

**Environment Engineering: Chemical Processes**  
**Prof.Dr. Bhanu Prakash Vellanki**  
**Department of Civil Engineering**  
**Indian Institute of Technology – Roorkee**

**Module No # 11**  
**Lecture No # 51**  
**Equilibrium of Redox – I**

Hello everyone so again welcome back to our latest lecture session so we have been discussing the relevant aspect with respect to kinetics right and I think the example we have been looking at was when we have hydroxyl radicle right.

Let us just look at what we have been up to hydroxyl radicle it can react either with the target or the scavenger right because again hydroxyl radicle is a very strong oxidant or oxidizing agent and it also relatively non selective so depending upon the relevant kinetics with respect to either the targets or with respect to scavengers you have a relatively more efficient system or in efficient system right.

And we looked at how we can analyze that particular aspect right in terms of rate of production of radicle and rates of the oxidation of the relevant target right we looked at those particular example and I guess we also looked at how to be able to estimate the rate constant of your particular what do we say reaction of hydroxyl radicle oxidizing your target right usually have a target and you do not know the rate constant right of these particular what do we say reaction that you are looking for specifically.

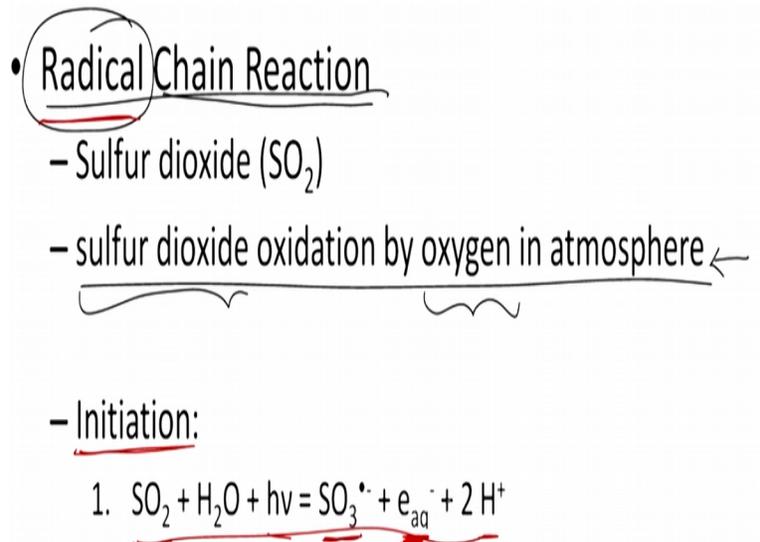
But you will have what do we say data available but usually the next database right NIST database and that you will have the relevant rate constant of hydroxyl radicle with most of the usually you know encountered compound or scavenger right. So give an particular rate constant as in think with respect to K if you had KS we saw how we can set up the equation and then by regression come up with your unknown rate constant which is KT.

So again we are going to have you know spend few more minutes on kinetics right and this aspect here obviously we are going to look at is mostly relevant to what you would see in the atmosphere right I guess the example we have is sulphur dioxide right and sulphur dioxide right.

Let us say depending upon the type of quality of particular fuel you have what do you say sulphur di oxide like being emitted into the atmosphere right from various power plants or during the combustion or of the relevant fuels or obviously again during let us say volcanic eruption you can have sulphur di oxide give out into the considerable concentration right.

So again we know that sulphur di oxide can lead to what do we say acid rain I again acid base relevant chemical process right sulphur di oxide can lead to formation of what do we say acid rain and also sulphur di oxide can also toxic too human beings right but obviously not obviously i guess but there is a mechanism in the atmosphere that lead to this particular oxidation of sulphur di oxide to sulphate  $\text{SO}_4^{2-}$  which is less toxic and deny too.

**(Refer Slide Time: 03:12)**



So let us look at that particular system and how that go about I guess so obviously here it is depend upon a radicle chain reaction so again when ever you have a radicle I guess right you are going to have chain reactions yes you are going to have a either forming what do we say multiple or further radicle that can lead to other relevant reactions right. So let us look at what we are up to here right I guess.

So here we are talking about sulphur di oxide right sulpher dioxide oxidation but oxygen in atmosphere oxidation how people look at or what people look at with respect to what do we say decrease in sulphur di oxide concentration the atmosphere. But you know this is the simplistic

explanation let us look at actually happens their referring to sulphur di oxide oxidation by oxygen right.

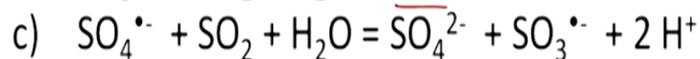
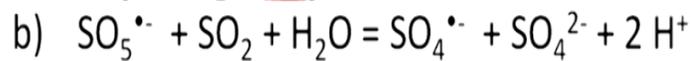
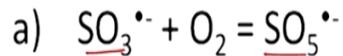
So let us look at what happens out there so obviously we are going to have what do we say reaction leading to information of your particular radicle right of your particular radicle so you are going to have the radicle formation so usually we call this step initiation reaction right again we are taking about with respect to atmospheric chemistry here right.

So let us look at the relevant reaction so sulphur dioxide in the presence of you would usually I believe right can form the sulphite anion radicle right and again release the electron aqueous electron which has relatively low what do we say half –lives right this obviously the strong reducing agent right and obviously H<sup>+</sup> here so here let us say sulphur di oxide leads to formation of radicle and an aqueous electron by itself to right.

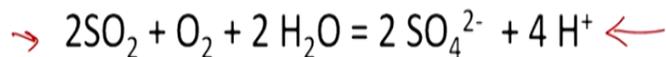
So this is what happens and let us see what happens here with respect to the different chain reactions right.

**(Refer Slide Time: 04:45)**

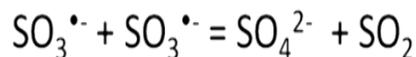
- Chain



Net Reaction:



Termination:



So here we have relevant chain reactions right this sulphide anion radicle reacts with oxygen to form SO5 or it is oxidized sulphur is oxidized what is what you can see here by oxygen and again this particular SO5 anion radicle right again as another chain reaction here. Again it is going to react with SO2 this is what we were looking at sulphur di oxide here right.

So let us look at where sulphur dioxide is being oxidized now so here we had sulphur dioxide right transforming into sulphate and anion radical and here we also see that one of the by products right which is  $\text{SO}_5$  anion radical can again react with sulphur dioxide to what we say now from I believe  $\text{SO}_4^{2-}$  or sulphate anion radical right. So and again next step you know another particular aspects with respect to again  $\text{SO}_2$  right oxidation of this  $\text{SO}_2$  by this sulphate anion radical.

And again  $\text{SO}_4^{2-}$  radical and  $\text{SO}_3$  are sulphate anion radical being formed right so these are the chain reactions that we see here right. So with respect to or based on the sulphate anion radical formed when let us say UV I guess right leads to formation of this particular anion radical from sulphur dioxide and then the relevant chain reaction you know chain reaction but if you look at the net reaction let us see what it turns out to be right.

The net reaction when you look at the net or overall reaction you see that it looks like its sulphur dioxide oxidation by oxygen to sulphate right. But obviously if you look at the relevant aspects you see that it is not just oxygen leading to what do we say oxidation of particular ahhh ahhh sulphur dioxide right but it is that you have a radical being formed the sulphate anion radical and then you have relevant chain reactions which lead to the consumption of your sulphur dioxide right.

And the key here is that you know in this particular reaction we are not consuming or leading to loss of your particular sulphate anion radical right what is that mean so if you not in this particular chain reaction you are not it is not net consumer of your sulphate anion radical right what is that mean now?

So the sulphate anion radical what do we say form earlier right anyway it is free to not free I guess concentration are not going to decrease due to these sets of chain reactions but obviously radical are remarkably reactive and there is going to be quenching or scavenging reaction let us say what it is?

So the termination or quenching or scavenging reaction it is the sulphate anion radical reacting with itself to form the form sulphate of sulphur dioxide I guess and this obviously happens when

the concentration of these radicles are relatively high right and so this what it actually happens when someone refers to sulphur dioxide loss due to it oxidation by oxygen right the key is that initiation of formation radicle and then the relevant chain reactions and then the overall reaction seems like it is oxygen oxidizing the sulphur dioxide right.

Again for this obviously if you are trying to build a model right it is going to be relatively complex because you have relevant I mean many radicles right we have many radicles right and you have many have the relevant reactions right so here we have not considered all the other compound that can be present in the atmosphere but you can build the model wherein let us say you can use let us say ordinary differential equation solver in matlabs let us say.

And you can build a model let us say and solve for this particular system let us say right or predict this particular system or I am sure that other air pollution related models that can exist in getting this done right.

**(Refer Slide Time: 08:35)**

Equilibrium ?  
Feasibility      Q/k      .pe

So let us move on so now we are going to (refer time: 08:35) move to equilibrium right so again the key here was that in the context of redox process what we understand now or what do we understand from our background we know that kinetics is the aspect that place a huge role right but what does equilibrium give an idea about you know what is that tell you about so it tells you whether obviously a reaction is feasible or not.

So obviously we will also look at equilibrium why? Because you want to know is the reaction feasible or not right so we are going to look at feasibility of particular reaction so keep I mind that in this context it does not let us what the concentration of equilibrium are going to be again because rarely with the system reach equilibrium but understanding the equilibrium will tell me other this particular redox reaction that in the first what do we say case thermodynamically feasible or not right.

So that is particular aspect we are going to look at let us say so with respect to understanding the feasibility of system there are what do we say different approaches right so the first approach would be with respect to  $Q / K$  one particular approach and then with respect to the redox potential  $P$ .

So we will look at these two aspects are these two sets of variables to understand let us say is my reaction or can I consider these particular redox reaction to be thermo dynamically feasible or not and also understand in terms of these variables especially PE right what would you expect with respect to the system if set at equilibrium right so let us look at these aspect I guess.

**(Refer Slide Time: 10:10)**

$$aA + bB \leftrightarrow cC + dD$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$Q = K \quad \text{At eq.}$$

Reaction Feasibility

$-Q/K$

a.  $Fe^{2+} + 2e^- = Fe^0 \quad \log K = -15.12$

b.  $O_2(aq) + 4e^- + 4H^+ = 2H_2O \quad \log K = 86.00$

*Redox*

So reaction feasibility obviously that is what we are looking at so  $Q / K$  approach  $Q$  again what is that now the ion activity product  $K$  is equilibrium coefficient right. So obviously  $Q$  will be equal to  $K$  at when the system is at equilibrium obviously right. So again how did we how do we write down  $Q$  have an activity product right so  $Q$  would be equal to activity or in this case

concentration and approximately by concentration products raise to their relevant stoichiometric coefficients right by the relevant variables for the reactants right.

And obviously when it is set equilibrium the  $Q$  and  $K$  values are going to be the same right and again as we know  $K$  equilibrium coefficient values are available in most of the standard values right and there available for standard condition at most in most of your relevant books right or in the NIST database. So obviously we are going to look at let us say  $Q$  relative to  $K$  and try to understand let us say system going to be equilibrium or not do right  $R$  is the reaction feasible or not for a given set of conditions.

So obviously  $Q$  less than  $K$  we know that what is that now the reaction is feasible  $Q$  and  $K$  are equal to we know that the equilibrium is already been reached right and it has now further motive to travel in any other direction right travel as in sense I am using laymen terms here obviously and if obviously  $Q$  is greater than  $K$  it means that the reaction is not feasible so let us look at one particular example here.

So we have 1 particular half reaction so obviously we are talking about redox reaction here so here we have what do we say relevant  $K$  to be  $-15.12$  for this particular reduction half reaction usually in your particular standard tables or such you will see that most of these half reactions are written as reduction right that is the way they are written and relevant what do we say constant are given right.

So let us look at the other particular what do we say equation too right so we have oxygen reduction right and we have the  $\log K$  value given here right so now let us say I want to know let us say I have feasible is it for iron to be oxidized you know  $0$  and entire let us say to be oxidized by oxygen right you know this is what let us say I am trying to look at as the two reaction is the reduction of  $2+$  to  $FE$  naught and obviously reduction of oxygen  $2 H_2O$  let us say right.

But obviously what is that I am trying to understand and trying to look at let us say how is it feasible for particular set of particular scenario that the  $0$  or iron can be oxidized by oxygen what is it mean for corrosion to occur right.

**(Refer Slide Time: 13:11)**

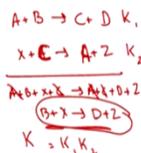
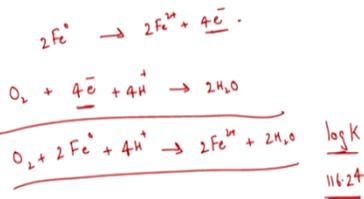
• Reaction Feasibility

- Q/K

a.  $2(\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}^0) \log K = -15.12 \leftarrow$

b.  $\text{O}_2(\text{aq}) + 4\text{e}^- + 4\text{H}^+ = 2\text{H}_2\text{O} \log K = 86.00$

$\log K = -2(\log K_1) + 1(\log K_2)$   
 $= 30.24 + 86.0$   
 $= 116.24$



$K_1 = \frac{[C][D]}{[A][B]}$   
 $K_2 = \frac{[A][2]}{[x][C]}$   
 $K_3 = \frac{[B][2]}{[x][C]} = K_1 K_2$

So let us look at that I guess right obviously now I need to look at the overall reaction right so I can look at the overall reaction but I cannot obviously sum them up at the way they are right and why is that obviously again first you would not have electron being accumulated right.

So what do I need to do I need to what do we say swap this particular reaction right as in and also multiple that by two times and why do I need to multiply this particular reaction by two times because I need to be able to see to it that the electrons being transferred or the same in half reactions right so I need to be able to look at that. So obviously transformed or log K the overall reaction what is that going to be equal to that is going to be equal to -2 - because I am going to swap this particular reaction right log K1 right + 1 times log K2 right.

So from that particular values I see that around let us say 30 so 30.24 + 86.0 that is going to be equal to 116.24 right log K for this particular overall reaction and what is the overall reaction let us try to write that down here oxygen + 4 electrons + 4H + goes to 2H2O and obviously you have swap in this and multiplying it two so this going to 2FE2+ + 4 electrons right again you know here we are looking at let us say oxidation of iron right so that is why I am swapping this particular reaction and multiplying with 2 because I want to be able to balance the electron transfer right.

So I am going to let us say sum that up so oxygen 2FE naught + 4 H+ is going to be what I am going to form here 2FE2+ + 2 H2O so this is the particular reaction for which we just found out

the log K value to be 116.24 right. So obviously I am going to now use this particular value to calculate and obviously look at calculation of Q by K for a particular scenario but before we go further let us look at you know how we end up with log K = this particular set of equation I guess right.

So let us say I have  $A + B \rightleftharpoons C + D$  and let us say  $X + A \rightleftharpoons C + Z$  right and I have a  $K_1$  or equilibrium coefficient for the first reaction  $K_2$  for the second reaction let us see right. So if you look at it let us say  $K_3$  or the overall reaction what is it now this is going to be I guess you know I should not have written this in this manner.

But if you write the relevant coefficient and such and see to it that the cancel out let us say as then writing it write it  $C + X + A + Z$  and now it is easier for us to understand so that now it is going to be equal to what now  $A + B + X + C \rightleftharpoons A + C + D + Z$ . So ACA I cancel them out this is more or less over all reaction is  $B + X \rightleftharpoons D + Z$  right.

So I want to know the equilibrium coefficient of this overall reaction right so how can I get that if you see that if you are summing it up the K is going to be equal to  $K_1$  times  $K_2$  right and that is what you see here why is that again  $K_1$  as we know  $= C \text{ times } D / A \text{ times } B$  and  $K_2 = A \text{ times } Z / X \text{ times } C$  but I am trying to calculate  $K_3$  which is from this particular equation as you see here  $D \text{ times } Z$  divided by concentration of B by concentration of X right.

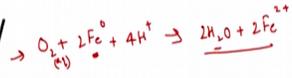
So what is that going to be equal to if you look at these two variable it is nothing but equal to  $K_1$  times  $K_2$  right so again I am just trying to show how it comes out here so why do I obviously you know multiply the -2 here minus because I am what do we say swapping the relevant reaction right and also two because I am multiplying the equation or reaction by 2. So that is how I guess you end with this particular kind of equation here.

**(Refer Slide Time: 18:05)**

$$\log K = 116.24 \Rightarrow K = 10^{116.24}$$

$$Q = \frac{\{Fe^{2+}\}^2}{\{O_2\} \{H^+\}^4}$$

• Reaction Feasibility



- Q/K

a.  $Fe^{2+} + 2e^- = Fe^0$   $\log K = -15.12$

b.  $O_2(aq) + 4e^- + 4H^+ = 2H_2O$   $\log K = 86.00$

$$Q = \frac{\{10^{-3}\}^2}{(10^{-4})(10^{-7})^4} = 10^{26}$$

$$\left( \frac{Q}{K} \ll 1 \right)$$

$$\frac{10^{26}}{10^{116}} \ll \ll 1$$

So again let us look back what we are up to so we see that log K value 116.24 right log K value = 116.24 so now I want to calculate Q and Q I guess what was that particular reaction I guess right so I am going to assume let us say some particular condition let us say PH7 and so on let us calculate what Q is going to be equal to again for that obviously in need the relevant what do we say overall reaction.

So let me right that down again so it is going to be equal to + 2FE naught + 4H+ right is going to go to 2H2O + 2 FE what is this here 2FE 2+ right. So obviously Q for this particular case what is that going to be equal to right so it is going to be equal to activity of O2.

Let us say the aqueous phase or dissolve phase it is aqueous concentration not the gaseous phase times activity of let us say I do not know I am going to assume is going to be equal to pure solid that is why it is equal to let us say 1 times activity of H+ right I guess I just met this up we need to write the reactants first divided by the products right.

So I am going to write down 2 here so that is going to be equal to activity of FE2+ (( )) (19:34) we know that it is going to 1 assuming that it is dilute solution by activity of O2 right and in again in the aqueous phase and the gaseous phase activity of H+ t the power of 4 right so let us say here I assume some particular standard condition and write this down right and again why did we say activity of H2O was equal to 1 and activity of iron was equal to 1 because I am assuming that H2O you know again it is dilute system right.

So again activity is equal to be 1 there and here let us say it is 0 was in solid right if it is a pure solid we know that the and here let us say it is a 0 solid and right if it is pure solid we know that the activity now is going to be equal to 1 and based on that we know the relevant what do we say equation for Q.

So let us say take one particular case obviously when PH is equal to 7 and let us say the relevant aspects so if I write down Q that is going to be equal to let us say at relatively low concentrations of  $Fe^{2+}$  which is I am assuming  $10^{-3}$  right I am assuming that  $10^{-3}$  concentration is  $10^{-3}$  power - 3 and  $H^+$  is  $10^{-7}$  to the power of let us say 4 right because PH is 7 I am assuming is PH 7.

And let us say it is  $10^{-4}$  concentration here of oxygen I am taking relatively low concentration of  $Fe^{2+}$  and which was you would presume or you know expect in your particular water and also I am assuming that the PH is still 7 the neutral what do we say PH I guess. So if we calculate thus I believe it is going to be equal to  $-64$  so it is going to be equal to  $10^{26}$  right pardon me.

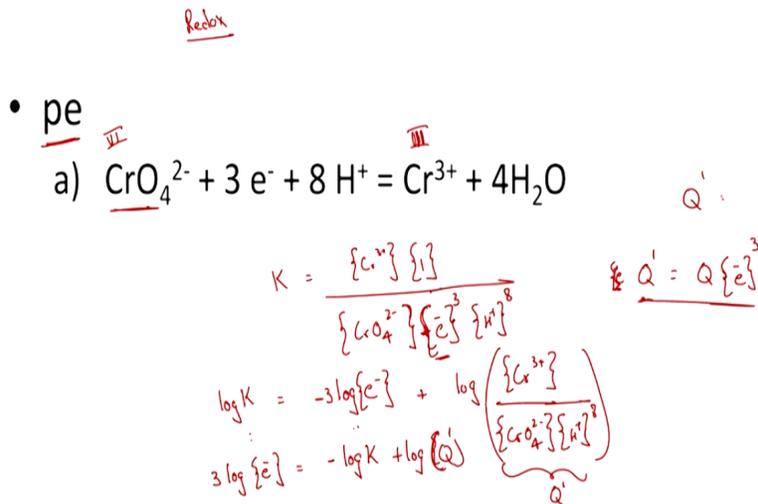
But as you see from here  $K = 10$  to the power of 116.24 right that is what you see here. What do you see when you calculate  $Q / K$  right it is very much less than what is this now 1 right so I calculated K from the relevant let us summarize what we have been up to I calculated K for the overall reaction of oxidation of iron by oxygen right or more or less corrosion of by oxygen right and I calculate the K value right and then I calculated Q the ion activity product for a particular scenario as in which was case in PH7 and I assume that iron and oxygen concentration are relatively low.

And obviously you see the Q is much lower right  $10^{26}$  and K something like  $10^{116}$  which is much less than 1 right. So again keep in mind if you look at this even if you change let us see the variables by few order of magnitude oxygen concentration in aqueous phase you only have a threshold right 8 milli gram or 9 milli gram per liter based on the what do we say temperature so that is more or less what do we say it would not change much.

But even if you vary FE2+ concentration a lot even if you increase FE2+ concentration a lot you still see that you know Q it is order of magnitude half by 80 right or 90 here so even if you increase the concentration of FE2+ still see that the corrosion of iron by oxygen is still feasible you know that is what you obviously observe in the nature right. So here that is the case that we just looked at right.

And obviously the oxygen concentration are relatively low in the aqueous phase right and that is why you know that is why you cannot vary this much even if you effect H+ match it does not effect your corrosion let us say the feasibility of corrosion greatly.

**(Refer Slide Time: 23:28)**



So let us move on to the other aspect you now we are going to look at the reduction potential the PE approach i guess right and here are we are going to call that redox potential reduction potential or so on and hence so forth but let us try to understand what it is that we are trying to talk about here right. So here let us say we have a particular equation for what do we say now reduction of chromium right here I guess in +6 state and here it is in +3 state right.

So we are going to try to understand this term called PE I guess right so here I have CR3+ and I have CR6+ let us reduction of this particular chromium. So let us try to first write down the equilibrium coefficient for this particular equation now K is not going to be equal to activity of CR3+ times activity of water which is equal to what right by activity of CRO42- + into activity of an electron to the power 3 into activity of + to the power of 8 right.

So let us say I try to transform this and what can I transform this into as I guess I take the logarithm and then let us say I try to transform this so  $\log K$  is going to be equal to  $-\log$  of 3 log activity of electron right and what else do you have I have  $+\log$  of I am going to keep this terms as  $CR3+$  by  $CRO42-$  and  $H+$  to the power of 8 let us see if we have the right equation here so  $\log K$  at take the logarithm and taking this particular term the electron term out right that is into here right.

And obviously it is in the denominator thus negative here and 3 it looks like I am on the right track so I am going to swap these 2 variables right and what does this particular set of what do we say variable looks like right it looks like what now it is  $Q$  dash right but  $Q$  is obviously equal to what now what is  $Q$  dash = in terms of  $Q$  now. If we look at that it is the it is only missing the term with respect to the electron here right.

So if I multiply the activity of this particular  $Q$  with the electron right raise to it is particular stoichiometric I see that it is  $Q$   $Q$  dash right so that I what we need to understand here right so I am going to approximate this term by  $Q$  dash right and here I am going to swap this 2 what do we say variables here so it is going to be equal to 3 times log activity to electron right =  $-\log K$  right + log  $Q$  dash I will just write this as  $Q$  dash right and let me write this down here.

**(Refer Slide Time: 26:42)**

$$\begin{aligned}
 3 \log \{e^-\} &= -\log K + \log Q' \\
 -3 \log \{e^-\} &= \log K - \log Q' \\
 -\log \{e^-\} &= \frac{1}{3} \log K - \frac{1}{3} \log Q' \\
 \underline{-\log \{e^-\}} &= \frac{1}{n} \log K - \frac{1}{n} \log Q' \\
 \underline{pe} &= \underline{pe^0} - \frac{1}{n} \log Q' \\
 \boxed{pe} & \quad K = \frac{[oxid]}{[red]} \\
 \text{high } pe & \Rightarrow \text{red. form pred. at eq.}
 \end{aligned}$$

$O_{xd} + n e^- \rightarrow Red'$

$\frac{1}{n} \log K = pe^0$

$Q' = [e^-]^n Q$

So have 3 of activity of the electron =  $\log K$  or  $-\log K$  if I am not wrong I  $\log K + \log Q$  dash right. Because I want to express it in terms that I am going to use later I am going to multiply by negative 1 =  $3 \log$  electron is going to be equal to  $\log K - \log Q$  dash right and I am going to divide by 3 –  $\log$  electron =  $1/3 \log K$  right –  $1/3 \log Q$  dash right. So here let us say what is that particular aspect with respect to 3 I guess right.

It is the number of electrons being transferred right so oxidized form + number of electrons goes to the reduce form so that is what I see here. So if I am going to approximate let us say represent 3 by number of electrons being transferred I will be left with  $-\log$  activity of electron is going to be equal to  $1/N \log K - 1/N \log Q$  dash. So here these particular term right – particular  $\log$  activity of electrons in that let us say –  $\log$  activity of H + concentration I am going to call this the PE right.

So these is more or less definition PE is  $-\log$  activity of electrons so obviously this is value that you are going to approximate not approximate try to use to understand the system and we are going to look at that later obviously. So  $PE = 1/N \log K$  and  $1/N \log K$  I am going to say = PE naught right so  $PE = PE$  naught –  $1/N \log Q$  dash. And obviously what was  $Q$  dash is nothing but equal to the if you take out the electron term from your particular ion activity product right.

So  $Q$  dash so this is what we have here right so now we are going to spend some time in understanding the particular aspects with respect to PE naught PE and so on and hence so forth right. So let us just first look at what it is we can understand with respect to PR naught I guess right PE naught. So PE naught as you see is  $1/N \log K$  right so obviously again what is  $K$  again it gives us an idea about the concentration of the activity of the product by activity of the reactant right.

So what does that mean when  $K$  value is higher so when  $K$  value is higher it mean relatively the concentration of the product is high and in this particular set of redox reactions right or the reduction reaction as we have written so what is the product here it is the reduce form right. So when you have a high PR naught what does it mean? It means that use form would what do we say be present or be predominate when the system is at equilibrium.

So what do we understand from  $E_{\text{cell}}$  right high  $E_{\text{cell}}$  means reduce conditions or reduce form predominates at equilibrium that is what you see here and again what is the how did we get from here because we know that  $E_{\text{cell}} = \frac{1}{n} \log K$   $E_{\text{cell}} = \frac{1}{n} \log K$  right high value of  $E_{\text{cell}}$  means higher value of  $K$  the equilibrium coefficient from that particular reduction half reaction.

And that particular reduction half reaction this is the generalized form right and we see that when will  $K$  be higher when this particular variable is higher or the concentration of the reduce form of the relevant compound is higher right. So that more or less translates to when the higher  $E_{\text{cell}}$  value you know that high  $E_{\text{cell}}$  value you now for a particular reaction you see that particular  $E_{\text{cell}}$  is high it means that the reduce form is going to predominate at equilibrium right or it promotes reducing right

So again higher  $E_{\text{cell}}$  means it promotes reaction so I guess the next couple of sessions we are going to look at let us say understanding  $E_{\text{cell}}$  in terms of  $E_{\text{cell}}$  and then trying to understand the system in terms of aspect that we looked at earlier right but I guess due to time constraint I am going to end today session for now and we will look at the relevant aspect later on I guess and thank you.