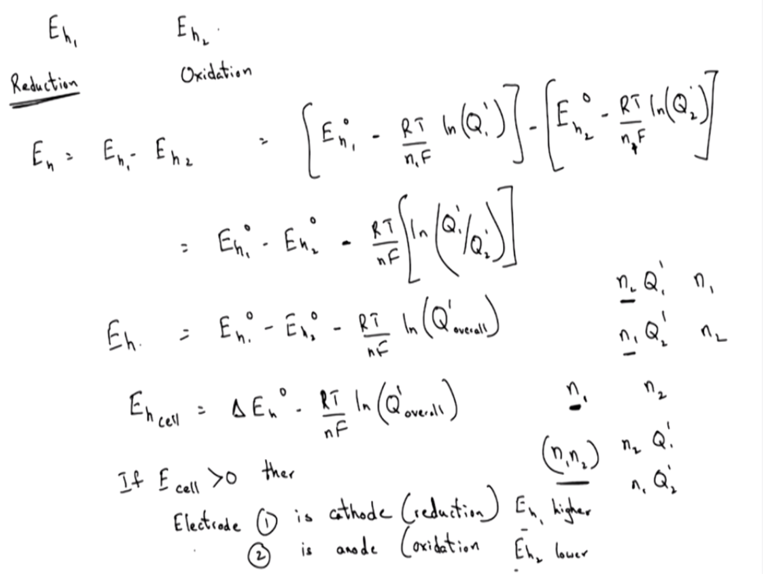

E_{h_1} E_{h_2}

Reduction Oxidation

$$E_h = E_{h_1} - E_{h_2} = \left[E^\circ_{h_1} - \frac{RT}{n_1F}\ln(Q_1')\right] - \left[E^\circ_{h_2} - \frac{RT}{n_1F}\ln(Q_2')\right]$$

$$= E^\circ_{h_1} - E^\circ_{h_2} - \frac{RT}{nF}\left[\ln\left(Q_1'/Q_2'\right)\right]$$

$$E_h = E^\circ_{h_1} - E^\circ_{h_2} - \frac{RT}{nF}\ln\left(Q'_{overall}\right)$$

$$E_{h_{cell}} = \Delta E^\circ_h - \frac{RT}{nF}\ln\left(Q'_{overall}\right)$$

$n_2 Q_1'$ n_1

$n_1 Q_2'$ n_2

n_1 n_2

$(n_1 n_2)$ $n_2 Q_1'$

$n_1 Q_2'$

If $E_{cell} > 0$ then

Electrode ① is cathode (reduction) E_{h_1} higher

② is anode (oxidation E_{h_2} lower

So again let us moving on so you have two cells here let us say EH1 and EH2 let us say so how would these particular reaction proceed or how do I understand this particular system let us say right. So let me assume that EH1 proceeds as reduction right and EH2 proceeds as oxidation let us say the EH would be equal to EH1 – EH 2 right so let us try to plug that in here.

So that would be equal to EH naught of 1 – RT / N1 F into natural logarithm of Q1 dash right – EH2 naught – RT / NF and 2F N being the number of electrons being transferred in the half reaction let us say the same number of electron is being transferred let us say N1F right into natural logarithm of Q2 dash right.

So what do we end up here it is going to be equal to EH1 naught – EH2 naught – RT / NF and natural logarithm of Q1 dash / Q2 dash right Q2 yes that be the right way to express that yes I believe that is true and how would that transform into that is going to be equal to EH1 naught –

EH 2 naught – RT / NF natural logarithm of Q over all reaction right Q of the overall reaction right.

So when is this particular value going to be positive now right so this PH cell could be equal to delta of EH naught – RT / NF natural logarithm Q dash overall right Q dash of the overall reaction right. So here let us say if it is not only N what do we say the same number of electrons being transferred as in one half reaction if we have N1 and then N2 so the N would have replaced by N1 N2 right the number electrons being transferred and Q dash 1 and Q dash 2 would have to be 1 you would have multiplied let us say Q2 dash by N2 and Q2 dash by N1 right.

So we are looking at the case as in let us say for 2 dash relevant half reaction we had N1 electron transfer and for the Q2 dash relevant reaction we had N2 electron transfer but we have the same number of electrons being transferred we need to multiply Q1 dash / N2 and Q2 dash / N1 right. So then here the N would be N1 N2 and the relevant Q dash Q1 dash and Q2 dash should be modified such that you multiply Q2 ash / N2 and Q2 dash by H1 and the relevant stoichiometric coefficients I guess right.

Anyway so that is one particular option here not option pardon me the way to go about it so obviously when if E cell is greater than 0 then what is that mean now then the electrode 1 let us say is cathode right or where reduction occurs right and electrode 2 is the anode where the oxidation occurs right as in EH is higher EH1 is higher than PH2 right. So again we can understand this in terms of what we had the half reaction we had earlier the relevant set up here.

So here EH1 is higher than EH2 right so again what do we see here that would mean reduction with respect to this couple and oxidation with respect to this couple right so again the relevant cathode and anode out here so again that is one particular case to go about it.

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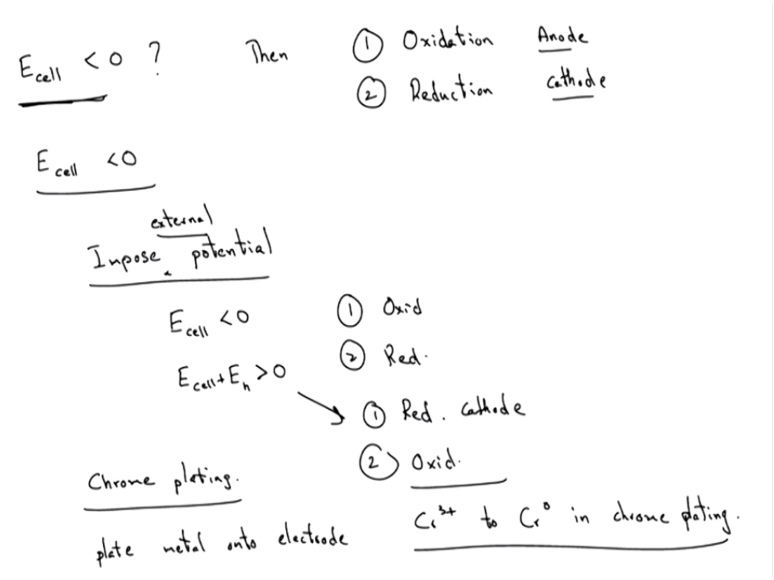

$E_{cell} < 0$?   Then ① Oxidation Anode

② Reduction cathode

$E_{cell} < 0$

Impose external potential

$E_{cell} < 0$ ① Oxid

② Red.

$E_{cell} + E_h > 0$ → ① Red. cathode

② Oxid.

Chrome plating.

plate metal onto electrode Cr^{3+} to Cr^0 in chrome plating.

So obviously IF E cell right is less than 0 what is that mean then the reverse needs to be applied right then what do you see now one right is going to have to be oxidation right or 1 the electro cell1 would have to proceed as or could be the anode and 2 would be the reduction let us say right and that would have to be the cathode if E cell is negative I guess right. So these is 1 particular case though so the major aspect is say I have a unfavorable reaction or the E cell turns out to be negative let us say right.

So here let us say we are talking about redox potentials right and electro chemical cell and we looked at the electro chemical cell calculation and saw that let us say when EH1 greater than EH2 we looked at reduction oxidation but let us say if it is less than 0 we see that it is unfavorable or the oxidation should takes place as anode and reduction it cathode.

But let us say if I want to force a particular reaction to proceed as reduction even though the thermo dynamic or such let us say that you now it is not going to proceed as the relevant what do we say relevant redox process I guess so what can I do now. So in that context obviously I can impose an external potential now right so I am going to say I can impose right a potential or a external potential right impose let us say an external potential.

By imposing this external potential I can term this E cell which is less than 0 right now right so that one proceeds as oxidation and two proceeds as reduction right by imposing these particular what do we say external potential I can see to it that E cell + this external potential that I am applying will turn out to be 0 right.

And in that case again we are going to have reduction at your particular electron chemical cell1 right which will then be act as the cathode right and oxidation here and again what are the applications obviously if there is a compound let us say that the compound reduce and under thermo dynamic conditions is not going to be reduce now so you have these external potentials applied to be able to force these particular what do we say reactions or half reactions or the redox reactions needs to go through.

And let us say practical application what do we look at we at chrome plating I guess right as in what are we trying to do we are trying to plate the metal on to the electrode right and as in CR3+ we want this male this favorable which is usually not so for that let us say we apply the external potential. So how do we go about chrome plating or someone refers to chrome plating right.

I want to be able to reduce CR3+ to CR naught I will mutual charge let us say right and let us say this reaction is not favorable though so how do I go about that or how do I make that happen I make that happen by imposing a external potential right. So again there are again application with respect to these particular aspects but here with respect to understanding the system with E cell and the external approach people I guess need to look at the terminology or relevant science involved now.

So here as in to which particular electrode would you connect the positive terminal and to which particular electrode would you come the negative two terminal and so on we are going to look at these aspects and then look at also what measurements right as in what we measurement as in to be able to get what do we say generic over view of these reduction potential right oxidation reduction potential of a particular solution you have these ORP meter you can use I mean there are some application but not a great log.

So we are going to look at or in greater detail with respect to these terms respect to or with respect to science with respect to the external potential and also look at with respect to the ORP measurement and then move on to let us ay understanding how corrosion happens and how you can limit corrosion in the next session I guess right. So I guess wit that I will end today session and thank yo.