Environment Engineering: Chemical Processes
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Module No # 11
Lecture No # 53
Reaction Feasibility based on Pe- I

Hello everyone so welcome back to latest lecture session so let us review what we have been up to in the last session. I believe we have started the discussing or discuss in greater detail any way reduction potential and then applied to a few different kinds of examples right.

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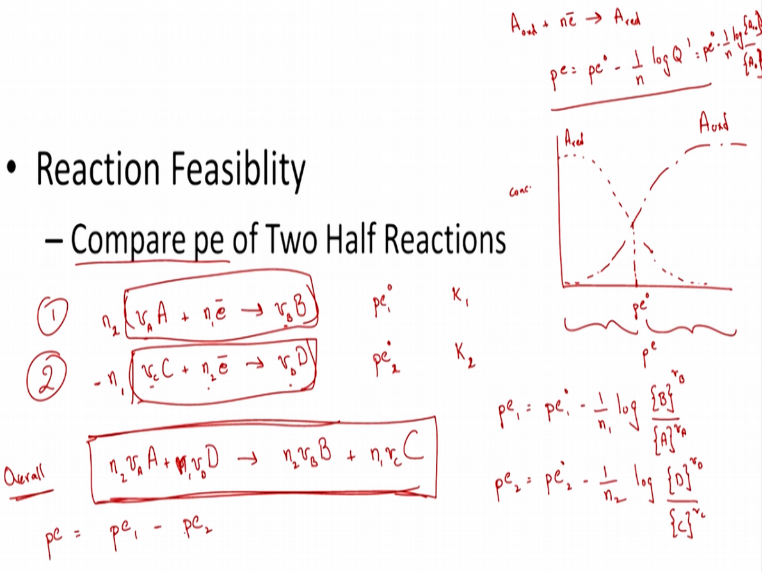

- Reaction Feasiblity
  - Compare pe of Two Half Reactions

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

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

① $n_2(\nu_A A + n_1\bar{e} \rightarrow \nu_B B)$ pe_1° K_1

② $-n_1(\nu_C C + n_2\bar{e} \rightarrow \nu_D D)$ pe_2° K_2

Overall $n_2\nu_A A + n_1\nu_D D \rightarrow n_2\nu_B B + n_1\nu_C C$

$pe = pe_1 - pe_2$

$pe_1 = pe_1^\circ - \frac{1}{n_1}\log\frac{\{B\}^{\nu_B}}{\{A\}^{\nu_A}}$

$pe_2 = pe_2^\circ - \frac{1}{n_2}\log\frac{\{D\}^{\nu_D}}{\{C\}^{\nu_C}}$

And I guess the basic cases is PE = PE naught right -1 / N log Q dash right and obviously this would be applicable for which kind of reaction now most obviously but we looked at different cases one would be oxidized form accepting electrons and being reduced to its reduce form right. So for this particular case you know for this e-generic case too we can apply this reaction of PE = P naught -1 /log Q dash right.

And then we try to vigilize the system in terms of concentration on the Y axis and PE on the X axis right for that obviously the reference was your PE naught right and that similar to your PH and PKA graph that we looked so just summarize that again so what we have looked at concentration here and PE here right.

So obviously if I try to represent this what is Q dash here so I am going to write this as PE naught 1/N log activity of the reduce form by activity of the oxidized form right that is what we have here so how do I write this we know that the reduce form is going to be something like this A reduce and the oxidized form is going to have this behavior A oxidized right so when would both these particular what do we say concentration or activities be the same when PE = PE naught right.

And then we looked at those particular cases when we are also had H+ right and also when we had the relevant present and so on but the take home message was when the PE is low right and especially with reference to is PE naught what is it mean it would mean that reduce condition would prevail relative to equilibrium and that is in this particular region obviously when PE is less than PE naught and also we looked at the other case when PE is high or PE is greater than let us say PE naught right so PE – PE naught is high what did we look at in that particular context we know that the activity of that electrons is going to be lower.

That means obviously the oxidizing condition would prevail meaning you would have the oxidized species predominating and that is what you see in this particular region yes again this scale is obviously not to graph. So now let us move on now so we can understand what it say looking at PE or PE naught W values and so on what it is we understand at the system at equilibrium right.

So now we are going to look at let us say standard system feasibility so I am going to look at let us say understand system feasibility so I am going to look at the PE of two half reactions right and then I need to be able to figure out let us say which reaction will stay as the reduction half reaction and which one you know have to be transform as the oxidizing reaction as in what are my talking about here.

So let us consider two particular half reaction stoichiometric of A + A right + N1 electrons goes to let us say it is what do we say reduce form B right and let us say these as PE1 naught okay and K1 and let us say relevant half reaction is C times C + N2 electrons goes to VD D stoichiometric coefficient of A stoichiometric coefficient of B stoichiometric coefficient of C and stoichiometric coefficient of D and the relevant reaction potential standard deduction potential and K2 equilibrium coefficient values right.

So here we have two half reaction right but we know that let us say for particular redox reaction to go through you need to have not just the reduction reactions which both these are reduction reactions as in their accepting electrons and the reduced forms are being form here right acceptance of electrons. So that more or less nothing but reduction but as you know you can never have both just two reductions right you need to have both the reduction and oxidation taking place simultaneously right.

You need to have a transfer of electrons so now let us say I need to be able to figure out looking out my particular values of PE and 1 and PE2 right and having the values of PE1 naught and PE2 naught let us say or K1 and K2 how can I let us say estimate not estimate I guess understand which particular half reaction will stay as return as in which way half reaction will go as reduction and which one needs to reversed and be written as or considered as oxidation right.

So one of these half reaction needs to be swapped right because that means it needs to written as oxidation. So from now from my particular case for our particular example right let us consider that the reaction 1 is going to stay at as it is as an reduction is going to do through and let us consider the case when the second reaction is written as oxidation right.

So in that case let us say what it will my overall what do we say reaction be and again now because now I have different electrons I mean numbers of electrons in involved here right as in N1 N1 case N2 in the another case I need to multiply the second reaction by innocent to and the first reaction by N1 right.

So again let us try to do that and have the overall half reaction right and what is that going to be equal to i need to multiply the first one my N1 and the second 1 – or the first one by N2 and the second one by – N1 and why is that obviously I need to be able to cancel out the relevant electrons or the electron transfer need to be the number of electrons being transferred need to be the same.

So let me write out here so it is going to be into N2 stoichiometric coefficient of A into A will go to N2 stoichiometric coefficient of times B or into pardon me times B and here I am going to have + stoichiometric coefficient N1 times stoichiometric coefficient of D and here i have going to have again and 1 times stoichiometric coefficient of C right. So this is my overall what do we say reaction now right and I need to be able to understand this particular system right so let me also write down PE1 and PE2 values here.

So PE1 is going to be equal to what now for non-modified or unmodified reactions I guess PE1 naught – what is this please -1 / N1log right and activity of B raise to its stoichiometric coefficient by activity of A raise to its stoichiometric coefficient this is for just this particular half reaction right and same case for this what is the PE value let me write that down.

So PE2 = PE naught of the second half reaction / 1 by N2 because N2 electrons are being transferred – log right and what do I have here activity of D raise to its stoichiometric coefficient right by activity of C raise to its stoichiometric coefficient.

So these are obviously PE1 and PE2 values and considering the case let us say these particular reaction 1 goes as reduction and 2 goes as oxidation I came up with this particular what do we say overall half reaction right. So what is that mean now let us say I will be able calculate PE of this overall reaction it is going to be equal to PE1 right – PE2 right that I am also going to have consider the case when what is this now I multiply this by 1 2 and this by N1 right.

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$$pe = (pe_1^\circ - pe_2^\circ) - \frac{1}{n_1 n_2}\log\frac{\{B\}^{\nu_B n_2}}{\{A\}^{\nu_A n_2}} + \frac{1}{n_1 n_2}\log\frac{\{D\}^{\nu_D n_1}}{\{C\}^{\nu_C n_1}}$$

$$= (pe_1^\circ - pe_2^\circ) - \frac{1}{n_1 n_2}\log\frac{\{B\}^{\nu_B n_2}\{C\}^{\nu_C n_1}}{\{A\}^{\nu_A n_2}\{D\}^{\nu_D n_1}} \leftarrow$$

$$\boxed{n_2\nu_A A + n_1\nu_D D \longrightarrow n_2\nu_B B + n_1\nu_C C} \rightarrow Q$$

$$Q = \frac{\{B\}^{n_2\nu_B}\{C\}^{n_1\nu_C}}{\{A\}^{n_2\nu_A}\{D\}^{n_1\nu_D}} \leftarrow$$

① $n_2 K_1$

② $-n_1 K_2$

$$\rightarrow \boxed{\log K = n_2\log K_1 - n_1\log K_2}$$

$$pe = \boxed{(pe_1^\circ - pe_2^\circ)} - \frac{1}{n_1 n_2}\log Q$$

$$pe_1^\circ = \frac{1}{n_1}\log K_1 \Rightarrow \log K_1 = n_1 pe_1^\circ$$

$$pe_2^\circ = \frac{1}{n_2}\log K_2 \Rightarrow \log K_2 = n_1 pe_2^\circ$$

$$\left(\log K = n_2 n_1 pe_1^\circ - n_1 n_2 pe_2^\circ\right.$$

$$= n_1 n_2 (pe_1^\circ - pe_2^\circ) \leftarrow$$

So let us look at that and take that through I guess right so the PE of that particular over all reaction is going to be equal to PE 1 naught – PE 2 naught of this modified or with the reactions we are not going to expand upon that now because it is going to be a erroneous so let us just understand that it is a difference in the standard reduction potentials right and what do we have here.

S PE1 = - so now let us say if it multiplied by N2 the electron transfer would be N1 and N2 – 1 by N1 N2 log and obviously again if this particular half reaction is multiplied by N2 that is going to be the case when what would that be now this particular case would have to be times N2 here or to the power of N2 right.

Log stoichiometric activity of B by activity of A stoichiometric coefficient of B times 2 right stoichiometric coefficient of A times N2 right + 1 by N2 this is the second or from PE2 right log stoichiometric coefficient D raise to its stoichiometric coefficient of D multiplied by N1 right by C raise to stoichiometric coefficient multiplied by N1 right.

So now let us say I want to look at it or simplified further so here again we are requested you not to just you know transform into because it is going to be erroneous just try to understand this particular set as the what is this now the different in this standard potentials of these half reactions right if I say this is minus here 1 / N1 / 2 right will be analog so it is still going to be an activity of B activity of A right and here it going to be equal to activity of C by activity of D raise to relevant stoichiometric coefficient ties N1 right.

So now let us again have a look at or overall reaction not half reaction pardon me over all reaction and let me write that down here so that it makes better sense N2 times UAA right + N1 stoichiometric coefficient D go to and 2 stoichiometric coefficient of VBB + N1 stoichiometric coefficient of VCC right. So if we look at these particular reaction right and look at these set of variable here or variables here what is that equal to now we see that it is nothing but equal to Q right Q for this particular overall reaction yes so again what is Q here.

Q is nothing but activity of B raise to it stoichiometric coefficient which is in this case N2 times UB and activity of C raise to it stoichiometric coefficient right which in this case is N1 you see by activity of A raise to it stoichiometric coefficient which is N2 Mu A times D raise to it stoichiometric coefficient which is N1 times Mu D again as we see this is nothing but equal to this particular variable right.

So now I can write PE overall reaction as the difference in the standard difference potentials – by N1 N2 right log Q right N1N2 is obviously the number of electrons being transferred that is what we see earlier when we try to modify the two half reactions N1 N2 Q is the relevant activity product of the overall half reaction right.

So here we did say that this is just the different in the two standard reduction potential it is the particular reason why you cannot just expand upon it as 1 / N1 into log K and get that done you should try that out you see that it is going to be erroneous let us see how we can get that I guess. How can I get the overall K value so I am going to look at log K so for the particular first half reaction I know the equilibrium coefficient was 1 let us say for 2 it was K2 right and how did get for the overall half reaction to do that I have to multiply K1 / N2 and K2 / -N1 right.

So obviously we know from what we did in couple of session that is going to be nothing but equal to what now N2 times log K1 right – N1 log K2 right and this is something that logical too this is something we looked at a couple of sessions ago right. So from here though A I know that PE1 naught = what now 1 by N1 log K1 right and I know that PE2 naught = 1 by N2 log K2 this is something that I know.

And obviously what is that mean K1 = N1 times PE1 naught and log K2 = N2 times PE 2 naught right so what is this transform into right this particular what would that transform into log K of the overall reaction K of the overall reaction is nothing but N2 times N1 PE naught N2 times N1 PE naught right P1 naught – N1 times N2 PE 2 naught so that is equal to N1N2 times PE 1 naught – PE2 naught.

So substituting this particular expression that we have out earlier equation where we had let us say log Q here and PE here and we are going to substitute this particular variable here so let us see how it is going to transform into right.

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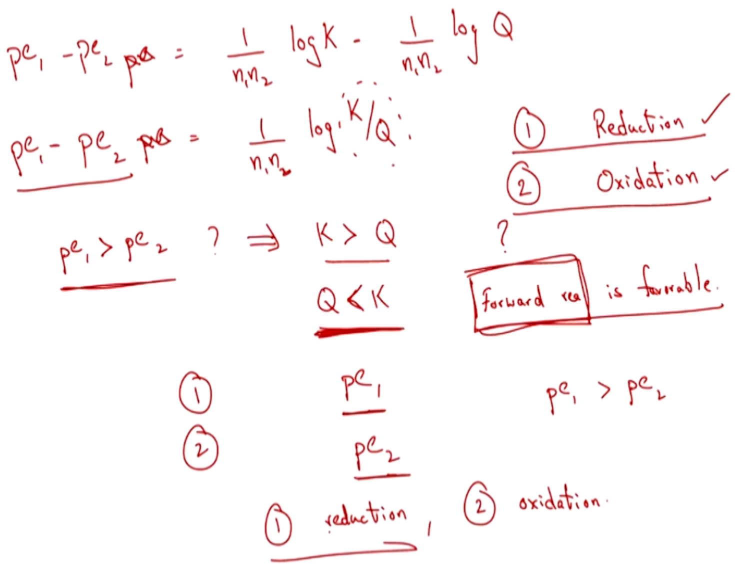

So we end up with PE = 1 / N1 and N2 log K – 1 / N1 log Q right and it is guess I am taking a familiar shape so PE = 1 / N1 N2 log K / Q right. I guess I should have written it has PE I should have written it as PE1 – PE2 right so let me continue writing that is the better way of expressing it right or correct way let us say PE1 – PE 2 = 1 / N1 N2 log K / Q now I guess we are at the stage where we can try to understand the system.

Anyway I guess we looked at the relevant basic derivation but you do not obviously to mug that up but you need to understand how to be able to understand the basics here right. So obviously what would the assumptions we looked at the case when the half reaction 1 is written as reduction right and reaction 2 we consider that to be oxidation right that is why multiply that by I N1 right.

So again in that case what is it that you see here when will PE1 or when PE1 is greater than PE2 right what do you observe here you observe that K is greater than Q right. So PE1 greater than PE means it is positive and one that would that be the case when K greater than Q or Q is less than K right again what is this mean now when Q is less than K you know that forward reaction will be favorable right forward reaction is favorable.

And how did we write the forward reaction or how did we get this particular forward reactions you remember that we consider reduction to be the half reaction 1 but we swap the second half reaction as oxidation right so again these case obviously works out when you see right when will PE1 or when will these particular reaction be feasible when Q less than K right when Q is less than K or when K is greater than Q obviously when K is greater than Q what is that mean again you know inversely here or conversely means that PE1 is greater than PE2.

And obviously where did that come from again from considering that reduction is half reaction 1 and oxidation is half reaction 2 and only in that context we will have the forward reaction is feasible. So again you know let us try to understand what we have here so what it mean is that when you have two half reactions and one of the half reactions is greater than other let us say in this case we are talking about PE1 greater than PE2.

So we had two half reactions right and for 1 case PE1 the other case PE2 right and when did we see that the reaction would be feasible so let us say if PE1 is greater than PE2 right what would be the scenario the particular reaction or redox reaction would be feasible it would be case one stays as reduction right that 2 is considered as oxidation right.

So obviously what is this mean now when PE1 is greater than PE2 will consider one as reduction itself right or as you now the half reaction stays as it is but the second case or the second or the lower PE2 value or because of the lower value will have to see to it that it is considered as oxidation right.

So again that is the particular case of obviously if PE1 is less than PE 2 when will the redox reaction and that is the particular case obviously if PE1 is less than PE2 when will the redox reaction be feasible when one is written as oxidation or considered as oxidation and 2 is considered as reduction which is the way we write it anyway right.

So we need to now compare 2PE1 to PE2 values let us say the PE value or 2PE values and the we can identify let us say which reaction is going to go forth as reduction and which reaction is going to go forth as oxidation right.

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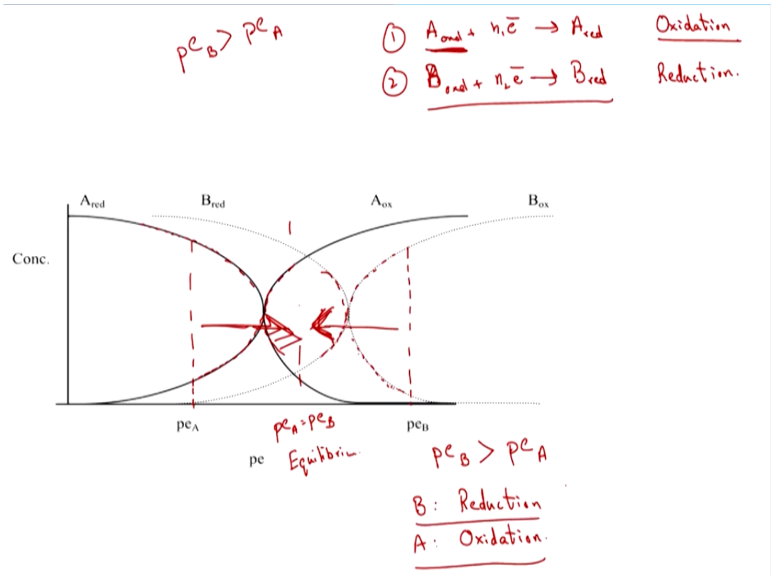

$pe_B > pe_A$

① $A_{oxd} + n_1\bar{e} \rightarrow A_{red}$ Oxidation

② $B_{oxd} + n_2\bar{e} \rightarrow B_{red}$ Reduction.

So in this context also let us try to look at one particular graph here that I have right so here let us say I try to understand the system here let us say. So similar to the example let us say we had here we have to say 2 redox couples 1 A reduced and A oxidized right A reduced and A oxidized and also B reduced and B oxidized right.

So let us just write it down here so A oxidized + M1 electrons goes to A reduced right similar to let us say reaction 1 that we looked at and A not A pardon me B oxidized + N2 electrons goes to B reduce right and here I have this concentration versus P graph and we have both the relevant Piece of information here right.

And here let us try to understand the particular scenario let us say right let us try consider the case when let us say the second reaction is goes as oxidation okay. So what am I considering here I am considering that here one will proceed as reduction right and 2 will go forth as oxidation as in these as to the inverse of this particular half reaction. So let us try to consider that case I guess right and then let us consider two cases let us say I have PE 1 let us say to be somewhere here let us say PE of A right this is the case and PE be somewhere here yes.

So let us say this is my case here right and now let us say I am going to consider that it goes through as oxidation here so let us see if that is feasible or not feasible or so on now let us say. Or let us say you know let us look at particular case here so let us say now I say that when PE1 is less than PE2 right that is what we see here right.

And in this case PE1 is less than PE2 but I am saying that PE2 is going to go through as what is this now oxidation now or the reverse reaction for this particular half reaction is going to go through so what is that mean obviously your concentration of oxidized form of B is going to increase right. So as the reaction go through initial concentration of B oxidation B in its oxidation form is here and let us say it is oxidation reaction of the of the inverse of this not the I guess the backward half reaction here right.

So then obviously as you see the B oxidized form is going to increase right and obviously you see that B reduced form is going to decrease right that is what you see and obviously then where will the PE be shift it is going to keep shifting to the right PEB values is going to shift to the right so obviously now let us understand what is going to happen with these particular PE one case I guess.

So here if that considered at one stays as reduction right so if it stays as reduction as in this forward reaction is feasible what is it mean as it goes through or goes forward A reduction increases and A oxidation decreases let us try to plug that here. So A reduction increases in this direction right and A oxidation decreases in this direction as in PE of A is moving in this direction right.

So what do you see here PEB is moving out here and PEA is moving out here so they were never approaching each other so which is not going to the case so your particular system would try to approach or as in come to a particular equilibrium let us say but when do you know that equilibrium will exist that will be case when PE of A will be PE of D right. So for that to the case in which the direction should be the values of PA and PEB travel they need to travel towards obviously each other right.

So obviously what does it mean are assumption initial assumption of one going as reduction and two going as oxidation will take the system away from equilibrium right so that is not how it is going to go through in nature. So it wants to want to reach equilibrium or PA needs to be equal to PEB right in this case what is it we need to observe we need to consider that one would go as oxidation right and 2 would go as reduction right in this particular case and why is that that is because PE of B was greater than PE of A right and that is similar to what we discussed earlier to right as in PE1 – PE2 = 1 / N1N2 log of K / Q right this is what we discussed earlier.

So if I write this as PE of A – let us say PE of B equal to 1 / N1N2 log K by Q right but we know that PE of B is greater than PE of A PE of B is greater than PE of A. So that means this is a negative value that means what now Q is greater than K that means the reaction is infeasible right.

So obviously when is the reaction feasible let us see that when 1 which is A oxidized + N1 electrons goes to A reduction is inverse and return as considered as oxidation right and 2 which is A not A pardon me B oxidized electrons goes as goes to B reduction and it considered as reduction right. And why is that again because the PE of B is greater than PE of A and that is what you see from our particular starting case here right.

And now let us consider this particular case obviously when PE of I mean B is considered as reduction itself and case is with respect to B and the case with respect to A is considered as oxidation so let us say for B work it out if it goes as reduction right what is going to happen now the B reduce form is going to increase as in this is going to go in this direction and B oxidized form is going to decrease so it has to go in this direction right.

So that means this particular PEB is going to shift in this particular case and same case for A let us say what have needs to form A oxidized form needs to increase because it is written as oxidation so in which context or in which particular scenario will that increase as you see it is here and travel in this particular direction and obviously the reduce form is going to decrease when oxidation occurs.

So in this direction right so here and so when PE and PEA and PEB meet let us say and one particular scenario when PA = PEB obviously that is when have equilibrium right and I guess what was the starting point of this particular scenario when PE of B was greater than PE of A that is why we had to write for the case it would be as case as reduction and for AK it would stays as it would have to be return as considered as oxidation right.

So that is something we have to understand so we are looking at two particular cases here right or to sets of half reaction so how do you determine the feasibility or the overall reaction. So the overall reaction would be feasible when that half reaction whose reduction potential is higher is written as written as reduction or in these case PEB because it is higher than PEA it is going to be considered as reduction and that half reaction whose reduction potential is lower.

Or in this case PEA right that is from my starting point here right is lower it will be considered as oxidation. And only then will your overall reaction be feasible right so I guess that is our particular what do we say session for today and I guess I am going to look at the relevant application from the next class or next session pardon me right.

So we are going to try to bring everything together in the next session as in if you remember I guess we consider initially only what do we say now acids and basis and then looked at complexes precipitation and reduction potential. So the next couple of session anyway should be able to bring everything together and pretty what do we say good manner let us say if that how is it all these 3 or 4 environment process relate to each other right. So let u take that in next couple of session I guess and I guess but for today I am done and thank you.