Environment Engineering: Chemical Processes
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Module No # 11
Lecture No # 55
Effect of complexation on Redox

Hello everyone so again welcome back to latest lecture session so let us quick recap of what we have been up to in last lecture session so we have been looking at or trying to look at let us say the understanding system holistically right so in that context we started looked at one particular example as in reductive dechlorination of this perchlora tetachloro ethinil by FE2 + right.

So in that context you will see that it is feasible or not feasible we looked at when particular scenario where in we assume that all the activities were equal to I guess 10 + -3 but the PH was it 7 right. So in that context we went to head in calculated the relevant PE values and from our background we know that let us say if PE of particular half reaction is greater than the PE of another half reaction right.

The PE or the half reaction with the greater PE right would go through as reduction and the other half reaction would need to proceed as oxidation right. So that is something that we understood or derived to I guess right so we looked at the equation as in we had this particular equation as in PE1 – PE2 = 1 / N1 N2 log K / Q right so we had this particular equation and we also looked at looked particular graph let us say right or a finger where we try to understand that let us say the case that for PE1 and PE2 to approach each other or the system to reach equilibrium right.

We saw that when PE1 greater than PE2 for the system to approach equilibrium we saw that PE1 needs to go through as reduction and PE1 needs to go through as oxidation and that is something again we need to understand from this particular equation that we have just written down right where in PE1 – PE2 = 1 / N1 and N2 log K / Q right.

So only when it is positive as in the left hand side is positive and PE1 is greater than PE2 we know that K is what now greater than Q or Q less than K meaning the reaction would go from left to the right or proceed from left to the right and the way we have written down the overall reacting who was when 1 went through as reduction and 2 and through as oxidation right. So again understand the particular system both in terms of the relevant aspects and also the relevant math I guess right.

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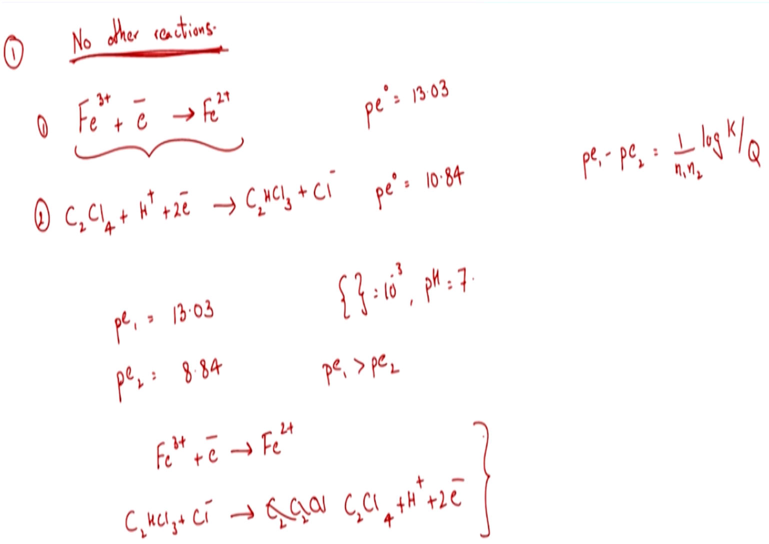

① No other reactions.

① $\underbrace{Fe^{3+} + \bar{e}} \rightarrow Fe^{2+}$ $pe^{\circ} = 13.03$

② $C_2Cl_4 + H^+ + 2\bar{e} \rightarrow C_2HCl_3 + Cl^-$ $pe^{\circ} = 10.84$

$pe_1 - pe_2 = \frac{1}{n_1 n_2} \log K/Q$

$pe_1 = 13.03$ $\{\} = 10^{-3}$, $pH = 7.$

$pe_2 = 8.84$ $pe_1 > pe_2$

$$\left.\begin{array}{l} Fe^{3+} + \bar{e} \rightarrow Fe^{2+} \\ C_2HCl_3 + Cl^- \rightarrow \cancel{C_2Cl_2Cl}\ C_2Cl_4 + H^+ + 2\bar{e} \end{array}\right\}$$

So again let us go back to our example here so the first case we consider was there where no other reaction right no other reaction other than redox yes and I believe we calculated the PE values for this half reaction and the second one came out to be 13.03 and PE2 came out to be 8.84 obviously the case was we assume that to the activities was equal to 10 power -3 and that system was it PH = 7 right.

And obviously the major aspect or assumption for this particular scenario was that we assume that there would no other reaction. And from this we see here that PE1 right PE1 which is this half reaction is greater than PE2 right so what is that mean that PE1 or the first half reaction pardon me is going to proceed as reduction or FE3+ is going to be reduced to FE2+ right and because PE2 is less than PE1 right we are going to have swap that particular half reaction as in C2HCL3 + CL- would have to proceed as being oxidized as C2CL4 C2 CL4 + H+ + 2 electrons.

So this is how the electrons should proceed if there were no other reaction and that is because PE1 right was greater than PE2 right what is this mean that C2H CL3 is going to reduce FE3+ or ferric iron to ferrous but again this is something that odd with odds with what you would observe their so we are trying to understand that we are going to try to understand why this is the case right so again we are going to look at the other scenarios obviously.

So before we go further obviously we want to be familiar with how to be able to use VMINTEQ in such scenario to be able to estimate the PE so let us go ahead and look at that for this particular scenario right or I guess okay VMINTEQ will always consider complexes so that is going to be difficult I guess right anyway so we have to skip VMINTEQ here so because we not take in hypothetical scenario when we exclude the complexes anyway.

So we are going to go through and go through the other scenario that we have to have for that today.

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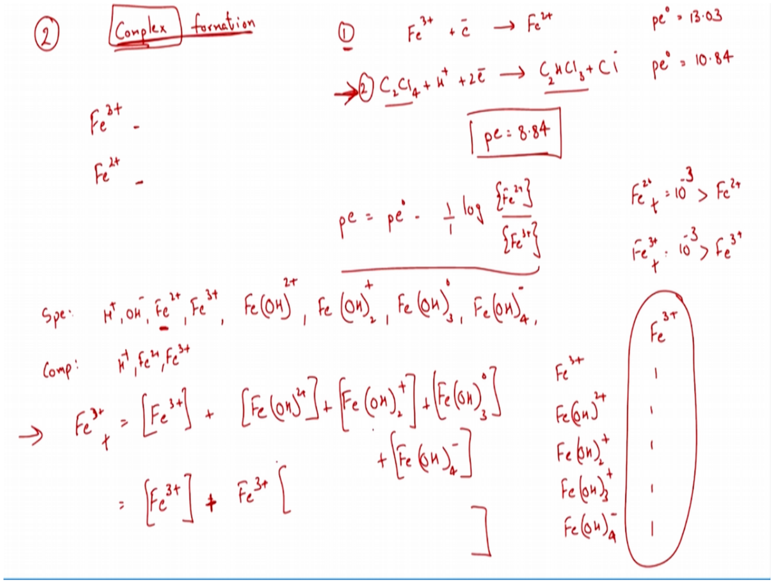

So we are going to consider other than redox we also have complex formation right so we are also going to consider the case when complexes are formed and same reactions as in FE3 + + electrons goes to FE2+ we are going to start with that right and also we have the relevant half reaction C2CL4 + H+ + 2 electrons goes to C2HCL3 + CL- right and we have the PE naught value to be 13.03 I believe and PE naught to be 10.84 right.

And obviously here with respect to complex formation right it as no effect on C2CL4 or C2CL3 or the relevant other what do we say the compounds their in this half reactions. So the PE which was 8.84 right from the earlier case is still going to be the same case here right and so we are going to skip having to re calculated the PE for this particular half reaction when we consider complex formation.

But obviously with respect to half reaction 1 you know that FE3 + can or will form complexes right and FE2 + not to a great extent but you do know that FE2+ 2 will or can form a few complex right. So here we are going to you know shift from the theoretical or you know the hypothetical scenario where we assume that only redox reaction go through and no other reaction go through and shift towards the realistic scenario and this will help in understanding.

Let us say how let us say the relevant other chemical process we have discussed thus far or relatively important and how they fit into the bigger picture right. So let us look at now so obviously we are midway or now considering that we also have complex formation and this something obviously we know right the metal FE2+ and FE3 + their electrons poor compounds right so they tracked the electron rich compound will ligand here and they can form this coordinating relationship r have the aqueous complex is being formed right.

So you know that so obviously let us say for total FE of let us say 10 power -3 right that is what we assume in our previous examples right FE3 + 10 power -3 and FE2+ was 10 power -3 but you know that you put in a total what do we say FE3 or 10 power -3 concentration the actual concentration of free metal FE3+ is going to be much lower why is that because most of the metal is going to stay as complex and not exist as what do we say the free metal right.

So obviously this will lead to a change in your particular what do we say variables in these equation right PE = PE naught -1 / N which is 1 electron transfer here log activity of FE2 + right by FE3+ right so this is the equation for which we are going to try to recap it the relevant what do we say numbers considering that we have complexes being formed right.

And we now know that FE2+ and FE3+ concentration or not going to be the same as this FE2+ total which was 10 power -3 and FE3+ total which is also 10 power -3 we know that FE2 + and FE3 + free metal concentrations right or going to be lower than the total FE2 + and total FE3+ that is present in the that you are you know putting into the system let us say right or you have in the system let us say.

So let us try to work these out first by hand and then by VMINTEQ right again to refresh the memory and also to be able to understand the system holistically. So let us say for the case of FE3+ we are going to work this rather than working it for everything but we write on the tableau right so let us say for what do I need to come up with I need to come up with all my species so the species here are going to be obviously H+ OH- and then the free metals FE2+ and FE3+.

So for ease of calculation right and digging into the relevant background that we have had with the relevant aqueous complexes based right we know that FE2 + will form complexes but not to a great degree say at least for working out by you know hand working out system by hand I am going to consider that FE2+ does not form any complexes and most of the or let us say all the FE total for 2+ stays as FE2+ itself.

So it is not a bad assumption as we are going to look at with respect to VMINTEQ later on I guess but with respect to FE3+ you know that most of the FE3+ let us say would stay as or you know would form complexes right and very little FE3+ would stay as free metal FE3+ itself right. So let us try to just work out work it out with respect to FE3+ assuming that little to know complexes are formed by FE2+.

So FE3+ I need to look at the relevant complexes so FE OH right 2+ FEOH twice + FEOH thrice neutral charge this is still a complex aqueous complex FEOH 4 negative charge right so I guess these are the relevant complexes that I am going to consider so how do I go about it now I am going to let us say choose that H+ and FE2+ and FE3+ are my components right and these are my species right.

So if I write down the tableau right only with respect to FE2+ let us say FE3+ and what are the relevant what do we say species that are relevant here so right say I am going to have to write FE3+ here and the four complexes FEOH2+ FEOH twice + FEOH thrice + right and FEOH4- FE3+ 1, 1, 1, 1 and 1 here the contribution.

So obviously we are at these stage I guess these are relatively comfortable enough what should be comfortable enough to be able to write the relevant tableau or get the relevant tableau with respect to the relevant component without having to write the formation equation right so that is what we are doing here. So if you are not at comfortable I guess obviously I guess writing down the formation equation.

So here we are going again with respect to the assumption that FE2+ forms little to know complexes and I am just trying to understand the system with respect to FE3+ so that I can help you know visualize it better so that is what we have here so here if I do the component balance right what is that going to be equal to FE3+ total is going to obviously equal to FE3+ right or concentration of FE3+ + concentration of FE OH2+ right.

And that is obviously from these particular tableau and relevant component balance and FEOH twice + + FEOH thrice neutral charge + FEOH4 negative charge. So obviously I need to able to transform from this particular equations into variable that I can what do we say use or solve for so I can what is this in terms of values again + FE3+ into what now how do I know the relevant equations here.

So obviously again we need to look at the relevant what do we say complex formation equations so obviously we need to look at the star value right where in we look at one step and protonated again let us just have a look with respect to one complex formation.

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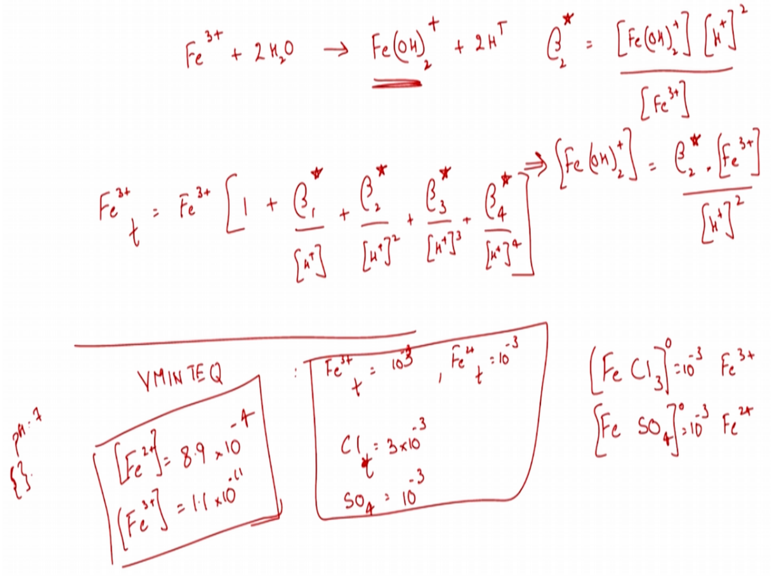

$$Fe^{3+} + 2H_2O \rightarrow \underline{Fe(OH)_2^{+}} + 2H^{+} \qquad \beta_2^{*} = \frac{[Fe(OH)_2^{+}][H^{+}]^{2}}{[Fe^{3+}]}$$

$$Fe^{3+}_{t} = Fe^{3+}\left[1 + \frac{\beta_1^{*}}{[H^{+}]} + \frac{\beta_2^{*}}{[H^{+}]^{2}} + \frac{\beta_3^{*}}{[H^{+}]^{3}} + \frac{\beta_4^{*}}{[H^{+}]^{4}}\right] \Rightarrow [Fe(OH)_2^{+}] = \frac{\beta_2^{*} \cdot [Fe^{3+}]}{[H^{+}]^{2}}$$

VMINTEQ

pH: 7

$$[Fe^{2+}] = 8.9 \times 10^{-4}$$

$$[Fe^{3+}] = 1.1 \times 10^{-11}$$

$$Fe^{3+}_{t} = 10^{-3}, \quad Fe^{2+}_{t} = 10^{-3}$$

$$Cl_{t} = 3 \times 10^{-3}$$

$$SO_4 = 10^{-3}$$

$$[FeCl_3]^{0} = 10^{-3}\ Fe^{3+}$$

$$[FeSO_4]^{0} = 10^{-3}\ Fe^{2+}$$

So let us say I am trying to form let us choose one of let us say these FEOH twice FEOH twice + charge right. So here obviously I am trying to have the protonated form of ligands right H2O right and obviously we has to be direct right it has to be 2 here and so I am assuming it into to be 2H+ here. So to balance it to H+ OH and here it is 4 okay that balance it out we know that the relevant coefficient is given by beta 2 star I guess right and that obviously = the concentration of FE OH twice + H+ square by concentration of FE 3+ right.

So obviously FEOH twice + concentration = beta 2 star right into FE3+ by H+ square right so similarly the relevant equation for the another complexes right. So obviously I am trying to refresh your memory and obviously you get your guess right so here we again let me just try to write down these equation here right in the form of what we want here.

So it is obviously going to be equal to FE total or FE3+ total is going to be equal to FE3+ times 1 + and here it is going to be first complex beta 1 star / H+ right + beta 2 star / H+ square which is this particular complex right and for the other two complexes two we can write it down similarly with the 3 star by H+Q + beta 4 star by H+ to the power of 4 right.

So obviously we now have the relevant equation in terms of 2 unknowns FE3+ and H+ and obviously relevant constant beta 1 star 2 beta 4 star I guess right and obviously if you do the balance total similarly you can then what do we say solve for two equations and two unknowns and get the relevant answer by hand right. Obviously we are not going to go through that but let us say let us use VMINTEQ to find out what is this concentration or actual concentration of FE3+ and FE2+ are right so let us go back to VMINTEQ here.

So I am going to put and plug in FE3+ right and where is that here FE3+ and let us say I am going to go through with the molal so we went to 1 power -3 concentration so we are going to continue with that right so it is going to be equal to 1 milli molal add to the list and the other case is FE2+ also 1 milli molal right so I am going to add that to the list but again keep in mind that here we are having total component balances right we are giving the system initial total component right.

So obviously if you giving a FE 2 + or FE3+ right you cannot provide FE2+ and FE3+ independently right the ions to the solution. So in general for the charge balance to I guess let us say assume that we provided FECL2 or such or FE3 pardon me FECL3 is the source of FE3+

and let us say the ferrous sulphate source of what is it now the ferrous I guess and let us go ahead and let me see what we had here and we had back to main menu right okay.

So again what I am saying is obviously so we are trying to work it out by VMINTEQ right VMINTEQ and VMINTEQ give the total component balance total component concentration FE3+ total we say is 10 power -3 and same case FE2+ total is 10 power -3 but for the relevant charge balance let us say we are going to assume that we are having FECL3 right and FESO4 let us see right and this obviously the source for the FE3+ and this for FE2+ I guess right.

And for that obviously I need to put in CL total = 3 times 10 power -3 right 3 times 10 power -3 right and SO4 total is also going to be equal to same molal concentration which is 10 power -3 right. So if I am having FECL3 naught at 10 power -3 and FESO4 naught at l0 power -3 right these are the relevant components right. And let me plug into the relevant ahh CL and SO4 i guess right.

So CL here CL is 3 milli molal right so this is what we have seen 3 milli molal add to the list and then SO4 and looking for SO42 – there it is and here we have 1 milli molal again right so let us look at the edit list so FECL3 and FESO4 right so we are fine there and now I am going to run it let us say right and let us say what is the actual concentration of FE3+ than FE2+ are and then plug them in so FE2+ is 8.9 into 10 power -4 right.

So I see that FE2+ concentration is slightly lower but still similar to 10 power -3 8.9 into 10 power -4 right and let us see what the actual concentration of FE3+ is right and where is that here that as is much lower 1.1 into 10 power 11 so 1.1 into 10 power -11so there you have it so this obviously is the case of when PH = 7 and the activities of the relevant total metals are equal to 10 power -3.

So now after plugging in the relevant what do we say components into VMINTEQ we saw that the actual free metal concentration of this FE3+ right is much lower right and that is order of magnitude what 8 times earlier to the 10 power -3 now it is 10 power – 11 right so order of magnitude difference of around 8 right which is huge difference obviously.

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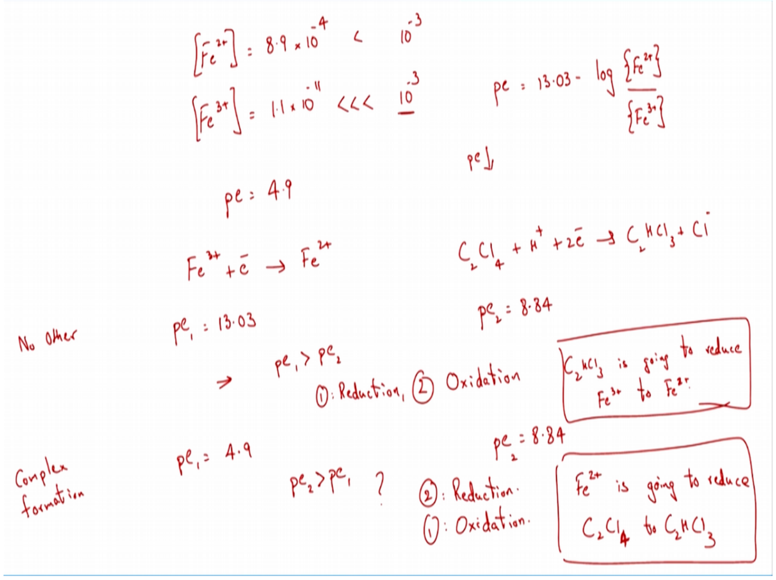

$[Fe^{2+}] = 8.9 \times 10^{-4} < 10^{-3}$

$[Fe^{3+}] = 1.1 \times 10^{-11} <<< \underline{10^{-3}}$

$pe = 13.03 - \log \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}}$

$pe \downarrow$

$pe = 4.9$

$Fe^{3+} + \bar{e} \rightarrow Fe^{2+}$

$C_2Cl_4 + H^+ + 2\bar{e} \rightarrow C_2HCl_3 + Cl^-$

No other

$pe_1 = 13.03$

$pe_2 = 8.84$

$\rightarrow pe_1 > pe_2$

①: Reduction, ② Oxidation

$\boxed{C_2HCl_3 \text{ is going to reduce } Fe^{3+} \text{ to } Fe^{2+}}$

Complex formation

$pe_1 = 4.9$

$pe_2 = 8.84$

$pe_2 > pe_1$?

②: Reduction.

①: Oxidation.

$\boxed{Fe^{2+} \text{ is going to reduce } C_2Cl_4 \text{ to } C_2HCl_3}$

So obviously let us come back to equation if this particular values so we have FE2+ concentration = 8.9 into 10 power -4 and as you see that still more or less similar to what we had initially 10 power -3 concentration and FE3 + though now equal to 1.1 into 10 power -11 right and again see is much lower right then 10 power -3 which is your initial total metal concentration right so obviously when we try to plug in the relevant values into our equation which was PE = PE naught – 1 / N log FE2+ / FE3+ right.

So what would you observe here obviously you see that FE2+ is more or less the same right but FE3+ is much lower right. So here I guess we are increasing the value of this particular variable here meaning that PE value will decrease I guess right. So I can plug this in into excel let us say and calculate that or obviously again let us see how to get this done in VMINTEQ I guess right so I am going to go back to VMINTEQ so fixed at 7 so I need to specify the redox couple right.

So we are looked at how to solve that and obviously I need to plug that in and get the relevant PE value but I can also use VMINTEQ to be able to get that. So obviously for that I need to specify what are the redox couple is here obviously the system is with respect to redox couple is FE2+ and redox couple he is with respect to FE2+ and 3 + that is what I am going to have here.

So I am going to ask the system to limit to those couples based on the components that I have so it is obviously only going to be FE2+ and FE3+ and I am going to add that to the list and here going to say that visual MINTEQ will have the fixed PE value of 8 which does not make any sense to me so obviously I need to go to the specify PE and PH menu okay we are going to do that back to main menu so here I guess parameters and specify PE and EH and it is not fixed PE right I am trying to calculate the PE so it is not fixed PE again will come back to that.

So PE or EH computed by supplying a guess or PE so guess with PE will give it be what it was earlier I think it was and let us say it was going to 3 that and save and back and now look at what the PE value is 15.03 8.84 and because PE1 was greater than PE 2 right what is that mean it means that 1 will go through a reduction while 2 or these half reaction will very oxidation right. But now in our case when we have complexes form 2 or complex formation complex what did we observe now.

We observed that PE1 now is now 4.9 right while the PE2 still going to be equal to 8.84 right the complexes do not effect these particular compounds here and now what do we see here we see that PE2 is greater than PE1 right so what is that mean now so 2 would go through as reduction right while 1 would go through as oxidation right and again what is that mean that more or less means obviously that if FE2+ is going to reduce C2CL4 to C2HCL3.

So obviously here you see that FE2+ is actually going to or trying to or try to reduce C2CL4 to C2 HCL3 right again so again why this change earlier yet what do we say PE1 to be greater than PE2 but here we have P1 less than PE2 and obviously again the whole point of it is that or the basis for that as here we are considering what do we see a more national case which is also the formation of the aqueous complexes right which we did not in the earlier case.

But here we see that if FE3+ concentration is going to be much lower that the total FE3+ right and why is that because we have FE3+ existing in various complexes. Let us look at that for a second again back to input menu or view output files pardon me and new species distribution.

As you see FE2+ 89% of this FE2+ stay as FE2+ but with respect to FE3+ I guess you know we do not even list FE3+ here because it is such low concentration 99.3 % exist as complexes are more than 99.9% exist as complexes and little or very little negligible amount what do we say of the total FE3+ exist as FE3+ or metal. So thus when you plug these values when your PE equation right for the reduction of FE3+ into FE2+ you see that the PE value is now much lower right.

So now as you see that in out their because of the complex formation right you see that iron would tend to receive or ferrous iron would tend to reduce your TCE pardon me PCE right or C2CL4 but if you consider no complexes you would have observed that if you had now complex formation you would have observed that it would have C2H CL3 I guess right what do we say oxidizing FE2+2 FE 3+ that is what you would seen earlier right.

So let us look at what we have earlier so if these was the case here what would have seen you would have seen these particular reaction to be swapped which as to be the oxidation reaction. So C2HCL3 would have then what do we say reduced FE2 + to FE3+ pardon me I guess I am misspelled it earlier. So in this case you would have C2HCL3 is going to reduce FE3+2 FE2 right and in this case where in you know complexes being formed right.

So obviously you know you now tend to understand or appreciate the relevant aspects so if someone did not consider the complexes or did not have the background that would have had what do we say an erroneous understanding of the system but again keep in mind that we are not yet done and why is that because in the practical scenario or out their in the nature what else would you expect now you know that you will have formation of the solid right.

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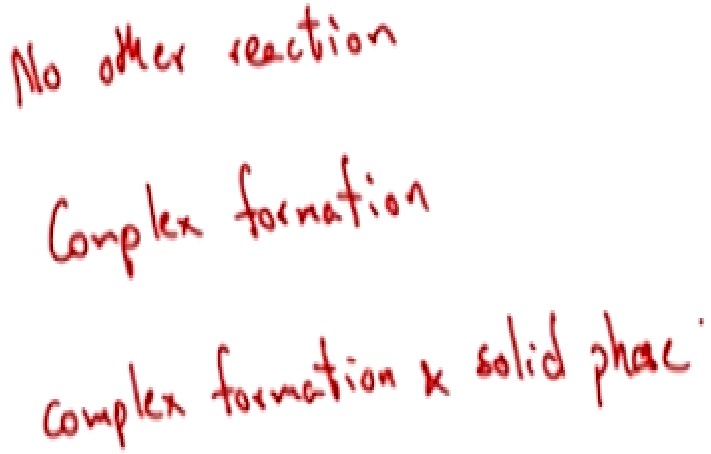

No other reaction

Complex formation

complex formation x solid phac

So here until we have looked let us say no other reaction other than redox right no other reactions right and then we considered complex formation and consider complex formation right and now we are going to move to the other case when we are also going to consider the most particular or natural scenario of their complex formation and sold phase or the precipitation I guess right.

So you know form your background let us say that you know ferric the ferric iron can precipitate out to and the let us try to understand how the system would change or what it is that you know we need to understand about system when we consider the natural case of the redox, the complex and the solid phase being present which is what would have been what do we say effect of their in the nature right I guess right.

So here i guess as we go through from just the redox what do we example to the redox end complex and to the more natural example or realistic scenario I guess right of redox complex and precipitation you will be able understand better I guess right why you need to have the relevant background in the complex formation and the precipitation and resolution and so on so I guess will continue this particular aspect in the next session and I guess with that I will be done for today and thank you.