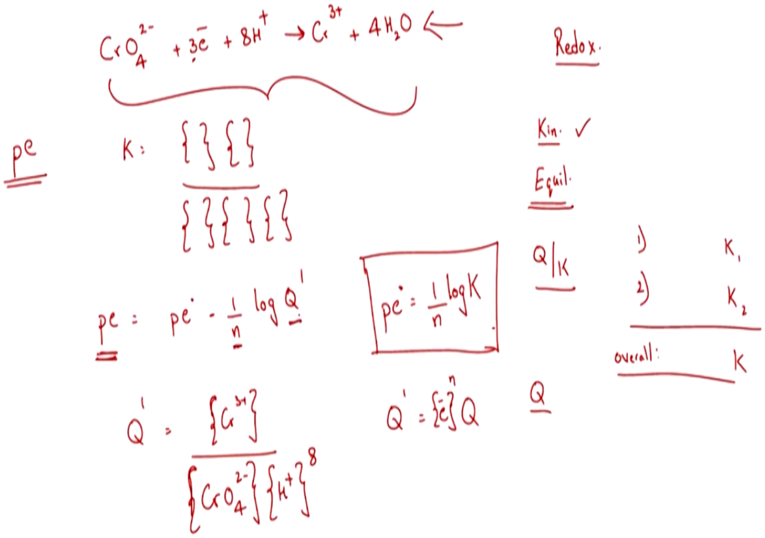
Environment Engineering: Chemical Processes
Prof.Dr. Bhanu Prakash Vellanki
Department of Civil Engineering
Indian Institute of Technology – Roorkee

Module No # 11
Lecture No # 52
Equilibrium of Redox – II & Reaction Feasibility

Hello everyone so again welcome back to our latest lecture session so let us have our customary review I guess for a few minutes about what we have been up to in last couple of session and then continue that where we left off right. So I guess we were looking at reaction feasibility or with respect to equilibrium right.

(Refer Slide Time: 00:43)



So we were discussing redox reactions yes and we looked at different terms and so on electron acceptors and donor and so on. And then we moved on to discuss in kinetics you are done with that and we started discussing about equilibrium right and I guess we are going to just quickly recap what we have been discussing with respect to equilibrium. So again as we mentioned or discussed right the most of these redox process though they are feasible right they will not go through because of the kinetics being way to slow right.

So in general what is the norm redox disequilibrium is the norm right so that is something that we have understood from our last couple of sessions. But obviously looking at equilibrium will help us in understanding let us say reaction feasible or not feasible right. So in the context we looked at two approaches and one of the approach was one of the approaches was looking at Q by K right.

So how did we get here so one half reaction we calculate K1 or we not calculate pardon me we can obtain the relevant K1 right equilibrium coefficient for the second half reaction get the relevant equilibrium coefficient again right.

And then you are going to sum up 1 and 2 right after modifying either reaction 1 or reaction 2 so that you know you will equate the number of electrons being transferred right and then we saw how we can come up with particular K for the overall reaction right for the overall reaction we looked at how to calculate that particular equilibrium coefficient right.

And obviously again the key is that we need to see to it that the number of electrons being transferred would be the same and both the reduction and oxidation process are the half reactions right. So again we did that and then you can calculate Q right based on the relevant concentration is that you have in our particular system. So Q will tell you an idea about what is the present scenario K will give us idea about what is going to be the system or how is it going to be at equilibrium right.

So when you look at Q /K and obviously Q / K is less than 1 it means that the reaction is feasible equal to K it means that the equilibrium and greater than K you now if not feasible right. So that is something that we looked at in some of these classes and that is something that obviously we looked at from the point of you of the redox process. And then we started looking at new approach right different approach something that we have not looked at yet.

You know the reduction potential or PE right so in these context we just obviously looked at how to get at the PE so how did we get that we wrote down the equilibrium coefficient for particular equation and this is the particular example I believe we looked at right we looked at the particular equilibrium coefficient right stoichiometric of the products right so the coefficient wise activities of the relevant what is it now the relevant reactants.

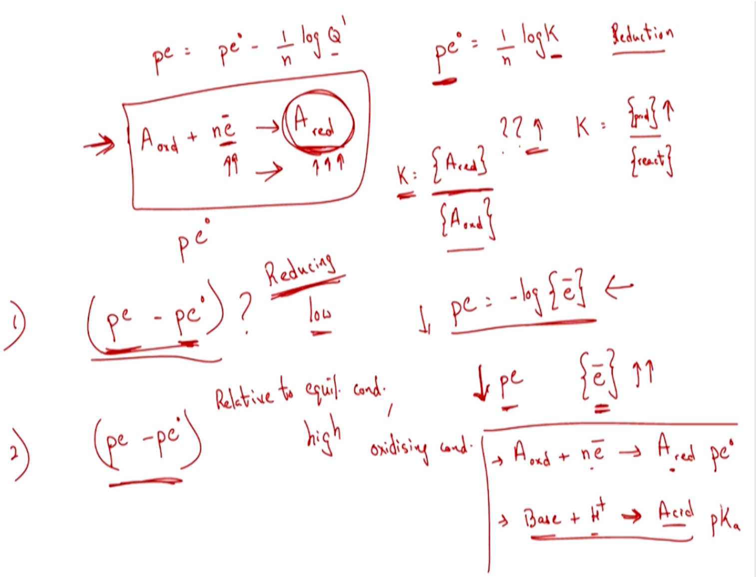
We got that done and then we plugged it in we transform the equation such that more of less we end up with PE = P naught – 1 / N log W dash. So again let us try to refresh what is that we need to understand with respect to each of these terms here. So P is the redemption potential which what we are going to consider with respect to determining or redox reactions feasibility right and P naught if we look at how we did that it was equal to 1 / N log K right.

So gives you have idea about the system at equilibrium of obviously right so again Q dash is nothing but I guess you multiply by the electrons raise to the stoichiometric of that particular or the number of electrons being transfer right and again what is N. N is the number of electrons being transferred which in this example obviously would be 3 right.

So Q dash let me just try to write down Q dash here for this particular example so S dash is going to be equal to activity of 3 or 3+ which we usually approximate that by concentration right by CR O42- right so we were not going to have the term electron term here divided by H+ to the power of 8 so that is Q dash here so what P dash is and from that we can obviously calculate PE right.

So again now we need to understand I guess this is where we were at last time so now we need to understand the significance of each of this variables that we have look at right. So obviously Q dash give you an idea about current state of the system right Q dash though is.

(Refer Slide Time: 05:30)



So we have PE = P naught -1 / N log Q dash so Q dash gives you an idea about current state of your particular system and PE naught right obviously gives you an idea about the equilibrium so in this context we need to understand what does it mean when there is a high value of PE naught or low value or such right.

So again for that we need to understand what does K tell us or it was an idea about as you see K is nothing but the activity of these what is it now the products by activity of the reactant right obviously product of the activity of the product divided by the activity of the product of the activity of the reactant right. So raise to their stoichiometric coefficient.

So obviously this is or equilibrium coefficient so when is this particular equilibrium coefficient going to be high when is it going to be high obviously when the products activity or the concentration of the products is going to be high right. And if you remember the way we wrote down the relevant equation or the half reaction was oxidized form of the compound + electrons right taking the electrons and goes to it is reduce form right A in its oxidized form right accepts electron and then transforms to it reduce form right and that is what we see here I guess.

This chromium and it is oxidation state number 6 I guess right SO42- S623 right it is taking an electron so it is and 6 oxidation state taking three electrons and thus the oxidization state of chromium is reducing to 3 so that it what you see here right so again generic form is nothing but A oxidized + with the number of electrons being accepted to the reduce form of the relevant compound right.

So obviously here what is it mean now if I write it down for this particular equation so K let us say will give me an idea about what now A activity of this particular reduced form let us say by activity of this oxidized form right in general yes. So obviously what is it mean to have a greater form let us say that mean the reduced form of this particular compound that would predominate right or that the reaction or you know would want to go in this particular forward direction.

So that is what the higher value of K would mean right or that the reduce form would predominate. So again higher value of K more of less as you know translates to higher value of P naught value. So for example from your standard tables if look at the relevant P naught values let us say of half reactions and you see that the relevant P naught value is high what is that mean?

That it means that for that particular system it what do we say now the reduce form would predominate at equilibrium or this particular forward reaction as written is going to predominate and which way do we write this standard half reactions I guess as reduction right.

The oxidized compound it is accepting the electrons and transforming into the reduce form so thus obviously we can understand that this is reduction process right also keep in mind that this is the way how the standard half reactions are written and obviously if we want to look at oxidation you need to transform the or swap the reaction yes. So again whenever we have P naught value to be high that means this forward reaction or the reduction is what do we say favorable I guess right.

So that is what we understand from PE naught I guess right so now let us move on to PE now right how do I understand PE in relation to what I have here as in P naught let us say. So for example what we usually look at is PE – PE naught right so if I look at this particular set of variable let us say what is it I can understand that two case obviously one when it is low and one that is high right and what is PE again thus we know it is –log activity of electron right and that too in the current state more or less right PE is the negative log negativity of the electron.

So it is obviously similar to PH right ah PH is the negative logarithm of the H+ or the activity of H+ right so obviously here let us say what does the low PE value mean similar to low PH value what do we say you know meaning that high H+ concentration again it is negative log right that is something that logical.

So again PE low PE value right low PE value would mean higher activity of particular electrons let us say if it existence in solution again as we discussed electrons would not you know exist in solution right both these oxidation and redox process or reduction process would go in congestion you will never have electrons pools right. So again that if for this theoretical half reaction let us say the if the P is less obviously this particular equation you can see that the activity of the electron will be higher.

So obviously if you look at this equation again if the concentration or the activity of electron is higher right what is that mean now then again the forward reaction would be much more favorable and that the half reaction would want to proceed a the forward direction right. So that is what it transforms into as in when PE then compared to PE naught is low what does that mean it means that reducing conditions prevail right.

So again where this from low PE means more or less higher concentration of or activity of electrons as we look at from this equation w it is a show that you know reduce from would predominate when would that be obviously when reducing condition prevail reducing conditions as in you have electrons right.

So if you have electrons obviously reducing conditions will prevail right and same case here so relative to P naught you are looking at PE and if that value is much lower right what is that mean P is pretty low and that means obviously the reducing conditions prevail so that is what we need to understand.

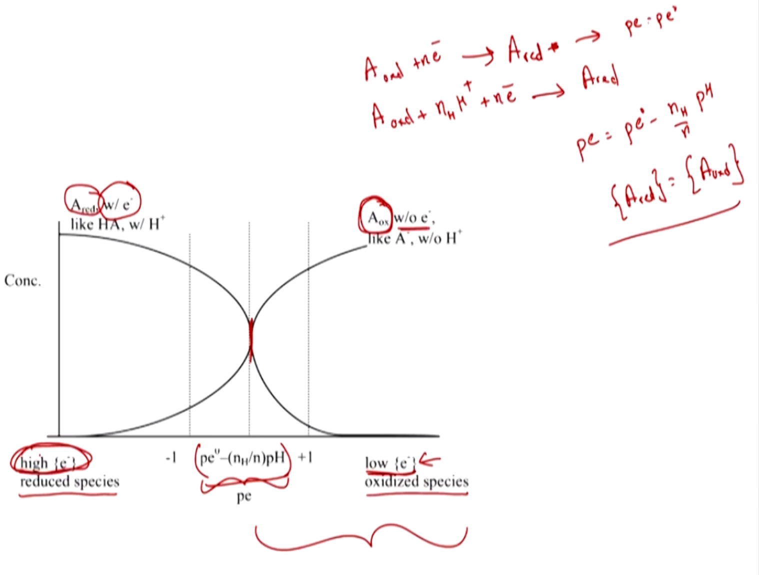
So obviously PE – P naught is what is that mean so relative to that so relative to equilibrium condition use see that oxidizing condition that will prevail so you have a high value of PE - P naught. So P naught gives you an idea about the system at equilibrium right so obviously higher value of PE – PE naught let us say right so it is going to obviously mean that you are going to have what we say oxidizing conditions prevailing or dearth of your electrons here you now that is the way to understand I guess.

So obviously here we have a graph that we before we go further let us say or try to understand that particular graph we should also be able to visualize what it is that we say right. So let us plug this in in forms of what we know so let us look at this equation again here that is the generic equation we have here for now. So oxidized form + the electrons right go to the reduce form right.

So what is this you know similar to let us say right it is similar to let us say the base +H+ right going to or my acid right. So in this redox process when we have the acceptance of the electron you know leading to formation of reduce form of the compound it is analog us so write we similar to base accepting the H+ right and then the acid being formed yes so and from this particular equation 2 we can also try to draw what do we say comparison between P naught.

And let us say the PKA value let us say right and let us try to understand from the graph that we have in next couple of slides.

(Refer Slide Time: 13:50)



So let us try to understand this system in terms of these acid base reaction that we looked and let us try to draw that PH PK graph that we have always looked at so this is the concentration on the Y axis and let us say PH on the X axis right and what did we have we had our protonated form HA right and here we have our deprotonated form or A – right. You know this is for obviously the reaction where HA goes to A- + what is it now H+ right and again H+ right and again or in the way that we want understand now H+ +A- goes to HA.

And this particular point when both the concentration are equal is PKA right so what I am trying to understand or try to help the relevant people visualize is that so here let us say like this is the K compound without the proton and this is the compound with the proton similar to that what we are saying is the equation that we have electrons being accepted by the compound without the electrons and compound with the electron right.

So here A oxidized is the compound without the electrons A reduce to the compound with the electrons right after the acceptance of the electrons. So we are trying to show an analogy between these two acid base and redox process but it helps you to understand these relevant figure which we have here again right. So in this context again we remember we had our PKA right acid dissociation constant for these particular reaction right.

So again the concept is similar here right so here again we have concentration on the Y axis and on the X axis we have PE instead of PH for acid base cases we have PH so guess this figure is bit more detail for now I guess this particular point is going to be PE naught right. So we are going to look when these particular set of variable is going to be worthwhile but for now we are going to consider these point to be at P naught.

So again keep in mind that this is similar to your PKA I guess for your particular case of acid base right. So again you have concentration here PE and let us say P naught is when obviously both these compound would be at the same concentration right. So let us try to understand that to so we have PE = PE naught – 1 /M log Q dash and what is Q dash for this particular reaction A reduce form right by A oxidized form right and if you remember again thus I guess is similar to PH = PKA right – log activity of HA / activity of A-.

Again I guess it is this a Henderson (()) (16:56) equation that we looked at with respect to or acid base process right this is an Henderson (()) (17:01) equation or slight modification of it right so again look at the analogies here it guess here right. So A reduce as in compound with the electrons by the compound without the electron and here compound with the proton divided by the compound without the proton right.

So that is what we have here you see the analogies and similar to this let us say it is we have here the reduce form or with the form of electron right and this is the particular profile for that right and here we have the oxidized form or electron and obviously this is the profile for the oxidized form and you see that what do you see now one PE is less than PE naught or in this region right when PE this is PE X axis and PE is less than PE naught this is my PE naught right.

So in this particular region what do I see which form predominates which is the reduce form and obviously why is that again PE less than P naught is high electrons is activities right and thus obviously reduce species predominant right. So again this is you know obviously realization of the equation that we looked at earlier right or you know the explanation we looked at earlier. We looked at the case where I guess we had low values of P – PE naught that is what we need o understand or look at it here right.

So what do we have here right so if you look at these particular area what is this particular area now obviously when PE – PE naught values are low or PE is less than PE naught right this is the PE naught case the PE naught here right. So that is what you see again right when PE – PE naught is low or PE is less than PE naught let us say obviously the we have higher concentrations of activities of our electrons that would expect right these are theoretical values.

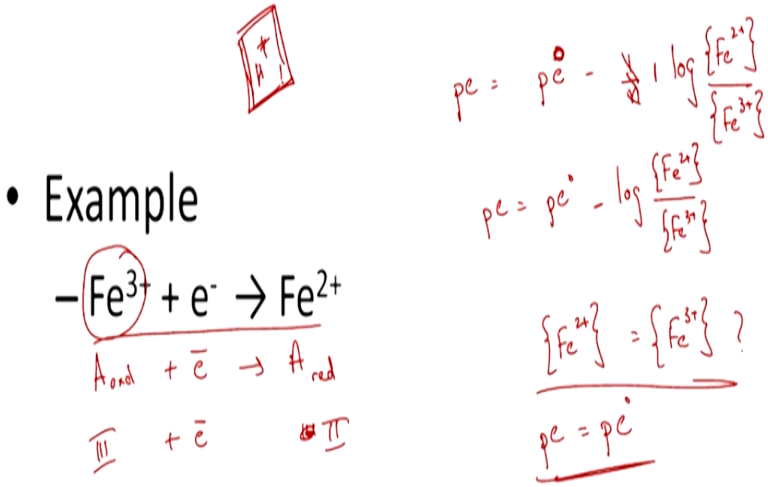
So obviously when you have higher concentration what is it mean A oxidized + N electron goes to A reduce right. So obviously when you have higher concentration of these electrons what is it mean you will have a higher concentration of these reduce forms right so that is what you see here as in A reduce form predominates when PE is less than PE naught right. So that is obviously the take home message here and obviously the similarly I guess in that region where we have PE is greater than PE naught right what do we see here.

Or when PE – PE naught values are what do you see obviously right you see that A oxidized form would predominant yes. S obviously when would both these reduced activity would be equal to activity of A oxidized right. So if you look at that we have the equation to be PE – PE naught – 1 / M log what is it now A reduced / A oxidized right so obviously when will these two variables be same when PE = PE naught then what do you see the activity of these particular reduce form of the compound will be equal to the activity of the oxidized form of the compound right.

And obviously that is what you seeing here in the graph at PE naught or at these particular point what do we see? You see that activity of the reduce form = activity of the oxidized form and again the cases is similar to PH and PKA graph right if these where the acid base relevant graph what would be here you would have HA or the portioned form here you would have the deported form right.

So similarly here we have A reduced form with these electrons and here you would have oxidized form meaning without the electrons so that is how you can help ahh you know understand of the system I guess right. So these was the case when we had a simple example of what do we say oxidized and electrons being accepted and reduced form I guess right being formed.

(Refer Slide Time: 21:23)



- Example
  - $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$

$A_{oxd} + \bar{e} \rightarrow A_{red}$

$III + \bar{e} \quad II$

$pe = pe^{\circ} - \frac{1}{1} \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$

$pe = pe^{\circ} - \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$

$\{Fe^{2+}\} = \{Fe^{3+}\}$?

$pe = pe^{\circ}$

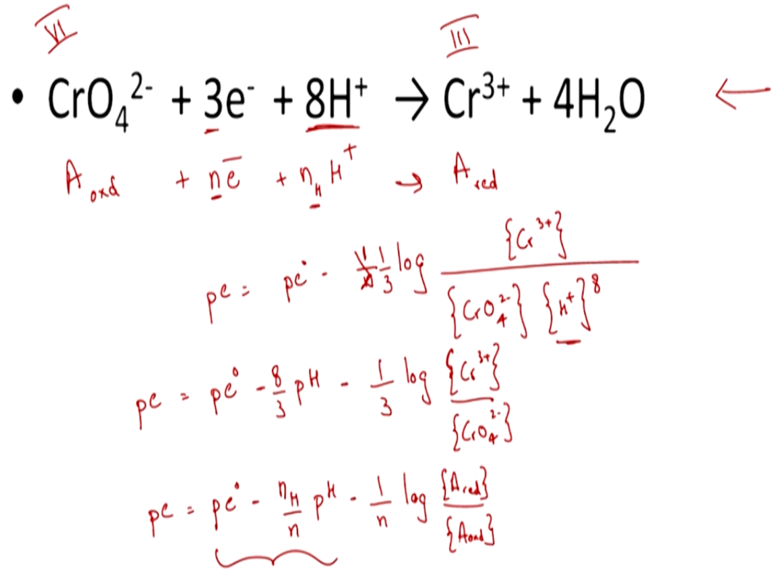
So now we are going to look at couple of examples I believe so for this case let us try to understand how to write the relevant aspects right so obviously PE will be equal to PE naught – 1 / N. N is the number of electrons that is being transferred here it is only one so I am going to write -1 into log Q dash right activity of FE 2 + which is reduce form / activity of FE 3+ yes.

So that is what you see here again PE = PE naught here pardon me PE naught – log activity of FE 2+ / activity of FE3+ right. And obviously again as we looked at it from the graph when is the when are the concentration of the reduce form and the oxidized form going to be equal right obviously you see that is going to be the case when PE = right I see something that obviously to understand so I guess this is the simplest case going to have only the oxidized form right you now taking in or accepting electrons and the reduced form being form I guess right.

And obviously this is a oxidized form right oxidized is taking an electrons and it is forming the reduce form right. Obviously oxidation state here is 3 and because accepting it is one electrons it is reducing to 2 that is a pretty simple to visualize so let us look at one another or couple more examples when we also have other compound present here primarily H+ right I believe the next particular example would be the one with respect to having H+.

So we are going to look at a particular example or couple of examples obviously when we are going to have other compounds primarily let us say H+ I guess.

(Refer Slide Time: 23:17)



- $\overset{VI}{CrO_4^{2-}} + \underline{3}e^- + \underline{8}H^+ \rightarrow \overset{III}{Cr^{3+}} + 4H_2O$ ←

$$A_{oxd} + \underline{n}\bar{e} + \underline{n_H}H^+ \rightarrow A_{red}$$

$$pe = pe^\circ - \cancel{\frac{1}{n}}\frac{1}{3}\log\frac{\{Cr^{3+}\}}{\{CrO_4^{2-}\}\{\underline{H^+}\}^8}$$

$$pe = pe^\circ - \frac{8}{3}pH - \frac{1}{3}\log\frac{\{Cr^{3+}\}}{\{CrO_4^{2-}\}}$$

$$pe = \underbrace{pe^\circ - \frac{n_H}{n}}\,pH - \frac{1}{n}\log\frac{\{A_{red}\}}{\{A_{oxd}\}}$$

So guess here is one example that I believe we have always looked at or considered until now right we have the reduction of chromium from oxidation state 6 to 3 right. But I unlike the earlier case where we had just the oxidized form and electrons being accepted and forming the reduce form right we also have what do we say H+ here 2. So N is the number of moles of electrons and H are the stoichiometric coefficient and NH is the stoichiometric coefficient of H+ here.

So here let us say how we can modify the equation for our particular case so let us write it down in the way that we know so we know that PE = PE naught right – 1 / N log of Q dash and what is Q dash in this particular case obviously it is activity of CR3+ by activity of water dilute solution CR = 1 and activity of CRO42- right and electrons we already considered that here obviously this is Q dash we are not going to have the electrons term here into H+ to the power of 8 right.

To the 1 / N this N should now have been 3 right so I am going to say 1 / 3 so again let us see how this is going to transform into PE = PE naught – and I am now going to bring this term out right so what is now going to be equal to now so that is going to be equal to – H right now is PH – log H+ right which is PH and let us say because it is denominator again – PH and it is going to be 8 here right.

So it is going to be 8 by 3 right – 1 / 3 log CR3+ / CRO42- so if I want to write the generic term from this what is this going to be obviously PE = PE naught – NH / N into PH – 1/ M log activity of the reduce form / activity of the oxidized form and the reason we express you know H + outside this set of what do we say variables is that you know usually let us say when we calculate PE P naught values is 1 / N log K values are remarkably you know are not remarkably I guess are significant compared to this Q dash or log Q dash value.

But let us say PH though will have considerable roll to play yes so again what I guess I am trying to is that we had PE = PE naught right = 1 / M log Q dash right. In general though we have two variables here PE naught value is relatively high compared to this set of variables right but le us say thought when we have H+ involved though that will have the considerable what do we say effect on your PE right or PH will have a considerable effect on your reduction potential that is what we are trying to say here.

So for that particular reason we try to express that particular Q dash term and then come with something called let us say PE E naught W which is nothing but PE naught – NH / N times PH. So in the standard table many times you will see this particular variable expressed not just PE naught so obviously when you see that that means they are talking about PE naught - NH / N PH and usually at PH 7 right.

So that helps you to understand the system better rather than having H+ inside the set of variable Q dash right so that is one particular excuse pardon me so in that context let us look at the relevant what do we say the relevant figure with respect to concentration of these reduce and oxidation form in the PE. So again here unlike looking at PE – PE naught which is the case earlier we are now going to look at PE – PE naught – NH / N times PH right.

So this is what we are going to look at so the relevant relative term or variable we are going to refer to I guess or the reference term is going to be = PE naught NH / N times PH so the that is what we have here. So earlier if we refer for that particular equation which was just A reduced + or A oxidized + N electrons goes to A reduce form we did not have these particular PE naught – NH by N PH we just have PE naught but now when we also have A oxidized + NH H+ right + N electrons goes to A reduce forms right.

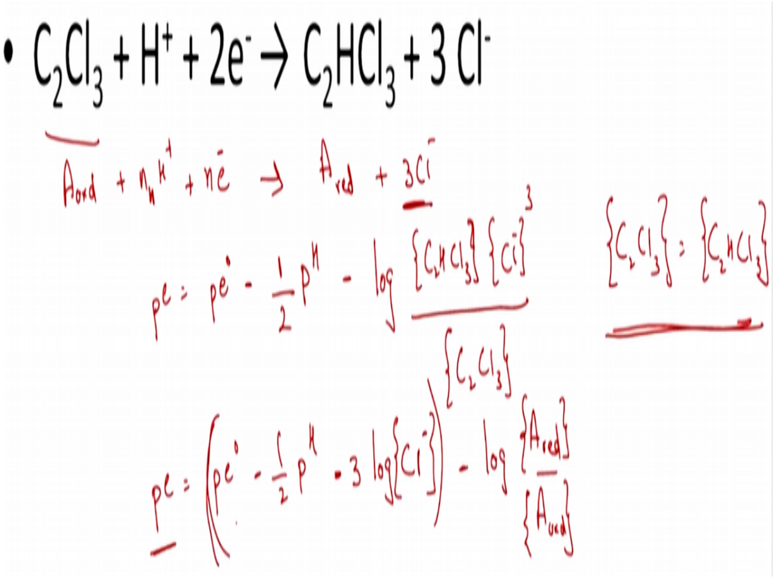
So obviously here the reference term is PE naught / NH/N PH right so again it is similar to that particular figure that we visualize earlier when PE is less than this particular set of variable obviously what would predominate now or what would that mean now so PE greater than or less than this particular reference means that PE is very low PE very low means high activity of electrons right that is what it means the high activity of electrons.

So obviously if electrons activity is high that would promote formation of our reduced species right. So that obviously means A reduce form would predominate or obviously the compound without pardon me with the electron right. So obviously on this particular side as in greater than this particular reference what do we see we see that the oxidized form would predominate why so that because low PE values right not low PE high PE values leading to low activities of your particular electrons low activity of your electrons means oxidized species would predominate compare to your equilibrium right.

And thus obviously your oxidized form or the compound without the electron with predominant right say again when would your particular what do we say concentration of these reduce oxidized species be similar or same pardon me it is going to be when the PE = this particular reference PE naught – NH / N PH right. So earlier when where they equal to earlier has not this simple case when PE was equal to PE naught right.

In this case obviously we have new set of reference that would be case when PE = PE naught – NH by N PH then we would have the activity of the reduced form equal to activity of the oxidized form right. So that is one particular you know set of case I guess right so now we will move on to another case I guess when we have not just the oxidized form and the reduce form but if you have another elements I guess right let us try to understand that.

(Refer Slide Time: 30:30)



- $C_2Cl_3 + H^+ + 2e^- \rightarrow C_2HCl_3 + 3\,Cl^-$

$A_{oxd} + n_H H^+ + ne^- \rightarrow A_{red} + 3Cl^-$

$pe = pe^0 - \frac{1}{2}pH - \log \frac{\{C_2HCl_3\}\{Cl^-\}^3}{\{C_2Cl_3\}}$

$\{C_2Cl_3\} = \{C_2HCl_3\}$

$pe = \left(pe^0 - \frac{1}{2}pH - 3\log\{Cl^-\}\right) - \log \frac{\{A_{red}\}}{\{A_{oxd}\}}$

So here we have let us say what else do we have we have the oxidized form here A oxidized + NH times H + + N times electrons goes to the A reduce form right + here we also have the other elements let us say in this case 3CL – right. So obviously here we need to again try to understand the system so we have PE = PE naught right – NH / N NH is 1 / N is two times PH right – log Q dash what was log or what i log Q dash it is C2 H CL3 right in to CL – activity raise to the power of 3 / C2 CL3 and it is activity here right.

So we will look at the simple case when our concentration of C2 CL3 would be equal to the concentration of C2H CL3 right. So obviously when would that be the relation of C2H CL3 right. So obviously when would that be the case right let us try to take this CL – term outside right so it is going to be equal to PE = PE naught – 1 / 2 PH right and we are going to have – 3 log CL – activity right – log of the reduce form by the oxidized form right.

And obviously when will this equation be valid when PE = this set of variables yes so again it is just for our purposes understanding we started with the basic example when we have just the oxidized for accepting the few electrons and transforming into he reduced form and then we also looked at the case where we also have H+ and obviously we are now looking at the bit more complex what do we say system I guess or the half reaction bit more complex half reaction right.

But again the objective here is to be able to understand the basic equation and how you need to transform it or visualize it so that you can look at the relevant variables and understand the underlying aspects and primarily obviously what do we understand here when PE is low or lower than your particular reference which is PE naught or PE naught – NH / N into PH right what is that mean that means your particular activity of electrons is high right.

Let us look at that equations here right we just summarize right for today and that means high activity of electrons meaning the reduce species concentration is going to be higher that means A reduce form is going to predominate when PE is less than reference that is what we see here and obviously the inverse of it when PE is greater right or greater than particular reference what is that mean low activity of your particular electrons.

And that would correspond to lower concentration of your particular reduce species or higher concentration of your oxidized species meaning oxidizing condition predominate right. So thus A oxidized form would predominate and again how can you understand this guess it is similar to your PA and PKA graph that you looked at let us say right and similarly I guess A reduce form would correspond to the acid which is to the compound with the proton right and A oxidized form meaning the compound without the electron would be similar to the compound without the proton or A- right.

I guess with that I will end today's session and we are now going to look at let u say how can I look at two half reactions let us say and the relevant PE 1 or PE values for the reaction values and then be able to understand which particular compound will then act as the oxidizing agent right and which one will then act as the reducing agent right anyway with that i guess I will end today's session and thank you.