Environment Engineering: Chemical Processes
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Module No # 11
Lecture No # 54
Reaction Feasibility based on Pe- II

Hello everyone again welcome back to latest lecture session so again have our customary review of what we have been up to in the last couple of sessions. So I guess we have been discussing about the reduction potentials in the standard reduction potentials yes and I guess we have been able to now understand what it is now I need to understand let us say PE or PE naught and let us say we look at too half reactions let us say right the half reactions written as reduction let us say which is the way standard half reactions are written right.

I then can by comparing the PE values right go about finding about let u say which reaction will stay as reduction and which reaction will proceed as oxidation right. So again let us try to quickly summarize again what we have been up to.

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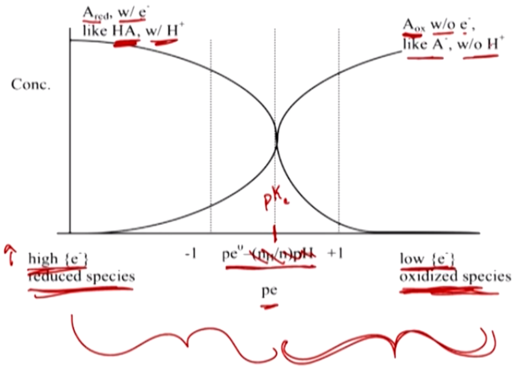
$$\rightarrow \boxed{A_{oxd} + n\bar{e} \rightarrow A_{red}}$$

$$Q' = \frac{\{A_{red}\}}{\{A_{oxd}\}}$$

$$pe = pe^{\circ} - \frac{1}{n}\log Q'$$



$$HA \leftrightarrow H^+ + A^-$$

$$H^+ + A^- \rightarrow HA$$

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

$$pe - pe^{\circ}$$

$$pe - pe'$$

So we looked up let us say developing the relevant equations for PE that is equal to PE naught -1 / N log Q dash right and this particular equation we derived from or particular simpler example of A oxidized form + M electrons going to it is reduced form right.

And obviously N here is number of electrons being transferred here and Q dash what is that nothing but activity of the reduced form by activity of the oxidized form of the compound right. So again then once we looked at this particular what do we say equation of PE right with then looked at the relevance of PE naught and then also looked at how I can understand the system by looking at let us say the variables or you know PE – PE naught for that particular example we try to draw the analogy with respect to the acid base reactions yes.

So I guess for the acid base reaction we had something like let us say HA can deprotonate right H+ +A- or you know written as this particular form right HA right so similar to our particular equation right which is nothing but N electrons + A oxidized form goes to the reduced form as in here it is the compound with the without the proton here it is the compound without the electron here it is the compound with the proton here it is the compound I guess with the electron right.

Again that is obviously layman term but helpful in understanding the relevant system I guess right. So in that particular what do we say example let us say we started looking at relevant aspects with respect the graph of PE right with respect to the concentration of the either the oxidized form or the reduce form of the compound I guess let us again look at the particular graph here.

So here we have PE obviously when you have H+ involved in that particular half reaction then you are going to have the reference to be PE naught – NH by PH right let us say for this particular case though it is going to be PE naught obviously right. So obviously let us say when PE - PE naught let us say is low right what is that mean that means the activity of electrons is going to be relatively high.

So what is that mean obviously looking at this half reaction again if the activity of relevant electron let us say is relatively high right of the theoretical activity obviously right then obviously the reaction would proceed to that right thus the reduced species would predominate and thus we see that the reduce species or A reduce which means with the electron is going to predominate in the region PE less than PE naught right.

And obviously that is the reference here right in this particular region but obviously the other particular region where PE is greater than PE naught or when PE – PE naught value is high what do we see here obviously you know the inverse of what do we discussed earlier right or the converse let us say so we have low what do we say expected activities of the electron thus what is that mean now.

So again oxidized species would be predominate right so low values of low what do we say concentration of these particular electrons right meaning the reaction to eh left would be what do we say preferred again this is for your particular understanding right. Again obviously these are half reactions you know when we talk about activities of electrons right you do know that these or more or less let us say the probable values or theoretical values because from our background we do know that electrons would not exist in solutions right or they would not accumulate in the solution yes.

So again obviously when we have low what do we say activities of electron oxidized species would predominate so that is why in this particular region we see that the oxidized form or the compound the electrons would predominate right so this is obviously simpler to out particular acid base relevant chemical process where on the left hand side of our PK I guess right.

We have our protonated form or with the H+ and here in this particular region again we have the deprotonated form or without the H+ right again that is for your particular understanding obviously.

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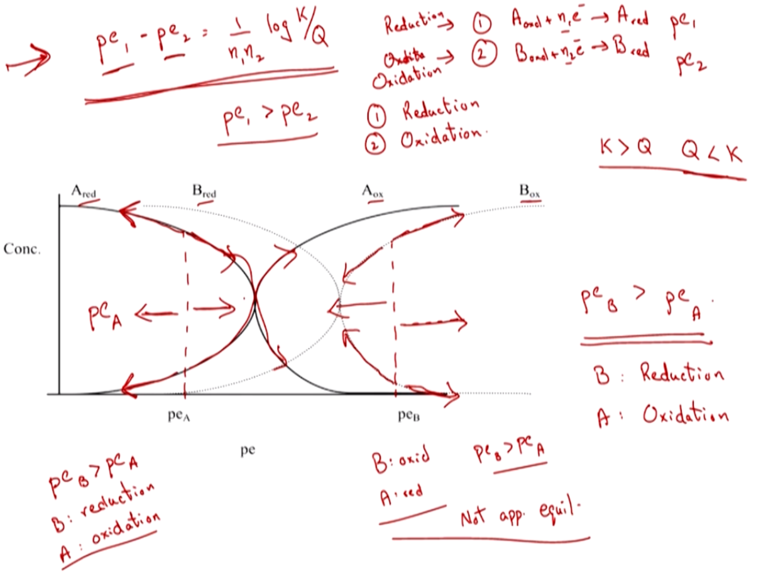

So let us move on to what we looked at then we started looking at let us say we had two half reactions I guess right let us say one and two half reactions and we have the PE 1 and PE2 for these particular half reactions let us say then we looked at ways to be able to understand which particular half reactions will go through as reduction and as you would go through as oxidation I think the example we consider was similar to A oxidized + 1 electron goes to reduce form and here B oxidized + N2 electrons goes to B reduce form right.

So obviously here both the half reaction as return as reduction right but for obviously the redox process to go through you need both an acceptance right and also donating of the electron right so both gain and loss of electron but here obviously it is only a gain of the electrons so obviously for redox process to go through one of these will need to go through as oxidation and the other will stay as reduction itself right.

So obviously to compare that to I guess we looked at relevant example and at the derivation I guess right we came up with some equation like PE 1 – PE2 right = 1 / N1 into right N1 and N2 being number of electrons being transferred let us say each half reaction right let us say right and log K / Q right so after looking at this particular equation or you know we can look at it now again 2 what happens when K is greater than Q.

So these term is positive K greater than Q meaning Q less than K right so obviously what do you see here you see that this term is going to be positive or PE1 – PE2 is going to be positive so obviously when Q less than K what is that mean the reaction would proceed as return and how did we write this particular what do we say equation so remember we said that this would proceed as reduction and obviously it is native here so this would consider would proceed as oxidation right and then we came up with relevant particular equation right.

And then we look at the relevant K and Q values and so on and from these relationship we can see that you know this particular term is positive obviously when PE1 is greater than PE 2 right so PE 1 greater than PE2 right when PE1 greater than PE2 what do we see that the first half reaction will go though as reduction right and the second will go through as oxidation right. And then to be able to bet in understand this particular aspect that we looked at in what do we say derived at we looked at relevant particular figure here right.

And obviously here we have a case of two redox couple here reduce at A oxidized B reduce at B oxidized so and then we choose one particular case when obviously PE2 I guess let us say if I starting from somewhere out here right of and from here let us say PEB and let us say for A here so let me choose this particular point right so we start out obviously I see here where PEB is greater than PE of A right.

So that is what you see here but we looked both the scenario's as in what would happen let us say B goes through as oxidation and not as reduction as in from these particular case we know that the redox process would go through in such a way as we know B would see reduction or reduction would go through in this particular half reaction and with respect to A it is going to be oxidation right that is what we see from this particular understand from these particular equation right looking at K values and so on here.

But to be able to better understand the system we looked at that particular case when we consider that okay what happens when oxidation goes through it with respect to B I guess. So let us see that again let us summarize that again so here let us say oxidation go through what would happen let us say if oxidation go through as in reverse reaction let u say than the oxidized form of the compound will increase and the reduce form of the compound will decrease right.

As in here this is what you see so these oxidized form is going to increase right and obviously this is the reduce form which is going to further decrease right if B goes through as oxidation right. So what is that mean that PEB is shifting here to the right and obviously then if B is going through as oxidation A needs to go through as reduction.

So if it is reduction obviously A reduce form will increase in concentration so that means this is what you are going to observe and also oxidized form of A is going to decrease in concentration right so it is going to go through in this particular direction so obviously PA will shift to the left and obviously as you see right PEB and PEA do not approach each other or they are moving away from equilibrium right.

So that is obviously not what you would see out their in the nature right so you would obviously see that or the system try to travel in such direction that PE of A and PE of B are same meaning the system reaches equilibrium right so what is it what happens here when PE1 and PE2 are the same that means K and Q right are the same means that the system has reached the equilibrium. But if you see as the equilibrium travels in one direction PE2 in the other right.

As we see in this case when we consider that B would go through as oxidation and A would go through as reduction for that particular when PE of B was greater than PE of A right. So we looked at in this particular example we saw that right the system was not approaching equilibrium right so that is what we see so obviously I guess we look at the other case PEB is greater than PEA.

Obviously still but we are going to go by what we understood earlier right that B will go through as reduction and A will go through as oxidation right and let us see this make sense right. So obviously if B is going through as reduction right the reduce form of B would increase in concentration so right this is reduce form right so this is going to increase right and the oxidized form would decrease.

And so it would this what this mean if P of B is going to travel in this reduction and with respect to A is going to be oxidation right so the reduced form of concentration will decrease and the oxidized form of A concentration is going to increase right in this manner right and reduce form is going to decrease in this manner what is that mean PA is going to shift to at the right. So in this particular case right.

When we saw that let us say for the case of PEB greater than PEA we consider let us say B consider as reduction A as then as oxidation you then see that the system approaches equilibrium right so that is what obviously go through so obviously we looked at in two aspects one with respect to the equation in PE1 to PE2 = 1 / N to log Q / 2 and also visual I guess right. So then we start discussing the aspect with respect to application of PE values so we are going so skip that and move on to what we sum of the application here I guess right.

So now let us say we are going to consider cases let us say when let us say we consider only let us say the redox process what would be the PE value and what would the PE value B considering all the relevant chemical process we have discussed that so on right as in complexion precipitation solution and acid base right. So that particular what we do we analysis now we are going to do couple of sessions right is going to give a clear picture of the relative importance of each of these process we have discussed that is what right.

So before we go further I guess we are going look at a few standard what do we say redox potential tables.

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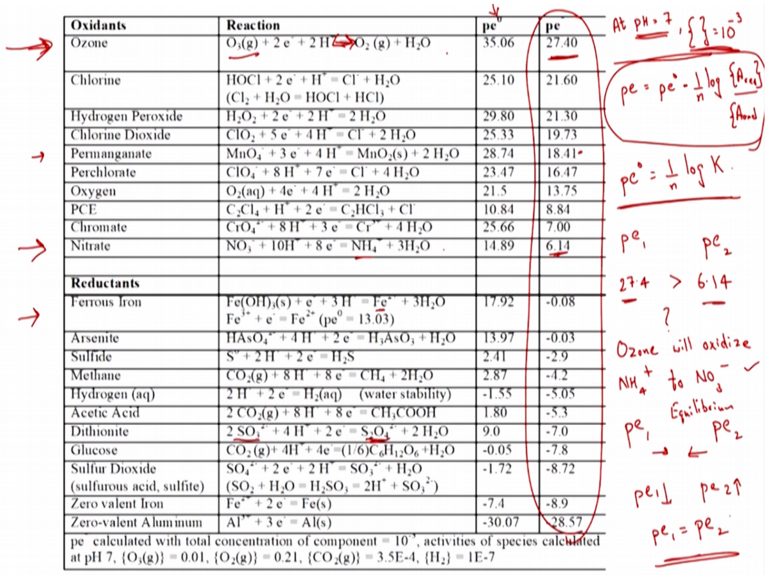

Oxidants	Reaction	pe^0	pe^-
Ozone	$O_3(g) + 2e^- + 2H^+ \rightarrow O_2(g) + H_2O$	35.06	27.40
Chlorine	$HOCl + 2e^- + H^+ = Cl^- + H_2O$ $(Cl_2 + H_2O = HOCl + HCl)$	25.10	21.60
Hydrogen Peroxide	$H_2O_2 + 2e^- + 2H^+ = 2H_2O$	29.80	21.30
Chlorine Dioxide	$ClO_2 + 5e^- + 4H^+ = Cl^- + 2H_2O$	25.33	19.73
Permanganate	$MnO_4^- + 3e^- + 4H^+ = MnO_2(s) + 2H_2O$	28.74	18.41
Perchlorate	$ClO_4^- + 8H^+ + 7e^- = Cl^- + 4H_2O$	23.47	16.47
Oxygen	$O_2(aq) + 4e^- + 4H^+ = 2H_2O$	21.5	13.75
PCE	$C_2Cl_4 + H^+ + 2e^- = C_2HCl_3 + Cl^-$	10.84	8.84
Chromate	$CrO_4^{2-} + 8H^+ + 3e^- = Cr^{3+} + 4H_2O$	25.66	7.00
Nitrate	$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$	14.89	6.14
Reductants			
Ferrous Iron	$Fe(OH)_3(s) + e^- + 3H^+ = Fe^{2+} + 3H_2O$ $Fe^{3+} + e^- = Fe^{2+}$ $(pe^0 = 13.03)$	17.92	-0.08
Arsenite	$HAsO_4^{2-} + 4H^+ + 2e^- = H_3AsO_3 + H_2O$	13.97	-0.03
Sulfide	$S^0 + 2H^+ + 2e^- = H_2S$	2.41	-2.9
Methane	$CO_2(g) + 8H^+ + 8e^- = CH_4 + 2H_2O$	2.87	-4.2
Hydrogen (aq)	$2H^+ + 2e^- = H_2(aq)$ (water stability)	-1.55	-5.05
Acetic Acid	$2CO_2(g) + 8H^+ + 8e^- = CH_3COOH$	1.80	-5.3
Dithionite	$2SO_3^{2-} + 4H^+ + 2e^- = S_2O_4^{2-} + 2H_2O$	9.0	-7.0
Glucose	$CO_2(g) + 4H^+ + 4e^- = (1/6)C_6H_{12}O_6 + H_2O$	-0.05	-7.8
Sulfur Dioxide (sulfurous acid, sulfite)	$SO_4^{2-} + 2e^- + 2H^+ = SO_3^{2-} + H_2O$ $(SO_2 + H_2O = H_2SO_3 = 2H^+ + SO_3^{2-})$	-1.72	-8.72
Zero valent Iron	$Fe^{2+} + 2e^- = Fe(s)$	-7.4	-8.9
Zero-valent Aluminum	$Al^{3+} + 3e^- = Al(s)$	-30.07	-28.57

pe^- calculated with total concentration of component = 10^{-3}, activities of species calculated at pH 7, $\{O_3(g)\} = 0.01$, $\{O_2(g)\} = 0.21$, $\{CO_2(g)\} = 3.5E-4$, $\{H_2\} = 1E-7$

At pH = 7, $\{\ \} = 10^{-3}$

$$pe = pe^0 - \frac{1}{n}\log\frac{\{A_{red}\}}{\{A_{ox}\}}$$

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

pe_1 pe_2

$27.4 > 6.14$

?

Ozone will oxidize NH_4^+ to NO_3^- ✓

Equilibrium

$pe_1 \rightarrow \leftarrow pe_2$

$pe_1\downarrow$ $pe_2\uparrow$

$pe_1 = pe_2$

So here obviously let us say pay attention to these particular names here right and so obviously here we have ozone chlorine peroxide and so on I guess we have same background will know that they are oxidants right and here we have ferrous iron, sulphide, hydrogen and so on and Dithionite let us say people with background will know that they are reductants or reducing agents right.

But let us say how do you but let us say you do not have the back ground so how will you let us say be able to estimate let u say which particular compound act as a reducing agent in general out their in the nature and which one in general act as a oxidized agent. So for that particular aspect I guess you are going to refer to your PE naught value here let us say right. So here you know the PE value is positive and pretty high.

So what is that is that mean again right that the reaction strongly favors going to the right PE naught if you remember what is that if it nothing but equal to 1 / M I believe log K right. PE naught value we define it as 1 / log K if you remember the relevant or if you can relevant derivations so greater PE naught means greater the value of K right and we know K is nothing but activity of the products raise to the relevant stoichiometric by activity of the reactants right.

And obviously if you look at that the greater value of K means this reaction would go through in the or go to the right. So obviously reduction is going to take place right as in these particular compound would act as a strong acceptor right. So electron acceptor we know it is oxidant right so obviously when PE naught value is high meaning K value is needs to be high what is that mean the reaction would go through or refer to go through in this particular direction right and thus what is that mean that these particular case in this right we can it is a strong oxidizing agent.

So when someone people or someone refers to I say particular compound as a strong oxidizing agent or a strong reducing agent keep in mind that we are all relative as you can see from this particular tables right. So for example ozone among the relevant oxidizing agent listed here or oxidants listed here you see that remarkably what do we say strong oxidizing agent right. So obviously compared to let us say chromate that is not a great example or compared to oxygen.

You see ozone let us say right is you know a much better or strong oxidizing while here P naught value is 21 here it is around 35 but keep in mind that here we are talking about logarithmic values P naught is 1 / N log K so you know factor let us say difference here we have what do we say different by 10 right that means it is a considerable difference here right so keep that in mind that PE values is 1 / N log K so we need to look at the logarithmic scale.

So right obviously reductants I guess right so here I guess it does not great picture as in you know these particular systems seems to be a at messed up. So obviously if it is negative right what do you understand if it is negative now right let us say so PE naught = 1 / N log K and if PE naught is negative right what is that mean that K value is pretty less or less let us say relatively less.

So if K value is less what is that mean now the reaction to the left low be favorable or we will proceed right. So the reaction to the left and then and then that case what do you see that it is going to be oxidation right or the relevant compound here would act as a strong bone or a strong reductants right.

So but obviously I guess PE naught does not give you the true or accurate picture for that particular case we have i guess looking a particular system where let us say we consider the relevant activities of these compounds let us say which is involved in our half reactions to be 10 power -3 and to the PH3 to be 7 and then I guess you can look at the PE values right for that particular hypothetical scenario which is more or less would be similar to what would expect in nature.

We are choosing 10 power -3 as relatively low concentration but not too low as to be hypothetical values right. So we are now going to look at what do we say PE values as then just PE naught the PE values is going to consider I guess is when let us said PH 7 right and also when all the other activities are equal to 10 power -3 yes we are looking at the particular calculation for PE right which is equal to PE naught – 1 / N log activities of the reduced form by activity of the oxidized form right and obviously if you have any other elements to I guess right.

So anyhow for that from that particular scenario we now have the PE values right and obviously this will also take into account the effect of PH right and so this will obviously or this will particular set of data will give us a better idea about trying to understand which particular compound let us say would act as a oxidant and which one let us say would act as reducing agent let us say for example dithionite here right yes.

So how do I go about that now so on so unlike PE naught right which is 1 by N log K which give me an idea about the system at let us say equilibrium right or obviously when the activity or theoretical activity of the electrons let us say when all the other activity are equal to 1 right. So again why do I say so because we know that PE equal to this particular case right.

And obviously what is this now when activity of all the other compound is equal to 1 you see that PE – PE naught. So again that is what we understood here so PE naught = 1 / N log K right so we can this particular case as in let us say which one should be a strong oxidizing agent or such but with respect to looking at PE let us say now I can compare PE1 and PE2 at any half reaction let us say for example let us look at these particular ozone and let us say nitrate here right.

So if I consider these two half reactions I see that PE1 which is 27.4 right is greater than PE2 and what is PE2 here it is 6.14 right. So again what does this mean this will help us understand that ozone right will oxidized ammonia to nitrate right and how did we come about that right again we looked at relevant derivation and such earlier. So here by looking at the 2PE values right for these particular scenario when PH= 7 and the activities or equal to 10 power -3 we see that we have these particular PE were ozone 27.4 and 6.14 for the nitrate relevant half reaction.

So by comparing the two PE values I see that 2 PE values is greater than PE2 right so obviously what is this mean this particular reaction will go through as written right or would proceed from left to right well these proceed from right to the left or these would not go as reduction but would go as oxidation right. So here we have reduction right gain of electron oxidation here we have the loss of electrons this is reverse I guess.

So that is what you observe so in any such scenario when it compare let us ay PE values of any two compound let us say so here permanganate let us say and let us say any compound here let us say ferrous iron right you will know that PE1 is greater than PE2 right so permanganate reaction will go through as this particular case right so NNO4 – will oxidized let us say right FE2 + 2 where do I look at so let us say for this particular case FE2 + 2 FEO thrice the solid right yes so that is what you obviously see here.

So again what is the whole point behind it so the system would try to reach equilibrium right as in PE1 and PE2 would travel in this particular direction as in you would try to reach equilibrium right and when will we reach equilibrium PE decreases in case PE2 increase in such a manner that finally we end up with PE1 to PE2 and we end reaching equilibrium right so let us try to understand that obviously.

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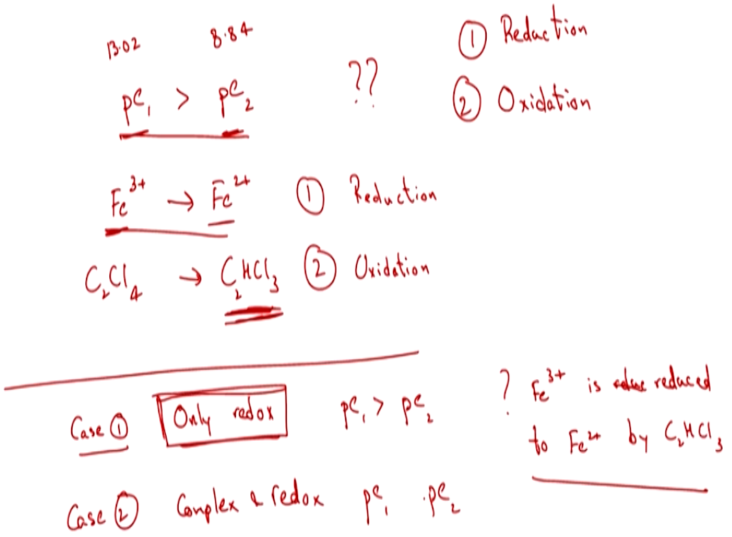

So looking at those tables I can compare any particular cases let us say PE1 and PE2 and once I identify which particular PE value is high let us say PE1 is higher than PE2 right but that ozone and ammonia relevant to half reaction so what happens now to system reach equilibrium you know that I should be PE1 = PE2 right. So for that to happen obviously we looked at the relevant figure to earlier right we see that PE1 has to decrease and PE2 bas to increase right and until PE1 to PE2 right.

So obviously again PE1will have to proceed as reduction and PE 2 will have to proceed as oxidation right so we are going look at this particular case of reductive defloration of carbon tetra chloride right or particular (()) (23:35) right. So here I guess the relevant aspect is that these chroniated solvents let us say or toxic to humans so obviously you want to be able to either remove them right either by phase change or let us say by degrading it right.

Or in this case degradation would mean reduction I would have say reduction obviously right we know that here carbon down by the CL – or CL right you know CL is relatively more electro negative than carbon right so you know carbon here obviously carbon being go into them be a oxidized form so here we are going to look at reductive dechlorination and for that obviously I need a reducing agent and in that case here obviously my reducing agent is FE2+ here right.

So again here we are going to look at the relevant aspects let us say with respect to redox chemistry right but the major aspect we are going to try to do or you know look at let us say with respect to next couple of session pardon me is that we are going to try to bring in the knowledge of previous major aspects as in acid basis complex formation and what else precipitation resolution and how they go hand in hand with the relevant redox process right.

So until now we looked at the four major aspect relatively independent or each other while we did look at few examples which try to look at the preceding aspects right here we are going to bring everything in right so here we are going to look at phase wise as in what would to be scenario you would expect.

Let us say if only one aspect is considered and then look at what happens actually out there in nature right or what happens out there in nature and how that compares your particular case or the theoretical aspect what we look at if only one particular process is considered right so let us go through guess. So we are going to obviously look at reductive dechlorination of (()) (25:26) right by ferrous right and here we have the relevant half reaction and the relevant PE naught values.

So here let us say I am going to start with the assumption that all the activities or going to equal to 10 power -3 and that the PH is =7 right. So let us say the PE for the first half reaction right PE1 is going to be as you know = PE naught – 1 / N log Q dash right so that is nothing but equal to PE naught here why is that because Q dash for that particular half reaction right 1 is activity of FE 2+ by activity of FE3+ right because both the activity of same Q dash = 1 so that is why PE1 is nothing but 13.03.

So the second case right PE2 it is going to be equal to PE naught – 1 by N log Q dash for this half reaction let us write that down PE naught is 10.84 – 1 by 2 and where is it 2 because two electrons are being transferred here or being accepted here right log Q dash as in activity of C2 HCL3 the reduce form + not + pardon me into CL – by activity of C2CL4 right into activity of H+ right.

So let us plug in the relevant values here so that is going to equal to 10.84 – 1 by 2 log activity of this particular compound which we know is 10 power -3 based on assumption 10 power -3 into

10 power -3 by 10 power -3 into H + we know that PH is assume to be 7 into 10 power -7 right so here we are going to look at the relevant value so 10 + -3 -3 get cancel out so I am going to be left with 10.84 – 1 by 2 log 10 to the power of -3 +7 0 to the power of 4 right that is going to be equal to 10.84 – 4 by 2 is going to be equal to 2 so that is going to be equal to 8.84 right.

So let us look at summarize what we have been up to here right so we looked at the case we are trying to look at dechlorination of C2CL4 / ferrous and then to look at relevant particular aspects right we calculated the PE1 and PE2 values and here even though we see that the PE1 right is greater than PE2 right so the PE1 is greater than PE2 right what is this mean you know that then the first half reaction will go through as reduction right.

And the second half reaction goes through oxidation right has in what do we understand as you know the relevant what do we say case we had was FE3 + going to FE2+ for the first half reaction and C2CL4 being reduce to C2CL3 in the second half reaction obviously I am not balancing it with respect to H+ and electron transfer but these are the couples right. But here as you know because PE1 is greater than PE2 let us look at the values I guess 13.03 and 8.84 right.

So what is that mean obviously that FE3 + is going to be reduced to FE2 + / C2HCL3 right but this is not what we expect or see out there in the nature now right so again what is the reason here right the reason here being that you know that ferrous or ferric can form complexes not can will form complexes or a aqueous complexes out their right. So that is one aspect we certainly have not looked at or considered right.

So I guess today let us say we have understood the particular case that you would expect let us say when you consider ferrous or ferric let us say as what we say just the free metals without considering the case of the you know possibilities that the complexes will be formed which you know does happen right. So here we until now let us say the past five minutes we looked at these theoretical case than let us say we do not have other chemical process we only have the redox process occurring.

And in that case do we see what do we say reduction of C2CL4 no we actually see what do we see here this is going to go through as FE2+ is what do we say FE3+ let us say is reduce to FE2+ by C2HCL3 that is what you see why is that because PE1 is greater than PE2 right. So in the next couple of sessions or next session right we are going to look at that particular case when we consider let us say FE2+ and FE3+ can form aqueous complexes.

And then we are going to look at the calculation of the actual what do we say concentration of these FE2 + and FE3 +metals or free metals that would been equilibrium with the complexes in the solution and then calculate the PE value right. So I guess for now we looked at case 1 let us say case 1 right what do we say only redox right and we see that PE1 is greater than PE2 right what is that mean that FE3 + is reduced to FE2+ / C2CL3 so that is what you see.

Because PE1 is greater than PE2 this will go through as reduction right and this will go through as oxidation as in particular compound will act as the reducing to reduce FE3+ to FE2+ right but why is that because we considered the case that only redox process occurs so in the next couple of cases we are going to consider the case let us say when we also have complex formation and redox and then calculate PE1 and PE2 and then try to understand that system accordingly right.

So I guess with that I will end today’s session and hopefully with next session you should be able to get the holistic approach right or understand the holistic aspects that are involved in these particular scenario right so and I guess with that I will end today’s session and thank you.