Environment Engineering: Chemical Processes

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Module No # 10
Lecture No # 50
Kinetics of Redox Processes

Hello everyone so again welcome back to our latest lecture session so we have been discussing the relevant redox reaction with relevant applications and the relevant terminology in last couple of sessions. So today we are going to discuss the relevant aspect with respect to kinetics and then move on to equilibrium right. So before we further again let us just refer what it is have been up to in last couple of sessions.

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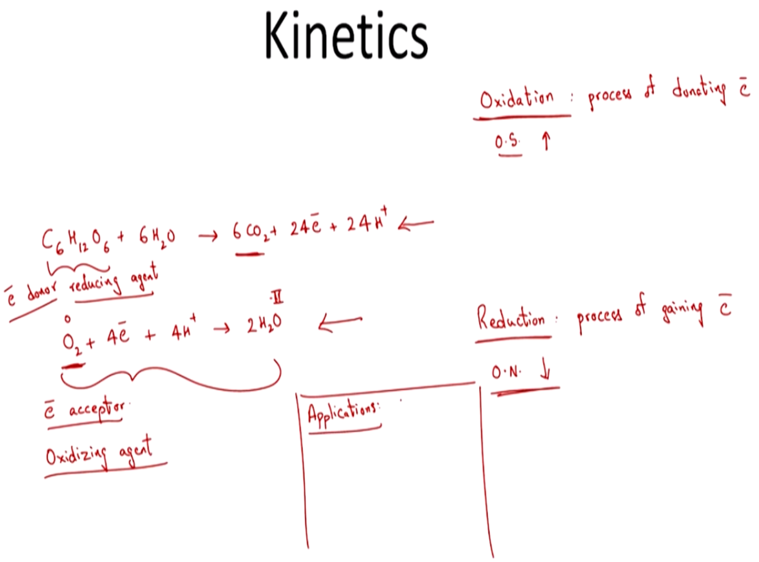

Kinetics

Oxidation : process of donating $\bar{e}$

O.S. ↑

$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24\bar{e} + 24H^+$

$\bar{e}$ donor reducing agent

$\overset{0}{O_2} + 4\bar{e} + 4H^+ \rightarrow 2H_2\overset{-II}{O}$

$\bar{e}$ acceptor

Oxidizing agent

Applications:

Reduction : process of gaining $\bar{e}$

O.N. ↓

So I guess we looked at understanding what is oxidation right and we know that it is process of donating electrons and yes reductions process of gaining or accepting electrons right. So oxidation again process of donating the electrons and reduction process of accepting the electrons.

So obviously by accepting the electrons what would you expect with respect to the change in oxidation state or oxidation number of the relevant atom here right so you are gaining the electron right so the oxidation state is going to be obviously are oxidation number is going to be reduced or it is going to be decreased so obviously if you donating the electrons what is going to be happen here the oxidation state right or the relevant atom is going to increase here right.

So again in reduction process of accepting the relevant electron or gaining the electron right so because you are particular atom let us say is gaining the electrons so you can obviously you know try to understand that that oxidation number is going to reduced or decreased and with respect to oxidation obviously because we are donating the electrons or loss of electron right so you are going to observe or increase in the oxidation state of your particular atom here right.

So I guess here we have two examples one would be obviously here this is the process of donating the electrons so this would be relevant example for oxidation and this particular half reaction is where we have process of accepting the relevant electrons right so that would be a particular example for reduction right. So again here I have we have glucose being what is it now oxidized by oxygen right.

So obviously let us look at the try to understand the relevant system here so here obviously oxygen is an electron acceptor right and that is what you see from this particular half reaction it is an electron acceptor or an oxidizing agent and this is something you need to keep in mind because you know oxygen right obviously prevalent everywhere right most natural systems right.

And obviously is role is that it is an electron acceptor right so either it places a role in most of the reactions itself or sometime you want to inhabit it is role as on electron acceptor but we look at those aspect later on I guess. And here obviously you know we see that glucose we really to release of what do we say electrons so here we say it is being the role of reducing agent right one which can donate electrons again electrons acceptor and electron donor right.

So obviously in these process of donating the electron what is going to the particular carbon oxidation state in glucose so you see that it is going to be increase in here so or it is going to be oxidized so reducing agent in the process of donating the electrons is going to be oxidized.

So now let us look at oxygen here I guess right oxygen is accepting the electron it is oxidizing agent so it is going to oxidize the other compound right but it is going to be reduce itself so that is what you see the oxidizing is the accepting the electrons right and being transformed into let us say H2O here and we obviously if we calculate the oxidation state we are going to look at decrease in the oxidation state here right.

So obviously if we look at in the oxidation state of oxygen here is 0 right and here it is going to be equal to -2 right. And obviously you see that it is decrease in the oxidation state here right so 2 electrons per each per oxygen atoms I guess. So here this is obviously something that you need to be comfortable with am sure that you will get that particular what will say familiar to say with respect to terms as you so along right.

So let us say look what else we have get I guess right so we also looked at applications right and I believe we looked at applications and we looked at various cases I guess one with respect to waste water treatment with respect to ferrous removal or arsenic removal or such right I am not obviously going to those aspects but keep in mind that obviously that the take home message is that the redox reactions are prevent everywhere in all the system that is more or less you know set site upon right.

And certainly as environment engineer redox reactions are probably the most relevant reaction that you would usually come across right. So again that respect to applications and then I believe we moved on to looking at too balance different redox half reactions right.

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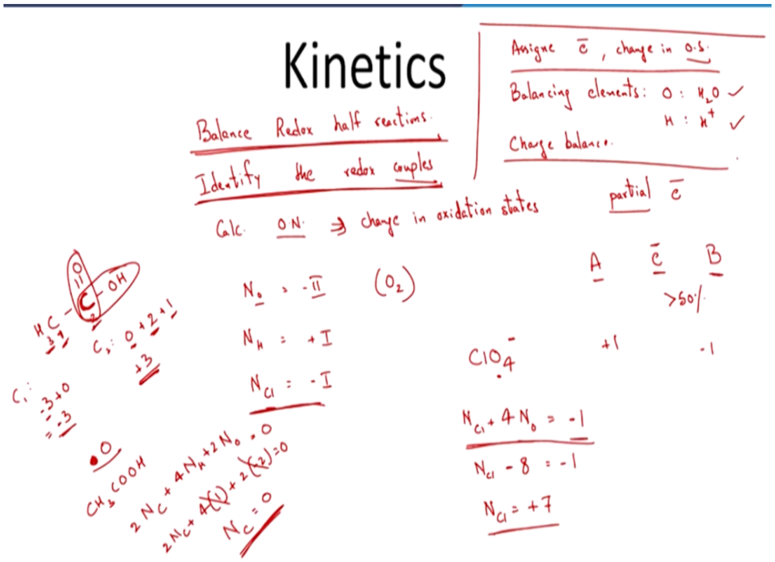

Kinetics

Balance Redox half reactions.

Identify the redox couples

Calc. O.N. ⇒ change in oxidation states

Assigne $\bar{e}$, change in O.S.

Balancing elements: O : H_2O ✓

H : H^+ ✓

Charge balance.

partial $\bar{e}$

A $\bar{e}$ B

>50%

+1 -1

$N_O = -II$ (O_2)

$N_H = +I$

$N_{Cl} = -I$

ClO_4^-

$N_{Cl} + 4N_O = -1$

$N_{Cl} - 8 = -1$

$N_{Cl} = +7$

CH_3COOH

$2N_C + 4N_H + 2N_O = 0$

$2N_C + 4(1) + 2(-2) = 0$

$N_C = 0$

So let us look all that so let us say second for summarize that right so here I guess what do we do we need to identify or we are going to talk about briefly balancing redox or half reaction redox half reactions right so the first aspect would be obviously right you need to identify the couples identify the redox couples and I believe in our example in the last session we looked I believe in oxidation state of oxidation state of pardon me oxidation of chromium 6 no I believe the reduction of chromium 6 to chromium 3 / sulphur dioxide right.

So that was the example we looked at earlier but here we are going summarize we have been approved so obviously we are going to identify the redox couples then we need to calculate the oxidation number right we need to look at change in oxidation states right yes so again how do we calculate these particular oxidation number now I believe we looked at set of rooms but in general more or less the major aspect need to keep in mind that this is a theoretical value right.

So this is that hypothetical charge that it would exist to the a particular atom right if the electron that being shared between two atoms is a science solely to the more electro negative of the atoms right. So obviously let us say if there is a partial transfer not to compete or full transfer of the relevant electron let us say right and this electron is being shared by atom A and atom B but let us say it is atom B is more electronegative than atom A it would have let us say greater share as in greater than 50% let us say of the electrons that is sharing with A right.

So what is it how do I calculate the oxidation state so with respect to this electron let us say I am going to assign this electrons completely to be right the oxidation state would be let be -1 and here it would be +1 for A so that is how we go about that so obviously in that context we looked at I guess a few of the known or you know in general oxidation states of the different atoms that we come across.

So usually oxidation state of oxygen = -2 right other than obviously it if it is in the form of O2 right why is that because above the atoms in O2 and oxygen have the same electro negativity right. So obviously you know the electron paid is going to be shared equally between the two oxygen atoms so thus obviously the oxygen state of O in O2 will obviously be 0 here right.

So in this case obviously here usually of hydrogen it is going to equal to +1 right and usually for chloride let us say or chlorine pardon me it is going to be equal to -1 or chloride right of chloride pardon me. But keep in mind that in general oxygen is more negative compared electro negative compared to chloride so if there is CLO4- let us say (()) (09:10) you know.

So the electron would be let us say what do we say oxygen being more electro negative you need to take into account that the oxidation state of this particular atoms or these oxygen atoms CLO4- would be -2 and then calculate the oxidation state or number of chloride atoms accordingly. So let us do that let us say oxidation state of CL + 4 times oxidation state of oxygen will be equal to -1 right and CL -8 4 times -2 is 8 -8 -7 so oxidation state of chloride here = +7 so that is what you see here but in general with most other what do we say compounds relatively most other compounds CL is electro negative right.

So again in general this is a particular way right more or less sum the oxidation state and you know equal that to the charge on that particular anion or the cation and obviously if it is neutrally charge molecule it is going to be 0 here right it charge balance more or less. And but obviously you keep in mind that here we are calculating the average oxidation state but for example is but let us say your particular organic compound you know sometimes let us say the average oxidation state of particular state of atoms can be confused right.

We will just look at one example here so let us say acetic acid CH3COOH right CH3COOH right so here let us say let us try to calculate the oxidation states of these 2 particular carbon atoms here right. So again keep in mind that how do we go about assigning the relevant oxidation state or numbers. So if a relevant what do we say electrons is shared between two atoms look at which of the two atoms is two electro negative and assign that two particular electrons to that particular atom right and then calculate that particular charge accordingly.

So obviously carbon here it is has three bonds right it is H right and one with carbon and carbon both or same electro negativity thus particular what do we say assigning their so how do I calculate the oxidation state of carbon is going to obviously be -3 + 0.

So that is going to be equal to -3 how is that why do we have -3 here because we are assuming that there are electrons that is shares with electrons is what do we say going to be carbon as a great share of the electrons that is shares with hydrogen that is why we assign -3 here for the three hydrogen atoms we see here and 0 because for the one electrons that shares with one electrons here the one and two let us say carbon 2 both as the same electro negativity so you know both share the electron equally.

So again -3 here so with respect to carbon 2 here let us say with respect to carbon 1 and with respect to carbon 2 let us say what do we see here now again carbon shares that is 0 there with respect to oxygen is more electro negative so I am going to say -2 there right and OH already have 1 here so it will have -1 here right so + + oxygen is -2 and oxygen is -1 here share here so that is going to be equal to +3.

Again carbon and carbon let us look at what we did carbon 2 and carbon 1 right both as a electro negativity so thus let us say no particular influence from no particular electrons shared on the oxidation number but with respect to oxygen share let us say the two electron pair let us say that right the two electrons being shared by carbon with oxygen right oxygen being more electro negative carbon we are going to assign those electrons to oxygen.

So thus +2 charge right for this particular case and obviously +1 from this particular case here right so with thus we end up with + 3 but you see that the average oxidation state is going to be equal to 0 right of carbon being average oxygen state of carbon and your particular acetic acid is 0 and obviously how can you obviously calculate that it is CH3 COOH right oxygen state two times oxygen state of carbon right +4 times oxygen state of hydrogen +2 times of oxygen state of oxygen or number pardon me is 0.

So 2 and C + 4 times 1 + 2 times -1 = 0 so obviously again these two cancel out you see that oxidation state of average oxidation number of carbon in acetic acid is 0 but as you see the carbon each the two carbon atoms here right in this acetic acid has different oxidation states or oxidation number right. So anyway that is one particular aspect the you need to be aware of but you know in general I guess if we look at the average oxygen states or oxygen number pardon me you should be able to give the relevant information.

Again so let us move on or we diagnose first we try to balance the redox of reactions in that case we identify the redox couples as in that particular case chromium six reduction to chromium 3 + so CR6 + CR 3 right I think CRO2 – and CR3+ and SO2 and SO42- these are the two redox couples and then I calculate the oxidation state of carbon chromium right in the redox couple and also of sulphur right in the two another redox couple their and then what do I do I guess I am going to continue here.

So and then I am going to assign the electrons based on the change in oxidation states or number right. So I am going to assign the electrons accordingly so once I assign the electrons than I need to move on to balancing the relevant elements right and how do I do that in general O I balance it with H2O and H with H+ and obviously with other elements chromium and sulphur we need to look at that particular balance anyway right.

So I need to obviously balance the elements and then move on to oxygen and hydrogen right and I am going to balance oxygen by you know looking at substituting or you know having H2O and hydrogen by having H+ right and then obviously I am going to do a charge balance right. So more or less again we are going to have the calculate change in oxidation state to calculate the what do we say the number of electrons being transferred you assign the electrons then balance the elements and then check for the charge.

And then you get the overall reaction by you know summing it up accordingly I guess so that your number of electrons right that had being gained and I being accepted or lost let us say or accepted right are going to be the same right because you cannot have a electron pool in solutions.

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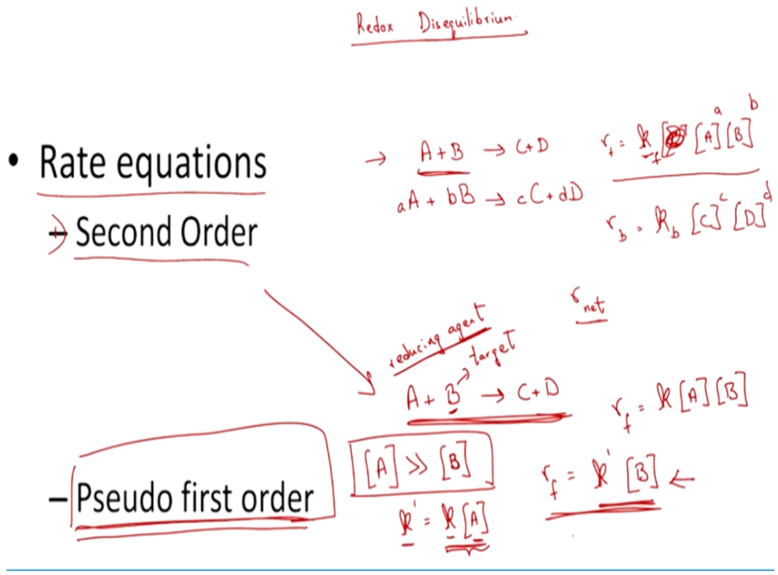

- Rate equations
  - Second Order
  - Pseudo first order

So again let us move on to the relevant aspect with respect to kinetics I guess so obviously in redox reactions right disequilibrium in what is prevalent so as we discussed earlier right many redox reaction are feasible but because the kinetics is or relatively slow for most of the relevant reaction right kinetics play a very important role right so in general though as you know what you would see out there is that even though many reactions are feasible because they are way to slow they did not go through.

So in general the norm is that disequilibrium is what is the norm I guess disequilibrium is redox disequilibrium is what you would observe out their right and why is that because the kinetic is too slow the kinetics are too slow right. So again once aspect is that we need obviously consider the rate of the relevant reactions right whenever we look at the kinetics of a particular system.

So here I guess we are going to look at a particular what do we say example here I guess not an example I guess a particular set of equation and then look at relevant model for particular set of examples. So rate equation just to refresh your memories right so let us say A + B goes to C + D let us say right and what is the rate of these particular reaction or the forward reaction.

Let us say if I am call that it is going to be equal to rate constant of the relevant reaction right times the concentration of the reactants right raise to the stoichiometric here I am stoichiometric coefficient or 1 thus that I let me write them down to be regular I guess if it is A times A and B times stoichiometric coefficient of ABC and D right and then rate of reaction is going to be equal to rate constant times A raise to stoichiometric coefficient and B raise to its stoichiometric coefficient.

So obviously again the take home message is that the rate of relevant reaction depends only on the reactants not the product right. So obviously again if you are looking the backward reaction right you will have for the backward let u say K backward K forward C to the power C but obviously when you are calculating or net let us say for each of these particular compound A, B, C and D then you need to take into account the relevant aspects right.

Again this is something we need to discuss in great detail with respect to kinetic section earlier when we discuss the fundamentals quite few sessions ago right but you know we just keep in mind again the rates depend upon the reactants not the product right. So again let us look at what you usually observe here let us say second order right.

So I guess that is the example that we just looked at second order reaction we know how to write the relevant rates of that particular what do we say the particular obviously as you see the initially let us say when you have high concentration of these reactants they rates are going to be high and as the reaction goes through the concentrating let us say A and B decrease because C and D are formed right we are assuming that the case is that the only the forward reaction is going through right.

Their obviously you see that the rate of the forward reaction is going to decrease right and obviously why is that because the concentration of A and B also decreasing right and obviously another case that we need to look at or we have looked at in the past I guess is Pseudo first order I guess you know it is self-explanatory it suits Pseudo first order let us say let us look at an example let us say let us first consider an example of second order reaction let us say A + B goes to C + D right.

So we are going go start with an example of an second order reaction right so as we know what is the rate of this particular reaction let us say or of the forward reaction let us say is going to be rate constant let us say times concentration of A and concentration of B right the reactants here so here in this case of Pseudo first order let us say and we are considering this first order example what would the system B or behave like let us say one of the concentration of one of the reactions is far greater let us say than the concentration of the other reactant here right.

So what is going to going to be the case here than let us say I can modify my what do we say reaction let us say or the rate of the reaction and as K start times concentration of B okay so obviously here what is the K dash here are going to be equal to the original rate constant times concentration of A right and I guess if you look at this particular modified rate equation here we see that it is a first order reaction but we know that it is actually a second order reaction right or the origin is second order reaction.

But it behaves like a Pseudo first order reaction why is that because concentration of A is far greater than concentration of B so over the course of this particular reaction A + B transforming to C + D right the concentration of A being far greater than D pardon me concentration of A is being far greater than B leads to a system behaving like pseudo first order right as in the change in A is so small compared to the change in B.

So that you can consider the concentration A to the constant consider of having just rate constant here we are going to have a modified rate constant which is sum of not sum of pardon me part of these two variables here and here the application are Pseudo first order reactions are many and mostly in national systems and also in engineering systems when you have let us say concentration of 1 of your what shall I say the redox reducing agent let us say to be very high and let us say B is your target let us say.

You usually consider cases let us say when you had a lot of reducing agent to reduce your target and application in such scenarios and such.

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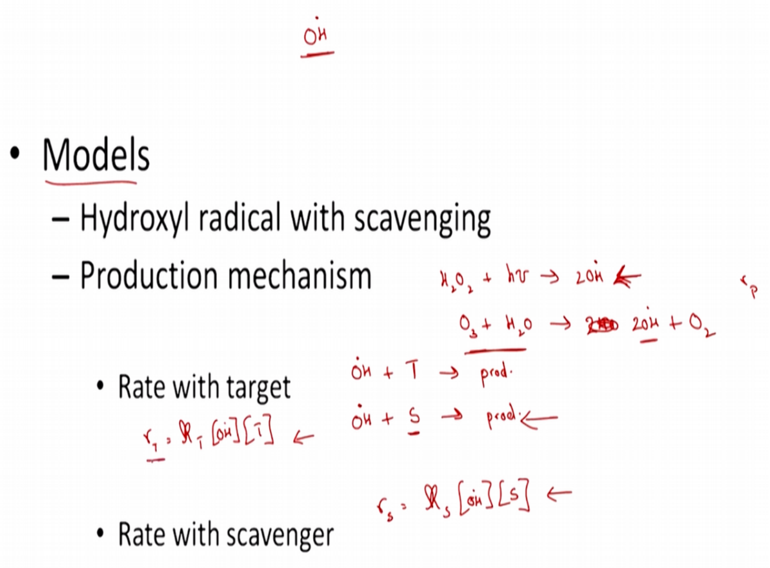

$\dot{O}H$

- Models
  - Hydroxyl radical with scavenging
  - Production mechanism

$H_2O_2 + h\nu \rightarrow 2\dot{O}H \leftarrow$

r_p

$O_3 + H_2O \rightarrow 2\dot{O}H + O_2$

- Rate with target

$\dot{O}H + T \rightarrow prod.$

$r_T = k_T[\dot{O}H][T] \leftarrow$

$\dot{O}H + S \rightarrow prod. \leftarrow$

$r_S = k_S[\dot{O}H][S] \leftarrow$

- Rate with scavenger

And so on now moving on to the next aspect let us look at couple of models obviously you never need to mug (()) (22:51) you just need to understand how to be able to manipulate the relevant aspects if and when required right. So obviously applications with respect to redox reactions or even the acid base reactions right are not limited to just the aqueous phase even the gaseous phase or in the atmosphere right.

So again different models are there so we are going to look at one particular model where we are going to have production of hydroceles radical right hydrosol radicle has we know has unpaired electron so it has a strong tendency to accept an electrons so the electron acceptor so it turns to be a very strong oxidizing agent or strong oxide right. So we can what do we say form hydroxyl radicle in different ways right I am just going to look at two mechanisms here.

So obviously hydroxyl radicle when it is formed when it atmosphere or you lead to its or you create the conditions to promote formation of hydroxyl radicle in the aqueous phase right what you see now let us say you are you see that hydroxyl radicle with would reach with what it is you want or which is your target.

So hydroxyl radicle will react with your target but being a strong oxidizing agent right it does not preference let us say for only one particular compound or such it is relatively non selective right. So it will also react with the other particular compound present in the solution obviously depending upon the type of compounds obviously right and the relevant rate constant rates I guess.

So obviously what you see is multiple parallel reaction whenever you have these radicles what do we say in your solutions so what do we need to look at? We need to look at relevant reaction with respect to what is the ratio of my particular radicle reacting with the target compared to let us say it is particular what do we say reaction with the scavengers is something let us say I would call an you know leading to let us say loss of hydroxyl radicle let us say right or all these unwanted reactions I would call them as scavenging reactions right.

So anyway let us look at one particular example here so I guess production mechanism I think we can have hydrogen peroxide in the presence of ultra violet light can lead to formation of redox radicle right and also ozone let us say it depending on the PH that you maintain usually at higher PH can lead to formation of the hydroxyl radicle right can lead to formation of hydroxyl radicle right or we just looked at two mechanisms for understanding.

So this can this is how people get it done in what do we say within the presence of UV light usually 254 nano meter wavelength right or UV photons let us say and obviously if you have ozone present in your solution present in your bubbling ozone through your solution and you have what do we or say if you adjust the PH you know in general you have hydroxyl radicle being formed at relatively higher concentration I guess.

So let us move on so here we have two aspects as in we just discuss that the hydroxyl radicle can react with my target or targets that can be multiple targets to right and form various products right various products or the hydroxyl radicle being non selective and you know that can also react with scavengers right and form various products right you know hydroxyl radicle you know here with everything right not everything let us say right but it is again the key is that relatively non selective it is going to have the relevant parallel reaction.

So some of them would be with your target which would be your reactions that you want to occur or promote some of them would be with you scavengers right which you would want to suppress right again you know and here rate with the target right rate of reaction with respect to ahh reaction of the target what is that going to be equal to rate of constant right times OH radicle concentration times the target concentration.

So keep in mind that when we write the rates here you know finding out the rate would be relatively difficult in this particular equation as we have written down why is that the hydroxyl radicle are have remarkably low half-lives so you cannot you know measure or cannot let us say it is remarkably difficult right to be able to measure the hydroxyl concentration right.

So that is one particular aspect that we need to keep in mind and rate with the scavengers so rate this scavengers be rate constant for this particular reaction right OH radicle concentration into concentration of the scavengers so obviously I am just using the generic terms scavenger to what do we approximate multiple compound that can lead to scavenging of my hydroxyl radicle right.

So here I have that so I want to be able to what do we say play around with my particular equations so that I can get the relevant information that I am looking for which let us say is how to be able to approximate or model the rate of target in terms of rate of the production as in let us say I can from these particular reactions calculate the rate of production of my hydroxyl radicle that i want to be able to get an understanding about how the target let us say or the rate at which the target is going to be removed by the hydroxyl radicle right.

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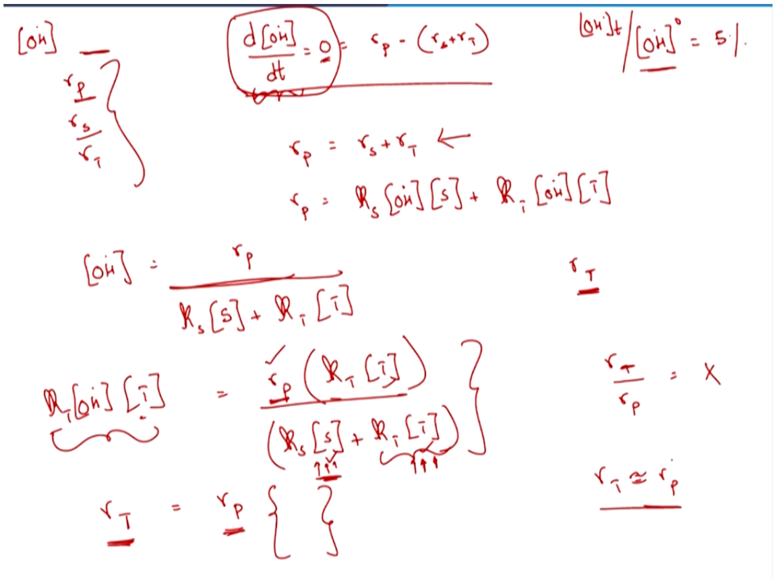

So let us look at that for a second here so here keep in mind that we mention OH radicle as very low half-life right yes in general and also let us say keep in mind that concentration of these what do we say hydroxyl radicle solutions are going to be relatively low at now point in time would have remarkably high concentration and obviously one the reason is that half-life if this particular radicle are very low.

So we can assume that you know with time right the concentration of hydroxyl radicle will dos not change right compare to obviously the rates of production and rates of production of radicle and rates of scavenging the radicle and rates of the reaction of the target. So what we are assuming here is that because OH radicle concentration are very low right and we compare to the rates of production are rates of reaction with respect to scavenger or target I can assume that I guess it is good enough assumption that the hydroxyl radicle concentration does not change with time right.

So that is going to be equal to obviously what now the rate of production of radicle – how is the radicle being lost either due to scavenging reaction or due to the target reaction right. So this is what we have and this is the assumption that we are making though. So keep in mind that let us say OH radicle concentration initially right and OH radicle concentration let us say time T can be (()) (29:52) can be 5% or so though right.

But with respect to time say with respect to time let us say and with respect to relevant rate this particular variable is very low or negligible or assume it to this 0 here. So here we have rate of particular assuming rate of production of radicle = rate of scavenging of the radicle rate of the reaction of the OH radicle with respect the target right. So in that particular case and then here obviously let us try to transform this particular equation rate of production = rate of scavenger is KS OH radicle times the scavenger + K target right OH radicle times the target right.

Again what are we expressing here the rate of production of hydroxyl would be equal to rate of loss of the hydroxyl radicle and which reactions are obviously leading to the loss of your particular hydroxyl radicle either reacting with scavenger or hydroxyl radicle reacting with your targets. So the relevant losses of these hydroxyl radicles right I can get them from the relevant rates form relevant reactions.

Because the stoichiometric we are assuming is 1 right that is what we have here as in one times RS and one times RT right. Again so I have these particular case so OH radicle let us say is going to be equal to rate of production which I can measure depending upon the number of photons and putting in or the amount of ozone and putting in the solution I can measure the rate of production by KS times scavenger + KT times the target concentration.

So again target concentration and scavenger concentration are something of the what I am presuming here that I can measure that in general or obviously what you would see right and you can measure the concentration of the scavengers and targets with time. But obviously here I still want to be able to come up with the way to approximate the rate of the reaction of the hydroxyl radicle with the target right.

So here let us say if we multiple that by OH radicle times KT times concentration of target right KT times target that is equal to rate of production times rate constant and target right. So I multiple with this particular variable on both the sides so obviously what do I see here you see this is nothing but the rate of reaction of hydroxyl that radicle with the target that is going to be equal to RP by this set of variables right.

So here obviously if you look at this particular variable I can measure target concentration I can measure the scavenger concentration right. So I can get the relevant information in this particular variable and I know the number of or amount of photons or ozone concentration that I am putting into the system.

So I can calculate rates of production right so once I have this particular information obviously I can express rate of this particular loss of the target or reaction of hydroxyl radicle with the target in terms of rates of production of the hydroxyl radicle. So again what is this help me with so once I know the rate of production of hydroxyl radicle I can also estimate the rate at which the target is going to be destroyed or degrade it or how it is going to be at the rate at which it is going to be oxidized.

Again why are we having to get the more because hydroxyl radicle concentration relatively difficult to measure out their but the way we have set it up now we can now express the rate of loss of your particular hydroxyl radicle or oxidation of particular target in terms of variable that we can measure or such.

And obviously if we look at this particular set of variable here right the KT times T by KSS times KT T what is that given an idea about if we look at it gives you an idea about rate of let us say target with respect to rate of your production of particular radicle right that is what we see here right.

This particular I call that X right X is nothing but the rate of loss of hydroxyl radicle while degrading the target right or rate of degration of target if you can transform with respect to the coefficient by the rate of production your particular what do we say hydroxyl radicle right.

So this will give an d idea about how efficient is your process obviously the higher the valuable of X this variable the more efficient the process but let us say if you are scavenger concentration is very high right what happens in that case with the scavenger concentration is very high right what you see obviously value of X would decrease right.

So that is what you would see here but if the value of this target here is high of the concentration of target is KT times T is high what would you see them right. You would see that rate of target would be equal to rate of production right let us just write that down here.

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$$r_T = r_P \frac{k_T[T]}{\underbrace{k_S[S]} + \underbrace{k_T[T]}}$$

$$k_T \uparrow$$

$$[T] \uparrow$$

So I have rate of reaction or rate of loss of hydroxyl radicle during it is oxidation of target would be equal to the production of radicle times KT concentration of target by KS S + KT T right. So let us try to understand this system I guess right in which should be inefficient either when you are scavenger concentration is very high or your rate constant is high or in this variable is high and this obviously can be high when either the rate constant is high or scavenger concentration is high.

Again what is that mean relatively high compared to KT times T what is that mean so if your hydroxyl radicle potentially react with what do we say the scalp scavengers relatively or the reaction of the hydroxyl radicle with the scavenger is relatively faster compared to the reaction of this particular hydroxyl radicle with the target obviously it is going to be the efficient or even if this scavengers concentration is going to be relatively high right that is what you see here your system is going to be relatively coefficient right.

But obviously if you see that inverse of it as in when will this variable be high and KT is high or the target concentration is high yes that is what you see here but an when will that occur obviously either the target concentration is high too to the concentration of scavenger or let us say when the redox radicle reaction rate is faster with respect to kinetics of hydroxyl radicle with reacting with target is faster compared to kinetics of hydroxyl radicle reacting with the scavenger right.

In that case let us say if this variable is high right what would turn out to be RT would be efficient but obviously as you see though as the hydroxyl radicle keeps reacting with the target what happens to the concentration of the target it keeps reacting right so obviously the rate it which these target is going to be oxidized is going to keep decreasing with time and that is what you would observe later on to right again that is for our particular understanding here right.

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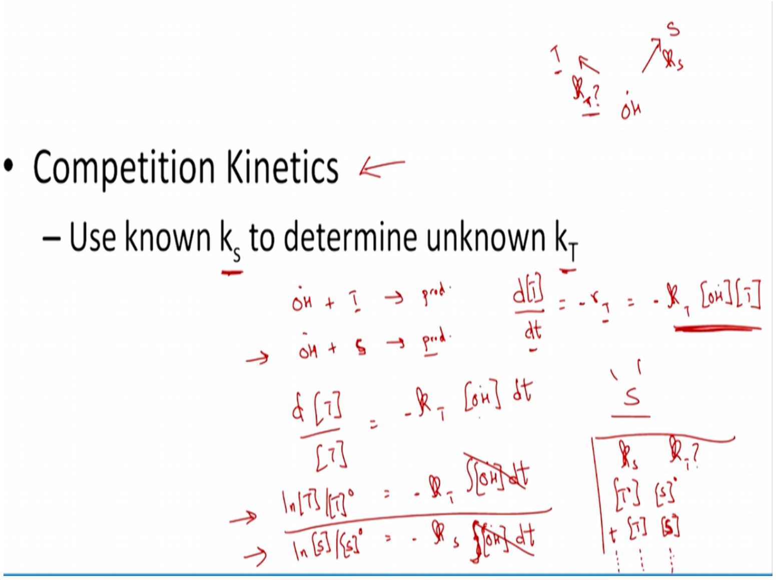

- Competition Kinetics
  - Use known k_s to determine unknown k_T

$\dot{O}H + T \rightarrow$ prod.

$\dot{O}H + S \rightarrow$ prod.

$\frac{d[T]}{dt} = -r_T = -k_T [\dot{O}H][T]$

$\frac{d[T]}{[T]} = -k_T [\dot{O}H]\, dt$

$\ln [T]/[T]^0 = -k_T \cancel{\int [\dot{O}H]\, dt}$

$\ln [S]/[S]^0 = -k_s \cancel{\int [\dot{O}H]\, dt}$

So let us move on to one let us move on to one particular aspect or another aspect I guess competition kinetics so obviously here I just looked at our particular earlier model we have multiple target we have multiple scavengers as in we have OH radicle it can either react with the target or the scavenger right so it is competition kinetics more or less right different parallel reaction it is occurring here right.

So obviously here let us say usually let us say know the rate constants with this particular reaction let us say of how we have the hydroxyl radicle it would what do we say or the kinetics of the hydroxyl radicle reacting the scavengers but for my particular target we do not know the rate constant let us say see right.

So how do I calculate that so let us just look at that briefly so I have hydroxyl radicle + target going to products right and hydroxyl radicle + scavenger go into products right and if I can write DT with respect to the time and how is the concentration of what do we say target changing with time right. Here we see that it is not being produced it is only being lost so it is going to be equal to – rate of this particular target reaction right and that is nothing but equal to – right rate constant K target right or let us say this is K target right at times OH radicle times the target concentration right.

And then obviously again I have here that is going to be let us say if I look at it that what is this form like so we have DT or differential of the concentration of the target with respect to time = to the rate of loss of that particular target and we know that the relevant what do we say rate for that particular reaction is here so let us say just try to see what we can express that I have DT / concentration of T = - KT OH radicle times DT right.

So obviously getting information about OH radicle is relatively difficult but let us say if I integrate on both sides here so natural logarithm of T right and T naught = - KT integral of OH radicle times DT again i do not have OH radicle times DT you know I do not have this particular value because I cannot have difficultly measure I say oxidation radicle concentration.

But let us say if I do the same with respect to this particular reaction or with respect to the scavenger right and what am I going to end up with natural logarithm of scavenger by S naught = - rate concentration of the scavenger times OH not times pardon me times integral of OH radicle times DT right and I can cancel this out and I have in measure T and T naught S and S naught right I can measure the targeted scavenger concentration with times so I have KT and KS .

So I can have what do we say how I go about the system now I already have KS right I want to calculate what is KT right but I have T naught and S naught right and I know how T and S will change with time right with different times I know how the target concentrations and the scavenger concentrations are going to change.

So with that this particular equation that as I have here right I can conduct regression and then get the value of that particular KT which would obviously give me least sum of squared errors minimum sum of squared errors and then that would obviously be my KT.

So obviously when you have competition KT kinetics and you know the rate constant of particular set of what do we say reactions you can use that for a to calculate I guess you know you can use that to build up on the model to calculate your known rate constant right. So I guess with that we will end today’s session and we will carry through continue looking at kinetics for a few minutes next session and then move on to equilibrium I guess and I guess again with that end today’s session thank you.