Environment Engineering: Chemical Processes
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Module No # 12
Lecture No # 57
Reaction Feasibility based on EH

Hello everyone so again welcome back to latest lecture session so let us have a quick review of what we have been up to in the last latest session. So I guess right now or you know we have the fag end of the course right. So we I guess need to be able to take an holistic approach to be able to understand let us say quantitatively and qualitatively any system that we look at right and in that context to be able to visualize that we looked at particular set of examples I believe over the last three sessions right.

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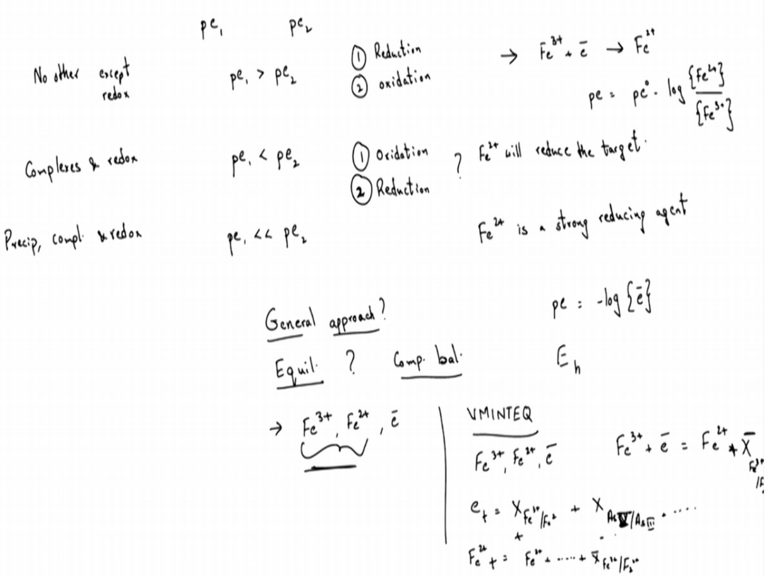

pe_1 pe_2

No other except redox — $pe_1 > pe_2$ — ① Reduction ② oxidation — $\rightarrow Fe^{3+} + \bar{e} \rightarrow Fe^{2+}$

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

Complexes & redox — $pe_1 < pe_2$ — ① Oxidation ② Reduction — ? Fe^{2+} will reduce the target.

Precip, compl. & redox — $pe_1 << pe_2$ — Fe^{2+} is a strong reducing agent

General approach?

$pe = -\log\{\bar{e}\}$

Equil. ? Comp. bal.

E_h

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

VMINTEQ

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

$Fe^{3+} + \bar{e} = Fe^{2+} + \bar{X}_{Fe^{3+}/Fe^{2+}}$

$e_t = X_{Fe^{3+}/Fe^{2+}} + X_{As(V)/As(III)} + \cdots$

$Fe^{2+}_t = Fe^{2+} + \cdots + \bar{X}_{Fe^{3+}/Fe^{2+}}$

So let us just quickly just summarize them so the first set we looked at one particular case where we looked at no other reactions right accept the redox obviously right and we calculated the PE value greater than PE2 right and from these you can then know that let us say half reactions one will go as written or as reduction right and the second half reaction would need to proceed as oxidation right.

But when we looked at what do we say the example with respect to the iron half reaction and consider the complexes right consider formation of complexes in congestion with redox process right. As in I believe we have these particular half reaction right FE3+ + electron goes to FE2+ this was her first half reaction right so when we calculate this particular PE value right so that is equal to PE = PE naught right – 1 / N 1 electron transfer right into log activity of FE2+ / FE3+ right.

This is from our understanding of the relevant system so when we looked at the particular case when we consider that no complexes would be formed and we would only have the redox reactions going through right or the redox process involved we saw that the PE1 for this half reactions was greater than the PE2 of the other reaction that we consider right. But with our knowledge or background that we had let us say we know right both with respect to or with FE2+ and FE3+ cations right.

So when we looked at that and then recalculate it that though we saw that PE1 was actually less than PE2 right. So what is that mean 1 would proceed as oxidation right and 2 the second half reaction would proceed as reduction or as written right and again what is this mean now this mean that now FE2+ will act as the reducing agent and reduce the other relevant compound right and reduce the target let us say let we leave that directly yes.

This was the other scenario we looked at but let us say the final scenario we looked at let us say our approach what you expect out there in system was you know we considered the formation of the solid or precipitation too right. So obviously out there in the nature you would have precipitation you would have complex formation and redox process all you know occurring simultaneous and obviously the relevant acid base reaction too.

So when we calculate for that particular scenario or analyze that particular scenario right we had precipitation we looked at or consider complexes right and obviously in conjuction with redox process. We saw that PE1 was far less than PE2 right indicating that for those conditions FE2+ is a strong reducing agent right so I guess hopefully these approach right or these sets of examples should have helped to illustrate what we have been trying to understand since the last couples of months I guess right.

So as in all these chemical process that we have discussed that is what the acid base complex for information redox precipitation they go hand in hand and interlink right. So it is a fine balance between all these process obviously at equilibrium right so we looked at these aspects right and now we are going to move on to what do we say the EH approach right until now we looked at understanding the relevant redox process form the context of PE right which is – log activity of electron right and understood the relevant aspects or analyze the relevant aspects.

But you know in general too the people are you might have heard about electro chemical cells or in general I guess you might heard of me referring to P as or the PE naught values as redox potentials will that slightly erroneous though you know when we say redox potential it is actually a EH values that we are talking about right again electro chemical cells these are relevant to electro chemical cells right.

So we are going to discuss these aspects though right again before we go further though right again similar to what we have done thus for with each of the process we will also briefly look at let us say how to set up these what do we say equations to be able to solve for the system at equilibrium right by hand now again we are going to have a very brief outlook again and the reason being that as you know in redox process mostly it is a kinetics aspects that are relevant.

These aspects that we are analyzing PE you know and such or using the VMINTEQ to be able to understand the system will only tell you what you would expect if equilibrium is reach right and you know what are the conditions prevailing let us say reducing conditions or oxidizing conditions are such that you would prevail if equilibrium is reached right but again keep as we know right the kinetics place huge role and you know we should be careful when looking at analyzing the system just looking at the PE values right.

For example in these particular case or the example we looked at just because we say that FE2+ is the strong reducing agent and will reduce the other compound does not mean that it can go through right because the kinetics can be relatively but at least you will e able to understand you know which compound would act as a reducing agent and thus which compound would be reduced and thus in so on right.

At least that will help you understand the system so again we are going to have very brief outlook right with respect to how to solve it. So I guess the general approach how have you solve these equilibrium problems now right the general approach what was that now right. How have to solve the equilibrium relevant aspect now right we always looked at components balance model right.

So similar we follow the component balance so let us say if I am looking at these particular set of example though. So what can the possible component be right so you usually would have chosen FE 3+ and FE2+ though but how would you know account for this redox reaction though right. So in such a case right you will choose your electron as one of the component too right. But you will consider that obviously let us say that relevant concentration of these electrons are relatively low right or negligible.

But you know choosing the electron as one of your what do we say components let us say will help analyze the or you know calculating the system I guess right or you will help in getting at the system but obviously again then you need to what do we say look at manipulating the other 2 component too right and how does VMINTEQ calculate this. Again with respect to VMINTEQ right what is this software about or hat will these help being understanding about.

Again keep in mind that VMINTEQ does not give you any idea about how fast or slow the reaction are VMINTEQ is software that we can use to understand what the system would be if and only if the system reaches equilibrium right. So when you try to use VMINTEQ or utilize VMINTEQ too analyze these redox what do we say process right or in redox reactions that is something to keep in mind that you are only understanding the system that would condition that would prevail equilibrium.

But again that the kinetics plays huge role so that you need to be calculate looking at relevant rate constant or such right. So VMINTEQ though again I guess the aspects here are obviously it will choose FE3+ FE2+ and what do we say electron as components right but I guess something that I have not mentioned out here the issue is that if these is written as these right with such formation equations right.

You see you can form one of components from the other two components with it said of the fundamental what do we say aspect of our what do we say now or components balance equilibrium right. So how do we how does VMINTEQ go about these component balance equations right. So how do we how does VMINTEQ go about these now right to able to get of out that these particular what do we say quandary i guess.

You know VMINTEQ introduces a dummy variable right you know FE 3+ FE2+ X is your dummy variable right and it now let us say here is this as a particular what do we say way to able to solve them relevant aspects. As in let us say what will your total electron balance be it is going to be equal to let us say X or FE3+ FE2+ right and if there are other two compounds let us say arsenic 5 to arsenic 3 for the relevant half reaction + so on and hence so forth.

So how will these electron transfer or the total electron balance what now so let us say if the electrons are being donating from these particular half reaction to these particular half reaction right. So then these particular term will be positive and these will be negative and so on right and again why is that electrons are being what do we say or FE2+ let us say acting as reducing agent in these case right.

So then that donating the electron so X in these case would be dummy variable here with resect to the balance of the electron would be positive here and then with respect to arsenic which receives let us say and this is oxidation state five for arsenic if that is not clear would be negative here and thus it would help to understand or analyze the system. So similarly again if i am writing FE2+ total balance it would be FE2+ relevant components not components species with respect to complexes right and also let us say X FE3+ / FE2+ right and so on right.

So again with respect to FE32+ it will be I guess to their right and so thus you know VMINTEQ tries to read the solution. So again in a such brief is good enough for us right once to understand the approach you can get that done if that necessary but obviously VMINTQ will cut down on the time.

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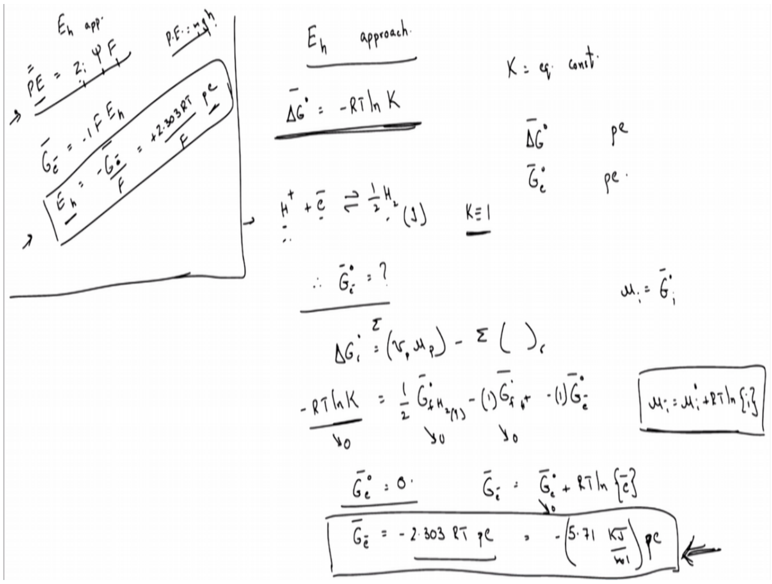

So now we are going to move on to the next aspect that we are talked about which is the EH approach right until now we have looked at the PE approach to understand the system and the relevant aspect but again in the environmental process are such you might have looked at people looking at electro chemical cells are such for promoting or populating certain kinds of reaction or such or utilizing the relevant transfer of electrons in worthwhile ah manner I guess right.

So in that context I guess right EH approach is worthwhile because it helps to understand the system in better manner right or the electric potential here let us see. So let us see what this about but before we go further we need to understand the few aspects here again keep in mind that everything down to one particular as in let us say one particular aspect as in every system.

Let us say or every process would be driven by the sole motive of decreasing its energy or the energy of the system you want to be decrease now and this is something we looked at in our initial process right and we looked at I guess the GIBBS energy of the system or GIBBS energy of the mixture right you saw that it is always driven towards you know being at its lowest possible state or valley right. So again keep that in mind we work our aspect.

So just to refresh your memory if you remember this we had delta G naught right was equal to what do say –RT natural logarithm of KK here is the equilibrium constant obviously right so I am just trying to state an approach where we are going to be able to try to link let us say this energy of system with the PE value or molar GIBBS energy of system let us say to be more specific and standard condition to the PE value right let us say how we can arrive at that particular aspect.

So people can refresh their memory at that fundamental aspect we say equation we clear on let us ay or very early what do we say as right and let us consider this particular what do we say half reaction let us say right + electron goes to half H2 this is gas and this in general difference = 1 let us say and now how do I calculate the molar GIBBS energy of these particular what do we say electron here right at standard condition I guess molal standard molar GIIBS energy of these particular electron how can I calculate that now right.

So if people remember that right this was based upon your particular what do we say the synapsis as in the delta G of the reaction as in the standard condition was equal to the stoichiometric coefficient right times the chemical potential right of the products summation – that of the reactants right. And again chemical potential was nothing but also equal to molal GIBBS energy of particular elements or compound molar GIBBS energy of compound if required right.

So how do we write this to this particular equation now here it is going to be half times GIBBS formation let us say standard condition H2 right hydrogen gaseous state as that of let us say what do we have here of that of H+ right –that of the electron and again 1 of the stoichiometric coefficient here right. But again these are the elements here let us say right and thus these 2 values would be equal to 0 right and here we know delta G of these particular reaction was equal to – RT natural logarithm of K right.

And equilibrium constant for this is 1 that is reference half reaction right so this value would also be equal to 0 now right. So now what do we have here I guess that GE naught = 0 right. So again taking this further right similar to our MU I at non-standard condition MUI naught right +RT natural logarithm into activity of that particular compound this is another particular equation that we analyzed we looked at trying to calculate the chemical potential of the system at non-standard condition right.

When the activity is no more equal to 1 so that is the case that we have here so if I apply these out here let us say the molal GIBBS energy of the let us say the particular electron but no more at the standard condition will be equal to that at the standard condition + RT natural logarithm of activity of the electron right. So as we just looked at these particular value = 0 so now I see for my system right and write this particular molal GIBBS energy of the electron to be -2.303 right RT times PE right.

And simplifying this further let us say looks like it can be written as -5.71 kilo joules per mole times PE right again we know we are just illustration these what do we say you know derivation here but just try to understand the system here right. So here what we have finally up to or what the take home message is that I can relate PE which gives me a measure of the activity of electron to the molal GIBBS energy of the electron here right.

So that will again help me understand let us say if let us say a particular electron you know a molal GIBBS energy of particular energy at particular state let us say higher energy state. So I guess how would the reaction proceed now the reaction would proceed such a way that the energy would decrease right. So you keep this in mind when we try to understand the relevant system later.

So here in such a manner right we can relate the molal GIBBS energy of these particular electron let us say in particular system with respect to the PE of that particular half reaction right. So let us move on that before we go further it guess there is one other aspect that I need to write up here.

So another approach that we need o also consider obviously is the EH approach say again here we people might be familiar with this concept of PE right or the molal electrical energy right and that is going to be equal to the part of the charge electric potential and faradize constant right molal electrical energy charge electric potential and faradize constant right. So it is more or less equal to potential energy is equal to let us say MGH I guess right you know that is an analogy here yes.

But H would be similar to analog us to what do we say now the electric potential here and constant and constant here and mass here would be with respect to charge. So applying this with respect to out particular electron let us say how can we write these as G = charge will electron = -1 so F times here we have the potential electric potential. So from these right what do we have here but PH = - G bar by F right and the again looking at the relevant equation that we have here what how can you write these as that is going to equal to + 2.303 RT by F into PE right.

So here from this particular set up right we now have a what do we say let us say if we have a particular value let us say P we can calculate the redox potential let us say we looked at the relevant aspect with respect to the energy let us ay right and the take home message is that here would be that we look at or try to understand the system you see to it that the system would always move such a direction as to decrease the energy of these system right.

So again in same case here let us say we looked at relevant aspect here as in with respect to the molar electrical energy right. And looked at that approach to be able to calculate your redox potential in terms of the PE values or the molal GIBBS energy of the electrons. Anyway now need to mug up these what do we say what do we say literal derivation that we are looked at – derivation of looked at pardon me but keep the background in mine.

So now I guess we are going to obviously try to link what we have been up to. So here we are going to look at two half reactions right. So here we have two half reactions SO42- being reduced to H2S right and also H4C right being reduce to CL- and here we also have the log K and PE naught values for these relevant half reaction here right.

Again what is we have here we have the relevant half reactions here obviously standard formation write them as reduction. For ease of understanding we have written them as one icon transfer let them we have written them as 1 electron transfer right so again here it is HOCL going to be say being what do we say reduce to CL – we can obviously look at relevant redox not redox pardon me oxidation states right.

So here let us say we are going to first understand in terms of what we have discussed thus for in try to understand in term of PE naught values that we have looked at right which we have here and we are going to understand these graphically and it should hopefully have understand the system or visualize the system in the better manner and at the same time we are also going to look at the molar GIBBS energy of the particular electrons and the redox potential here let us say.

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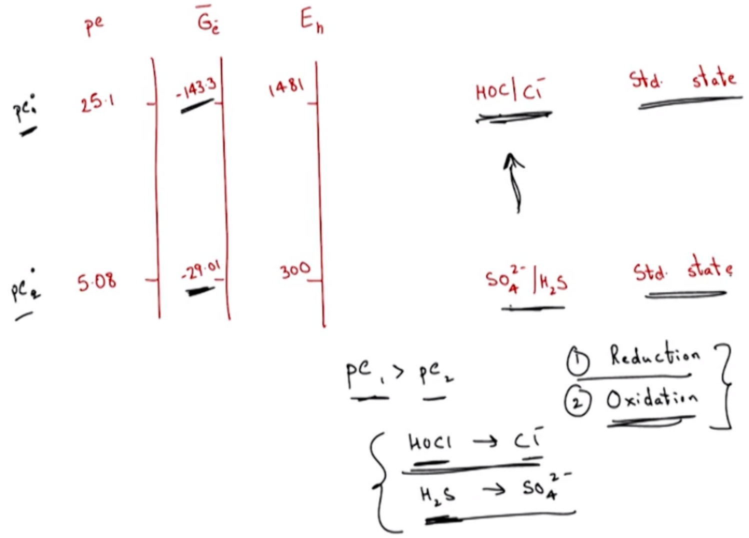

So let us say I guess I have a graph here right so I have graph and here we have a HOCL and CL- in there standard states so these would correspond to the PE naught values obviously right and here we have for HOCL and CL – right here it is higher PE naught value 25.1 and the other reaction it was 5.08. So for the redox couple HOCL and CL- the PE value is 25.1 is higher than the PE naught 2 value let us say right 5.08 the redox couple SO42- and H2S.

So at the standard state at the standard state the molar GIBBS energy of these particular electron let us say in equilibrium with redox couple HOCL and CL - would be at a lower energy state compare to and H2S so what does that tell you now let us say would the reaction would proceed let us say if it would at standard condition now let us say standard condition again as in temperature 25% centigrade pressure and the activity being equal to 1 right.

In would direction would proceed now again keep in mind that in a way that energy would decrease right. So has in the would the electron transfer would take place from these couple to the other couple right the energy is higher here it would want to travel from the higher energy state towards the lower energy state right. So let us try to understand the system in term of what way we have discussed in earlier in terms of the PE now.

So if you remember try to understand this system in terms of what way we have discussed earlier in terms of the PE now. So if you remember when we looked at or analyze the system in term of PE we said that if PE of 1 is greater than PE of 2 right what did we have or what did we understand about that now or we mentioned that one would proceed as reduction right reduction and the other one would proceed as oxidation.

So let us just try to visualize that here what would that mean that would mean here that HOCL will be reduce to CL- right and how will be reduce by H2S right. So here what have you written now 1 is written as reduction right this is reduction here and then not obviously writing down the balance half reaction here and 2 will be will go through as oxidation so what is happening here if you look at the combine system here H2S will end up reducing HOCL to CL-.

And again you do not two aspect to understand here one was that PE 1 naught right is greater than PE2 naught and in that case we are understood or we looked at relevant derivation to I believe right epically with respect to PE1 anyway that one would go through as reduction 2 as oxidation and again now here we can understand it in terms of the molar GIBBS energy of the electron and that it travel from let us say higher energy state to the lower energy state right.

But obviously these is at the standard state right let us look at what it would be let us say if it is at non-standard state.

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pH 7

$HOCl = \{10^{-4}\}$

$Cl^- = \{10^{-3}\}$

$$pe_1 = pe_1^0 - \frac{1}{n} \log \frac{\{Red\}}{\{Oxd\}}$$

$\{SO_4^{2-}\} = \{H_2S\} = 10^{-3}$

$pe_2 =$

So for that condition let us say we are going to consider PH to be 7 and I believe the example we are going to look at is going to be HOCL to be at 10 power -4 activity and CL – to be at 10 power -3 and SO42- and H2SO to be at 10 power -3 right and how can we calculate the PE value is now PE1 and PE2 right. So obviously as we are in general half reaction is PE1 = PE1 naught -1 by N and being the number of electrons being transferred times log Q dash right.

And Q dash is nothing but activity of the compounds in the reduce form by the oxidized right so in these particular half reaction what it would be I guess the PE value would be equal to right PE naught would be equal to 5.08 – 1 / N only 1 electron transfer right only 1 log Q dash right so would that be here so H2S power of 1 / 8 by SO42- raise to the power 1 by 8 obviously because we have H+ here 2 we need to consider that H+ to the power of 5 by 4 let us say right.

And these particular case it would be PE = PE naught is 25.1 right – log Q dash 1 / N again the number of electrons being transferred is 1. So it is going to be 1 times reduce form right. CL- to the power of half activity of water is 1 and divided by HOCL raise to the power of its stoichiometric coefficient half and again H+ raise to the power of stoichiometric half right so from here we can calculate the PE values right and let us see what the system would be.

So here I have the calculated PE values for these 2 redox couples as in HOCL and CL- SO42- and H2S and at PH7 and 10 power -4 and 10 power -3 respectively concentration for HOCL and CL – and PH7 is 10 power -3 for both these couples here not both these couples for the pardon me the couple of SO42- N H2S. So here we have the PE values not the PE values so here we have the 21.1 and once we have the PE value we know that it molal GIBBS energy of the electrons right.

And again how you can relate that to the redox potential and same case here we can calculate and we are able to calculate the PE value molal GIBBS energy and again the redox potential right so let us try to understand this in terms of what we had earlier let us say as in the standard condition right. So let us look at the standard condition so these where the standard conditions right and these where at the or at the non-standard conditions of PH7 and 10 power -3 and 10 power -4 concentration say again standard condition to non-standard conditions right.

Again from here I am looking at let us say the PE values or such you can understand which direction the or which particular what do we say compound or the reduce form would predominant or oxidize form would predominate right in relation to PE – PE naught right. So in one of the earlier classes right we looked at have let us say similar to PH and PKA by comparing the PE values with respect to PE naught we could let us say which particular compound would predominate.

Let us just try to you know suit through that particular aspect here so if I am looking at these particular what do we say couple. HOCL and CL – so PE here is 21.1 and PE naught is 25.1 right. So similar to the PH and PKA graph so what would it be like obviously there is H+ involved here too so that is going to be slightly erroneous and try to understand that here but that is fine here.

So if PE naught is 25.1 right and PE is left of it or less than PE naught 21.1 so which form would predominate now right the one with the similar to the acid base right the one with the proton or here one with the electron or the reduce form would predominate right so thus in these case in this non-standard condition or reduce form will predominate right. So same case here again with respect to the non-standard conditions.

In the non-standard conditions for SO42- and H2S right what do we see here we have tableted right 25.1 yes so again here to we see that PE is less than PE naught right. So again from the similar approach of what do we had earlier you will understand at the non-standard conditions which one would predominate now the reduce form or H2S would predominate right again that is just for understanding the system here.

And going to back to where we where we are now trying to see in which direction let us say would the reaction takes place now at the non-standard conditions right. So earlier we looked at the non-standard conditions where do we see or come across such standard conditions. So at the non-standard conditions the PE values the molar GIBBS energy PH values and so on but the redox potential and we again have the relevant what do we values of the activities and PH values right.

So similar to what we looked at with respect to our with respect to our standard condition right we will first analyze it with respect to the PE so here again PE one right let us say I will call these PE1 and this PE2. So PE1 is now still greater than PE2 right. So again what is that mean that means that the first half reaction will go through as reduction right as in HOCL will be reduce to CL-.

And how will that reduction takes place now right and that will be taking place because H2S will be oxidized oxidation the second reaction how half reaction will go through as reaction or H2S will be oxidized to SO4 2- in the process H2S will release the electrons which still be accepted by HOCL and then be reduced to CL- right. So that is from the PE1 or PE2 approach here right.

So but let us say try to understand let us try to understand this system with respect to molar GIBBS energy of the electrons here and here again you see that in the redox couple right the electrons that would in equilibrium in redox couple SO42- and H2S the it is at higher energy state right and you see that with the electron that in equilibrium with HOCL and CL – GIBBS lower energy state.

So again the electron want to transfer form these couple to the again this is layman understanding I guess but more or less you can understand the analogy with respect to then energy and the system wanting to move in such a direction that energy decreases right. So from higher energy to lower energy state and that is what you see here so the electron transfer would take place from this redox couple to this couple so that means this couple proceed in oxidation or H2S is going to be oxidized SO42- in the process releasing the electron which would reduce your particular HOCL here right.

So here I guess obviously now we should be able to understand the relevant aspects terms of both the PE values the molar GIBBS energy of the system right and you know if now immediately I guess now I have the intuition that happen in the system right. So now again in this context again you can look at redox potential too right as in relative to the other.

So these aspects we are going to start discussing in the next session right as in the electro chemical simple approach let us say how and how or what do we need to understand when we look at a self what is anion what is cathode what takes place at that and why is that relevant towards and so on right and I guess with that I will end today session and thank you.