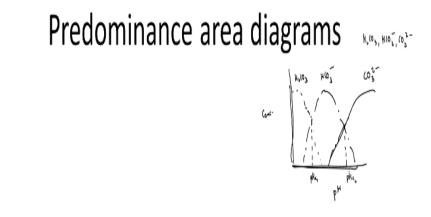
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Lecture – 47 Predominance Area Diagram & Introduction to Redox Processes

Hello everyone, again welcome back to our latest selected session so we are hopefully going to wrap up precipitation and resolution in this session. So, one of the last aspects that we are going to look at is the predominance area diagrams as we briefly touched upon or discussed them in the last session right we say that we are going to look at a summary of the relevant scenario right or a snapshot of the relevancy scenario and this is going to be useful let see.

And you want to obviously get a generic idea of which species will predominant at which particular pH or which particular scenario right or at which point particular set of conditions. So, I guess one example we are going to have a look at is.

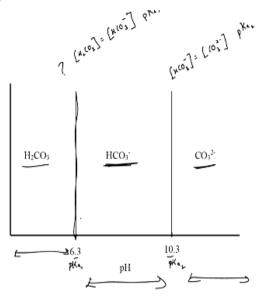
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Let us say the acid based speciation for H2CO3 HCO3- and CO32- okay we know that let us say this is the concentration and this is the pH here the true picture would be something like this right. So, this would be the H2CO3 concentration which would decrease with pH right and this would be the HCO3- HCO3- concentration and this would be your or let us say this would be your CO32- concentration.

Right yes and we know that these points of intersection of both the relevant variables are equal will be PK1 and PK 2 right so but obviously you know when I if I want to get at the predominance area diagram what is it that I am going to represent I am going to represent that region in which that relevant compound is going to be at higher concentration right or is going to predominate.

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So, obviously the graph that we had earlier is going to transform into something like this right so what is it that we understand this is the pKa1 this is pKa2 right. So, when pH is< than pKa1 what variable which compound is going to predominate H2CO3 and obviously that is what you see here too right when pH is< pKa1 or in this region which particular conjugate acid base in this particular system is predominating you see that it is H2CO3.

Right and that is what we have here right and obviously this solid line what does that represent that represents that concentration of that region where H2CO3 concentration is= HCO3-.Right so that is the key here the solid lines represent that particular region when the and the sideline obviously would represent the region when HCO3- is going to be=CO3- and where do you know that these occur.

This will occur at pKa1 and this will occur it pKa2 right and that is what you see here. So, again

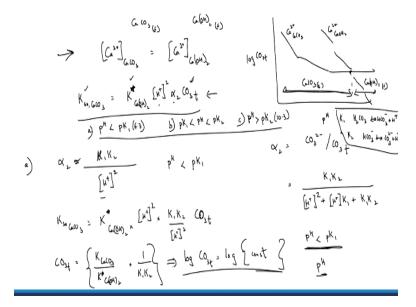
from this particular graph the predominance diagram right you know that HCO3- or this tells us that HCO3- will predominate between the pH of 6.3 and 10.3 and let us look at the graph that we have earlier and that is what we see here right between pHa1 and pKa2 even though you have HCO3 or CO32- which is the variable or compound that is going to predominant that is HCO3-.

And that is what we have here and similarly when pH is> pKa2 you know that CO32- is going to predominate and that is what you see here right. So, again keep in mind these predominance area diagrams give a snapshot right not the true picture as and you do know that between pH of6.3 and 10.3 while HCO3- concentration is relatively higher right it does not mean that there is no H2CO3 nor no CO32_.

As you know near let us say pH7 you still have some H2Co3 and near PH10 you still have CO32-. So, keep in mind that these what is it now predominance area diagrams gives you a summary right are obviously a snapshot of what variable or particularly which compound or what compound predominance. But that does not mean that there are no other compounds present in that particular region.

Right so in general again I know they give a snapshot that is the key keep in mind that they did not give a true picture of the relevant equilibrium related species concentration right. So, let us say now we are going to move on to one particular example which we did earlier.

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When we had both CaCO3 the solid and the CaOH twice the solid right so we looked at one particular graph right where I think for log total c and with respect to pH right and log CO3 total I believe right we came up with graphs as in this region right and CaOH twice would be this and we say that in this region CaCO3 is going to predominate right and this is when Ca2+ is an equilibrium CaCO3.

And this is when the Ca2+ is in equilibrium with CaOH twice because in this region this particular variable is< this CaCO3 solid is going to pre state and in this region right CaOH twice is going to precipitate. Right so but obviously let us say if I want to get a snapshot of what is happening the system I need to be able to draw what now or develop what I need to be able to develop the boundary lines.

So, let us just try to develop those boundary lines right so obviously how can I draw the boundary lines or when will both the solids pre state out right when the concentration of calcium in equilibrium of CaCO3 is going to be= the concentration of calcium in equilibrium with CaOH twice. Right as in what is that region obviously this is the region right were trying to look at and now I am going to say how to figure out how the it varies with pH right.

So, that is what we are going to try to plug in and I guess we looked at this particular equation in the last class. So, I am not going to write that down again but I think it is k solubility product of

CaCO3=K star right of CaOH twice right * I think H+square right * CO32- that would mean alpha 2*CO3 total right this was the relationship I believe we figured out when you were trying to look at the relevant what do you say case.

When both the solids would precipitate out so this was the equation and obviously when would that be the case when the concentrations of calcium that would be in equilibrium with both the solids they are going to be equal. So, now I am going to have to figure a way out of coming up with you know or breaking these down into sections where you know for a particular pH this is the solid that is going to predominate.

And for a particular pH which the solid is going to predominate right and let us see how we can go about that. So, obviously you know for a given CO3 total right of these two are constant, the solubility part of CaCO3 and the modified solubility part CaOH twice they are constants yes and for a given scenario CO3 total 2 this let us say the constant for a given scenario right so what obviously changes here.

You see that alpha 2 will change with pH right so keep in mind that in this equation you know you can see that alpha 2 is going to change with pH and we know that alpha 2 what is that that is nothing but CO32-/CO3 total right but we also know we can express that as what is it now K1 K2 right/H+ the whole square+*K1+K1 K2 right this is alpha 2 and K1 K2 obviously are those acid dissociation constants for H2CO3 dissociating*HCO3-and H+.

The K1 would be for this equation K2 would be for the second acid dissociation equation right HCO3- reaction part would be in equilibrium with CO32- and H+ right K1 and K2 so we are just trying to refresh our memories these are aspects that we have covered in great detail in our acid and base relevant process. Right so we know that alpha 2 is going to be this particular case but so now I am going to look at three cases right.

The three cases are going to be when pH is< pK1 pH is< pK1 and we know the pK1 means 6.3 and when the pH lines between pK1 and pK2 and the third case obviously is when pH>pK2 right pH>pK2 and pK2 we know is around 10.3. So, for these three cases we are going to work out the

relevant equation and you will see how it makes sense now with respect to understanding the predominance area diagram.

Right so let us go through that so the first case is when pH < pK1 right. So, that is we are going to work out now. Right so obviously alpha 2 right what will it transform into in this case. When PH is far< pK1 right so alpha 2 right so it is going to be K1 and K2 one k two is going to be cave in and k two but which term would predominate here in the denominator now when the pH is very less obviously H+ concentration is going to be very high.

So, this particular term is going to predominate as an alpha 2 is going to be K1 K2/H+square=1 the pH is<pK1 right. So, obviously keep in mind that we are making some approximations here right. So, alpha 2 is going to=K1 K2/H+square so I will plug this in into my equation here right so now what do I end up with now I guess right I am going to have KsoCaCO3=K star CaOH twice right *H+square * alpha 2 is now K1 K2 /H+square right *CO3 total right.

Or I can also express this obviously as CO3 total=K solubility constant CaCO3/K star CaOH twice right H+square and H+square obviously cancel each other out right and CO3 is total I am still going to have what else, I am going to have 1/K1 K2 right so what does that more or less turn out to be so if I take log write log CO3 total would be equal to log of this particular set of variables right and you see this is a constant right.

So, what does that mean when the pH is<pK1 right there is no dependency upon PH that is what you see here right. Is there any pH relevant relevant aspect in this particular what we say now equation right? So, what does that mean that that region when the pH is<pK1 right the predominant said area diagram of the relevant relationship where CaCO3and CaOH twice per state does not depend upon the pH right.

And that but to regain so it is going to be a straight line there I guess so keep that in mind. So, next aspect is obviously.

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When part b when I guess pH right is between pK1 and pK2 right so obviously in this case what will alpha 2 turn out to be. You all know alpha 2 was equal to K1 K2/H+ square +H +*K1+K1 K2 right. So, obviously in this particular scenario we know that alpha 2 is now going to be=K1 K2/ so which term is going to be predominant. So, obviously H+* K1 right H+*K1 so packing this in into that relevant question and so on.

So, we will end up with obviously CO3 total will be=Kso CaCO3 right/K star CaOh twice right and this is similar obviously to what we have out here right out here are the transformation here right. So, we are going to have the term and obviously it is now going to be equal to what else. So, H+square we used to have H+square * what do we have here we have K1 K2/ K1 K2 or thus is obviously going to be=K2/H+ right.

So, K1 cancel out and this is what we have so thus obviously it is now going to be=K2/H+ right so one H+ and H+ here cancel out. So, if I take the logarithm what is that going to be= log Co3 total= Log of Kso CaCo3/K star CaoH twice right / it is going to be /K2*H+ or /K1 k2/H + square here right. I guess I should have written that down in the different manner here so it would have been H+/K2 right *1/H+square right.

So, obviously because I am bringing up this term out here to the left hand side so that is going to be H+/K2 * 1/H+square. So, that is obviously going to be=1/K2 so this again is a constant right

and here we have logarithm of H^+ to the power of -1 right so logarithm of H1 what does that mean we know that pH=-log concentration of H^+ right and that is what we are left with here. So, it is going to be +pH right now it is going to be this is a constant.

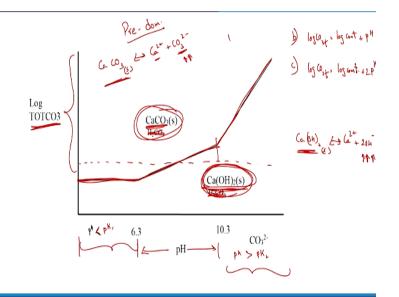
That we had earlier not the same one by K1 K2 I guess right. And now we also have +pH so in the region what this now pH is between 6.3 and 10.3 you know that the relevant boundary when CaCO3 and CaOh twice both state will increase linearly with pH right with increasing pH. Again once we draw the diagram it is going to be related to with. So, the next case is going to be pH>Pk2 what does that mean that means alpha 2 is going to be= we are looking at this.

So, obviously which particular term will predominate here K1 K2 will predominate in the denominator right and that means obviously alpha 2=K1 K2/ k1 K2 right that means alpha 2=1 right. So, obviously I am going to plug that in here and CO3 total is going to be=KsoCaCO3 right /K star CaOH twice right * what else you have here I have 1/H+square right and alpha 2 is 1.

So, 1/alpha 2 2 will be 1 right so now I take the logarithm of this particular equation what do I end up with. So, log CO3 total=log of this particular variable here right and what else you have log of 1/ H+square right and again we know that it is going to be=-2 log H+ if I take log of 1/H+square right and that is nothing but=+2PH right. So, it is going to be log CO3 total= log of this particular set of variable+2pH right.

So, the now the slope right is going to increase earlier when pH was<pK1 there was no effect of pH. When pH was<pK1 and pK2 increase with pH and here when pH>pK2 we see that it increases at the right of two times the pH.

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So, let us look at this in terms of the relevant graph right so here is the graph that we have seen initially you see that you know when pH is<6.3 right when pH<pK1 which is this region right and if you look at the relevant questions that we came up with we saw that it was a constant right for a particular log total C we saw that it was a constant and let us just try to go back to that graph or the equation.

So, this is what we had right the relevant relationship so logs CO3 total was a log of a particular constant right. So, for a particular CO3 the boundary was constant I guess right and that is what you see here and for the second case you saw that we had a particular additional term as in for logs CO3 total we had something like log of some constant +pH right and that was the case when pH was between 6.3 and 10.3.

So, that is why you see this particular increase right the slope right when the pH is between 6.3 and 10.3. This was for case B and for the case C if you remember we had something like log CO3 total=log pf some constant right+2 times pH. Right so obviously the slope is going to be greater and that is where you see that when pH is>pK2 which is 10.3 an in this region right what do you see that the slope is right or slope is greater.

So, what do I understand from this particular aspect now right so keep in mind that we are discussing the predominance area diagrams right and you are trying to draw the line predominates area diagram between CaCO3 and CaOH twice the solids. So, what does this mean now when let us say in this particular region that we see here we see that CaCO3 is going to predominate right.

And in this particular region I believe this particular line you are going to see that CaOH twice is going to predominant. Right so that is what we understand from this particular system. So, obviously what does this particular solid line indicate it means that at that particular solid line right we all went to the particular log CO3 or pH both the solids are going to precipitate make sense hopefully right.

So, in this region again let us try to understand this when the log total C is higher or Ca CO3 right the solid we know is in equilibrium with Ca2+ and CO3 2- right. So, when log total CO3 higher it means that in general CO3- concentration is higher right. So, obviously what does that mean this particular backward reaction would be feasible as in more of this CaCO3 would be formed leading to less Ca2+ as in CaCO3 would predominate.

So, that is why you see that at higher log total CO3 CaCo3 is predominant. Right but obviously again we know that CaOH twice is solid is going to be in equilibrium with Ca2+ and two times OH-. So, at higher pH right at higher pH you know OH- concentration is going to be higher and then this backward reaction is going to be relatively more favorable to the formation of CaOH twice.

So, that is why you see that as the PH keeps increasing right you see that CaOH twice right would precipice out rather than CaCO3 at the given conditions of the log total CO3 right. Make sense hopefully yes again so this will obviously try to help you understand the system so obviously a remarkably high PH right so for most of a values of log totals CO3 right. So, for example let us take this point low value of log totals CO3 right.

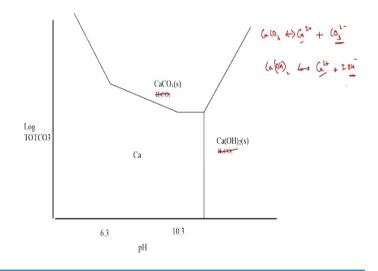
So, until it is pH of around 8.3 looks likes CO3 is going to predominate and from 8.3 and higher looks like COH twice is going to predominate right. So, that is what we understand from the system so now let us say but in this case right what is it that we have here we see that right we

consider that the solid is always form right but will not always be the case not really the right. Because sometimes you know how under such rigid solution this is what we talked about earlier.

I guess right we talked about saturation ratios and such so when the relevant concentrations of the metal or the cation and anion are not high enough what do you see though. Right you see that the solid was not precipitate out right so you will have those cases right well you might have no solid precipitating out. Here we are looking at in this graph this predominance area diagram we are obviously concerned that we either have CaCo3 or CaOH twice always.

So, what is the missing picture here we are missing the picture where we have the under saturated regions right. So, again we can set that up in the relevant equations and calculate that which we are not doing here.

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But I have the relevant graph here right so let us look at what we have here I guess right. So, here we have a new term variable here we also have Ca2+ so obviously what does this mean now in this region right it is under saturated right with respect to your precipitation let us see right. And Ca2+ is that what we say would predominate right. So, obviously as you keep increasing the PH right.

So, it lower PH lower log total CO3 you see that Ca2+ would predominate but and that is

obviously on the whole region right. So, when this region would correspond to relatively low PH right as you see here and relatively low log total CO3 right and that is what you would expect to right. But as you keep increasing the PH right what do you see now Ca2++2OH- you know are going to be in equilibrium with CaOH twice right.

And that is why you keep increasing the PH here for a particular log total CO3 you see that in this region CaOH twice is going to predominate right. But obviously let us say for a given PH if I keep increasing the log total CO3 what do I see that say in this region right I see that CaCO3 predominates yes so again keep in mind that at lower PH and at lower log total CO3 right as in we have two ways that Ca2+ can precipitate out right.

That is with CO32- right CaCO3 or CaOH twice right either with lower pH meaning OH- is less or at lower log total CO3 meaning CO32- is less obviously it is going to be which reaction is going to be favorable now. The dissolution solid will not be favorable right and that is why you would relatively high concentrations of Ca2+ in these regions right. And obviously as you see that the pH is increased right.

As you see the pH is increased right and you will have this particular equation predominating as in the backward reaction that is CaOH twice and with that same case out here right. Again I guess with that we are more or less about to be done with our particular case right. So, in general again keep in mind predominance area diagrams give you a snapshot right as and when we solve the example especially with respect H2CO3 HCO3- and CO32-.

You see that it gives you that particular area when that particular variable or compound is going to predominate. That does not mean there are not going to be any other compounds present so in general I always suggest you know when you want to go for detail calculations or use such you we may in take or obviously try to solve it by hand or use your intuition that you have or should have developed by now right.

So, I guess one particular aspect that well talk about before ending this particular session with respect to what is now precipitation in dissolution is going to be the Langley saturation index.

$$S \cdot I$$

$$= p^{H} - p^{H_{3}} \qquad (a^{2+}, A^{HK}, (a^{(0)})$$

$$= 0 \qquad \text{sat} \qquad (a^{(0)})$$

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So, we have a Langley saturation index right and I guess this is going to be equal to pH-pHs right and pHs is that particular pH would should be in equilibrium with Ca2+ for a given affinity right yes and for CaCO3.Right when equilibrium is reached for a particular affinity right and between CaCo3 and Ca2+ and that particular pH would be the pH at the saturation value I guess pHs right and saturation index is calculated as pH- pHs.

So, when this is positive means the situation is over saturated right and when it is=0 that is now where a guess right it is just a saturation and when it is negative it means it is under saturated. Right so again what is pHs that pH at which for a particular concentration of affinity Ca2+ and CaCO3 would be at equilibrium. Let us see right pHs so obviously when pH is>pHs what does that mean now it is over saturated and it will precipitate out further right.

And CaCO3 will precipitate out and obviously if it is under saturated that would not be the case and people look at this what is it now the saturation index of Langley saturation index. They have said to understand of the system can precipitate out our system can lead to precipitation of CaCO3 or not. And why do people look at this let us say because sometimes it is in your distribution networks right you are going to end up having corrosion let us say right.

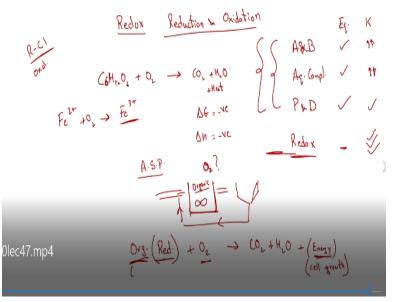
So, but let us us say if you maintain the pH or the relevant value you will have a protective layer

of CaCO3 formed. As and let us say this is what you say cross section of your distribution pipe let us say and let us say if you have a layer of CaCO3 scaling on your particular surface of your distribution system right. You know if you maintained the pH right well you are not too high there when you are going to have blockage.

Or decrease in the effective cross section area. But let us say when you maintain the pH at a sufficient value. Let us say which is over saturated you will have precipitation of CaCO3 on the what do you say surface of your particular pipe. And that will act as a protective film or a cup anyway that is one particular case when people try to maintain this particular pH right. So, I guess with that we are I am done with precipitation with dissolution.

So, now we are going to move onto the redox process right which are ever present yes. So, for now we will have a brief discussion for I guess a couple of minutes regarding what this redox process are and why they are relevant to us and then we will go on to move into more details in the next particular session right. So, now we are going to move on to redox process right.

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Redox reduction and oxidation reduction and oxidation right so let us just again try to summarize what we have been up to until now right. So, initially we did look at the basics for any chemical process that would be equilibrium as in how far the system can go to underspecified set of conditions right and kinetics as in how fast will the system go ahead right and in that particular aspect we looked at until now three measure aspects right.

And what were they we looked at acids and bases. And then we looked at aqueous complexes right and also we looked at precipitation and dissolution and in all these aspects we then looked at mostly applications of equilibrium or kinetics we know that in acids and bases kinetics are very high so that is why we end up only discussing obviously equilibrium. Same case in aqueous complexes kinetics is very high.

So, that is why again we mostly looked at only the relevant aspects with respect to what the system would be after the equilibrium has reached right. Again if the kinetics are so high right by usual what if we say timeframes you look at you would obviously reach equilibrium that is why we obviously only looked at equilibrium right. But with precipitation dissolution we know that precipitation reactions can be relatively slow.

Especially from amorphous to crystalline to more insoluble form. So, we also discussed kinetics and obviously equilibrium in that particular case. So, with this we were done I guess right but as you remember in one of the classes we did mention that all these cases there is no change in the oxidation state or oxidation number right of the relevant element here right but here now we are going to have redox reactions right.

Redox reactions right when there is going to be a change in your particular oxidation state of this particular compound of the element. Again we are going to discuss this in the later classes but keep in mind that all these three aspects that we have covered thus far right. Are co coordinative relationships right which is not the case with redox forces but one aspect with redox process.

I guess that I think we need to cover are not sure if I use this particular example I think I did in one of the initial classes was that right. If I have, I think I did right you know if I open up I know that let us say you know say C6 H12O6+ I think the oxidation right and that can go to the relevant products I think Co2 H2O and lot of energy. I think delta G was negative right but this does not give me an idea about the energy release and + heat right.

Delta H will give me an idea about that I think that H2 is negative and it was considerably high right so I think C6H12+O6 glucose or let us say if I open up a packed of glucose and throw it out here. Now let us say you know up a toffee bar or coffee bar and throw it out you know it is not going to lead to explosion or nobody is going to run away from here right and I think obviously the aspiration was that.

Even though considerable amounts of energy are going to be released it is the time that is required right. Time it takes for that energy to be released that is the key unlike an explosive that people use let us say right thus particular what do you say C6H12O6 does release considerable energy but over a considerable period of time. So, here what I am trying to stress upon is that unlike the relevant aspects.

We discussed as far as an aqueous complex as all acids and bases you know kinetics play a remarkable role in the redox reactions. So, rarely do you have more systems reaching equilibrium. But almost all of them are going to be dependent upon highly dependent upon your kinetics. So, whenever someone talks about redox reactions it is kinetics play a remarkably important role right.

And rarely do they reach equilibrium I mean some of the reactions can reach equilibrium right. But keep in mind again that we can understand equilibrium to see you know if it reaches equilibrium what would be relevant what you say the changes. But the key is that will we ever reach equilibrium given the certain conditions are such. So, we always need to look at kinetics with respect to the redox process.

Any redox process I guess right again that is one particular aspect that I guess I need to highlight so over the class or the over the next remaining sessions were going to talk a lot about kinetics. And then we are going to talk I guess about you know what would happen let us say if the system reaches equilibrium or what would the system look like I guess right. But again keep in mind redox process again every kinetics that plays an important role right.

So, in this aspect again why do we need to look at redox process why not the general

applications I guess right I guess I are you are a living example I am taking in oxygen again why is that for now you know you are eating food right and again what is that more or less now it is oxidation reaction right of the sucrose that you are going to digest or such right. It is again an oxidation reaction and you are going to release energy from that oxygen reaction.

Which I am going to use for either my cell synthesis or growth or you know my body functions right. Again I am breathing in oxygen taking oxygen or source of oxygen and it is going to help in oxidation of the relevant sucrose or glucose right and that is going to lead to release of energy right again that is a redox process oxidation of the glucose or sucrose or the relevant compounds right at a macroscopic level I guess.

I am sure there are relevant what you say reactions right between what you say you eating food and you ending up getting energy. But let us say that is one particular way to understand what happens in the system. So again let us see where else we come across these redox process you know that activated search process let us say sequential batch reactive are blah blah again that you use for your treatment of your organic compounds or your waste right.

So, again what are the key factors that you are usually putting in here let us say so let us say this is my ASP right and this is my second resettling tank here let us see right this is the recycling here and this obviously the inlet here right. So, here in this activated search process this particular tank here right which is always well mixed right and what else do you have are you supplying now you are always supplying a source of oxygen right.

So, why is that now right and you also have organic compound here which is the waste that you are trying to degrade right. So, organic compounds are usually to reduce forms or in the reduced forms right and why are we supplying oxygen because you want to oxidize this particular organic compound right. And obviously this is the relevant to reaction here right so this is they are going to compound which is really to be in the reduced form right.

And you are going to supply oxygen and the microbes right there are going to act as a catalyst the enzymes released by the microbes they are going to act as a catalyst to make this particular redox reaction go through faster. So, if there were no microbes. Let us say right it is going to take a remarkable amount of time the kinetics is going to be very slow right. But obviously the role of the microbes right they are going to assist in this particular process.

Was that the energy that is released the microbes are going to use for either the cell synthesis of cell growth repair and so on right. So, same case as us they to want to derive the energy that is going to come through based down this particular degradation or oxidation of your waste or your organic compound. Again why are we using microbes because we want to fasten this process which would otherwise take considerable.

Considerable you know practically impossible or infeasible amounts of time right. So, the microbes your play the role of catalyst right there fast in this particular process and why do they want to do so because they want to use this particular energy for themselves right and again keep in mind that the applications of redox reactions obviously here I give a generic example of where you would come across redox reactions right.

But maybe people do not play as important a role as you should but you know obviously again redox reactions are ever present right you know in the atmosphere any particular what do we say transformations that not any most of them are redox processing or let us say you take a bite of an apple and leave it out exposed to the atmosphere now. And what you see you see the what do you see exposed layer of the apple turning brown.

What is happening there you see that Fe2+ right is going to be oxidized. Anyway this is not a balanced reaction to obviously to Fe3+ right so whenever you bite an apple leave it out right and what you see the that it so I believe it is going to be oxidized to Fe3+ and that is what you see that the brownish color change right. So, again there are multiple applications are you know redox reactions are ever present everywhere right.

Let us say if I am trying to degrade a compound let us say a chlorinated organic let us say RCI usually that is toxic and carcinogenic. Now I degrade that so what do I need this is a oxidized compound right right so I need to add a reducing agent again we are going to see what these

reducing agents are and so on. So, that I can oxidize this already use this particular contain right. With that I am going to end todays session.

And were going to go through redox person with great detail over the next sessions and I guess with that I am going to end todays session and thank you.