Chemical Reaction Engineering

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Lecture No. # 12

Complex Reactions - Kinetics of Chain Reactions and Polymerization

Friends, let us continue our discussion on complex reactions, and so far we looked at several examples of this complex reactions, and simple schemes which are representative of complex reactions. And we saw some characteristics of such reactions using this simple schemes. We also saw two basic approximations that we use quasi steady state approximation or quasi equilibrium approximation, which allows us to simplify the kinetics of the process. Today’s session we will take a look at few examples, and see how we derive the kinetics of these processes using the approximations that we saw in the last class. Now the first question that we may ask ourselves is that how do we know that reaction is a complex reaction? So the first indication that the reaction is a complex reaction comes from the fact that the order and molecularity of the reaction do not match.

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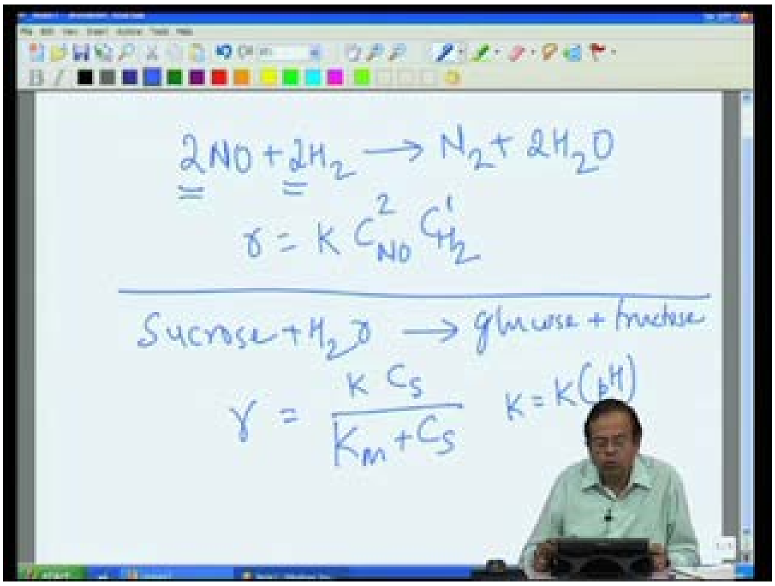

$$\underline{\underline{2}}NO + \underline{\underline{2}}H_2 \rightarrow N_2 + 2H_2O$$

$$r = k C_{NO}^2 C_{H_2}^1$$

$$\text{Sucrose} + H_2O \rightarrow \text{glucose} + \text{fructose}$$

$$r = \frac{k C_S}{K_m + C_S} \qquad k = k(pH)$$

For example, if we look at oxidation of nitric oxide or other reduction of nitric oxide to give rise to nitrogen and water. The order of this reaction is given or the kinetics is given by… So, the molecularity here is four, two moles of N O and two moles of hydrogen, so two plus two four, whereas the order is three, two, and one over here. So that is a clear indication that this reaction is not occurring as a single step interaction between two molecules of N O, and two molecules of hydrogen. But there is something else that is that is happening, so that is one example.

Another example, we can look at is sucrose when it undergoes hydrolysis to give glucose and fructose. The rate of this reaction is given by an expression, which looks something like this. It is not a order or power law kinetics but it is a little more complicated reaction kinetics and which says that rate is K some constant times C S divided by K n plus C S and it turns out that this constant K is also not really a constant but it is a function of p H of the media. So in reality the kinetics and or the order and the molecularity once again do not match. So, how do we now get this kind of kinetic expressions when we have complex reactions?

Now before we start looking at few examples and deal with them. Let us look at how do what is the approach for developing the kinetics of such reactions. So what we essentially do is we write a mechanism of the reaction. So mechanism of the reaction is nothing but the detailed description of the reaction as it takes place from reactant side to the product side. So mechanism is the detailed description of the reaction and we write the mechanism of a reaction with an understanding that each stage in this mechanism or each step in this mechanism is a elementary reaction.

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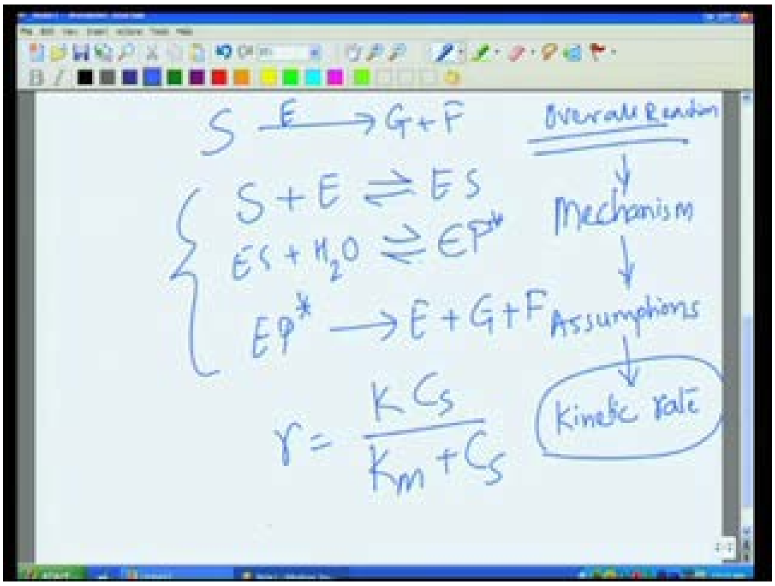

$$S \xrightarrow{E} G+F$$

$$\left\{\begin{array}{l} S+E \rightleftharpoons ES \\ ES+H_2O \rightleftharpoons EP^* \\ EP^* \longrightarrow E+G+F \end{array}\right.$$

$$r = \frac{K C_s}{K_m + C_s}$$

So we have a reaction, we have it does not occur as a single step process as we as I said earlier but it occurs as a multi step process and we further make a assumption that each step of this is an elementary reaction. If we take a example of sucrose so I am just going to write this as S going to glucose and fructose, this example actually is a example of a catalytic reaction and it involves an catalyst E, let us say we call that catalyst E. So this is a overall reaction and we write the mechanism of this reaction as a detailed description and we will discuss about this in detail little later on. But at this point let me just say that what happens in this reaction is this sucrose binds to this enzyme E gives rise to some complex.

This complex interacts with water gives rise to some other complex, which call it as P star then E P star gives us E plus G plus F. So, what we have done in short is we have written the overall reaction in terms of it is constituent elementary reaction. Now there are several things to be remembered when we write the mechanism. Mechanism of a reaction must explain the conversion of a reactant to the product. For example, I cannot have a mechanism of a reaction in which this fructose is not there. This is not a complete description because the overall reaction over here has a product fructose. But if we omit fructose from our mechanism then this is not a correct mechanism. So it has to explain the entire…

Now and each step of this mechanism we say that it is a elementary step and law of mass action kinetics therefore, applies to such elementary steps. Then we can work either quasi steady state approximation or quasi equilibrium approximation and derive the kinetics of the process, which eventually leads us to the expression that we saw earlier. So kinetics of complex process is consist of analysis consist of first of all the overall reaction, the mechanism then some assumptions and the kinetic rate expression. So now this is of course, not always one way street we are to remember that whatever mechanism we write and whatever kinetic rate expression we get it must be experimentally verified.

That is if I write a mechanism of this reaction and if I cannot experimentally verify that this is the correct rate that is I experimentally measure the rate of hydrolysis, I experimentally measure the sucrose concentration and see whether this kind of expression applies to that experimental experimentally determined rate. If it does not then I have made mistake either in writing the mechanism or writing or making certain assumptions and therefore, I will have to go back to my mechanism step and rework so that I get consistent kinetic rate expression. Now, in our discussions we will be following mechanism assumptions and what is the final kinetic rate that we get.

We obviously cannot in these video tutorials verify them experimentally but whenever possible I will try to show some data, which says that indeed, that is the case. Now before we go on to examples one more point to be noted that when it comes to mechanisms, there are two kinds of mechanisms. One what we call open sequences, this particular example or this particular case is an example of an open sequence that is what we have is starting with reactant we follow a series of steps, which end up in product.

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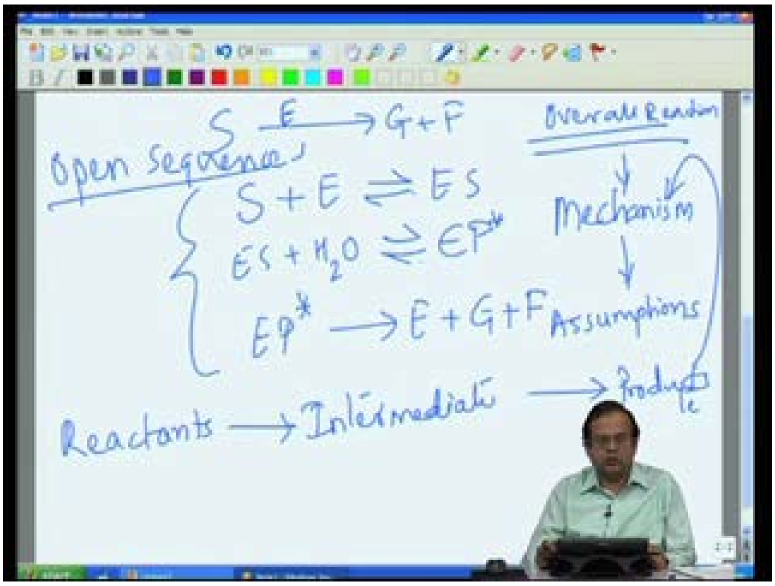

Open sequence

$S \xrightarrow{E} G + F$

Overall Reaction

$S + E \rightleftharpoons ES$

$ES + H_2O \rightleftharpoons EP^*$

$EP^* \rightarrow E + G + F$

Mechanism

Assumptions

Reactants → Intermediate → Products

So to be brief we have let us say reactant we have reactants, intermediates, products. It need not be a linear sequence like this but that is a order in which information is flowing and there is this is what we call open loop open loop sequences. This catalysis is an example of an open loop open loop sequence.

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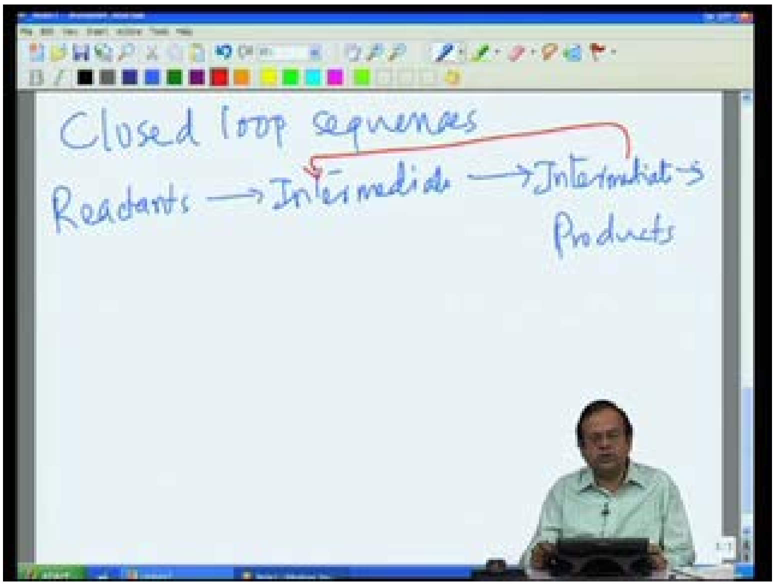

Closed loop sequences

Reactants → Intermediate → Intermediates →

Products

The other type of mechanisms are what we call closed loop sequences closed loop sequences. Now in these kinds of mechanisms, what we have is we start with reactants, they go to some intermediates some more intermediates, which goes to products.

However, unlike open loop so this is what happens typically in an open loop sequence. But in a closed loop sequence the intermediates let us say at the later stage go back to intermediates at an early stage in a way closing the loop in a in a sequence of events.

You probably are familiar with control terminology, open loop control, closed loop control and so on. So in that sense, this is a closed loop because you are going in one particular direction. But at some stage there is a feedback into a previous stage and this is what makes these sequences to be called closed loop sequences. So we will start with examples of closed loop sequences, two examples chain reactions actually chain reactions and polymerization reaction and see what happens to kinetics of these processes.

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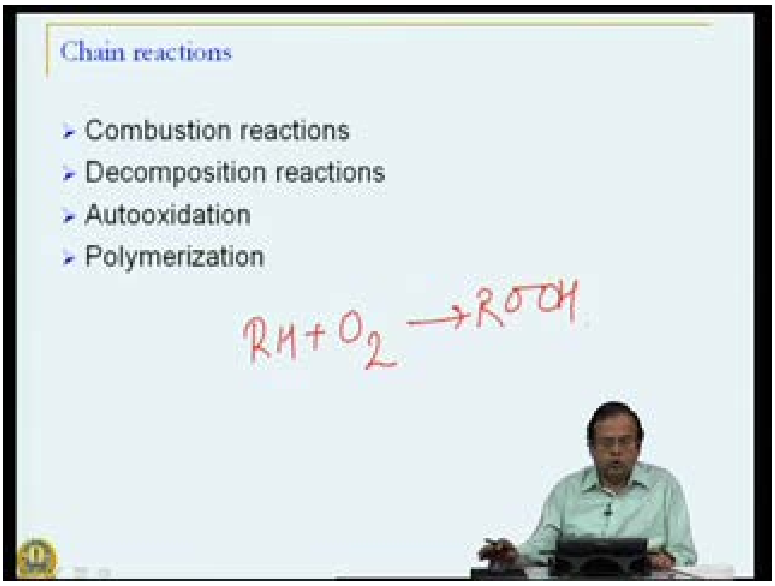

Chain reactions

- Combustion reactions
- Decomposition reactions
- Autooxidation
- Polymerization

$RH + O_2 \rightarrow ROOH$

So, let us look at chain reactions to start our discussion we are going to look at complex reaction, chain reactions as first example and there are several examples of chain reactions few I mentioned earlier but let me reiterate once again. We have combustion reactions which are chain reactions. We have decomposition reactions. We have auto oxidation reactions, polymerization reactions and so on. All important reactions, combustion reaction of course, as the name suggest any combustion process hydrogen and water combining to form hydrogen and oxygen combining to form water or burning of hydrogen a combustion reaction.

Decomposition reaction, that is break down of complex molecule into simpler molecule and we are going to see a example of that auto oxidation. Formation of peroxides that is we looked at that example earlier that is you have a hydro carbon we imbibe oxygen into it and it is a deadly combination because both fuel and oxygen are together and then of course, the polymerization reaction.

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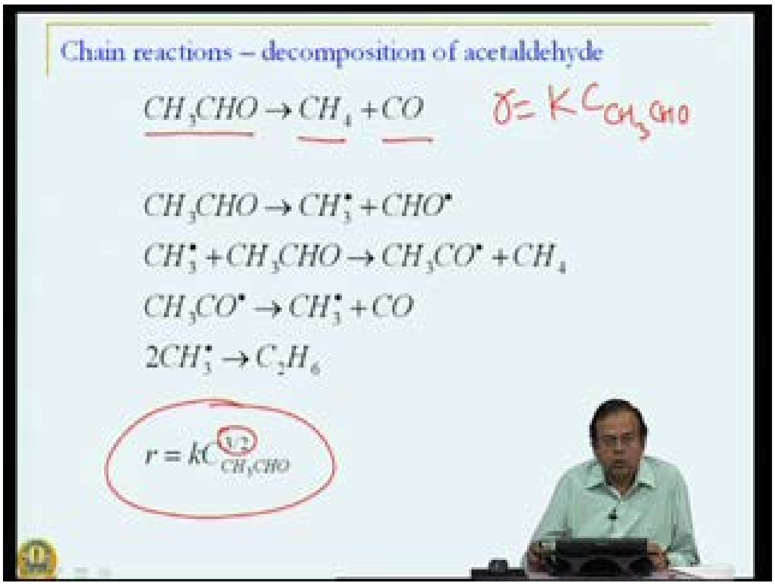

Chain reactions – decomposition of acetaldehyde

$\underline{CH_3CHO} \rightarrow \underline{CH_4} + \underline{CO}$ $r = kC_{CH_3CHO}$

$CH_3CHO \rightarrow CH_3^\bullet + CHO^\bullet$

$CH_3^\bullet + CH_3CHO \rightarrow CH_3CO^\bullet + CH_4$

$CH_3CO^\bullet \rightarrow CH_3^\bullet + CO$

$2CH_3^\bullet \rightarrow C_2H_6$

$r = kC_{CH_3CHO}^{3/2}$

So, let us start with an example of a chain reaction decomposition reaction, so decomposition of acetaldehyde. Now what we have is acetaldehyde giving rise to methane and carbon monoxide. The simple break down and if it was a simple reaction we would have expected the kinetics to be k into concentration of acetaldehyde. Because the order is one, so first guess would have been or first order reaction or rather the molecularity is one, so our first guess would have been first order reaction.

However in reality the experimental data suggest that this particular rate actually is has a order 3 by 2. So it is r is k into concentration of acetaldehyde raise to 3 by 2. A clear indication that it is not a complex reaction and in fact this reaction actually takes place through several steps8 and let us looks at first the mechanism and say example of closed loop sequence, so that will also tell us why we call this as a closed loop sequence.

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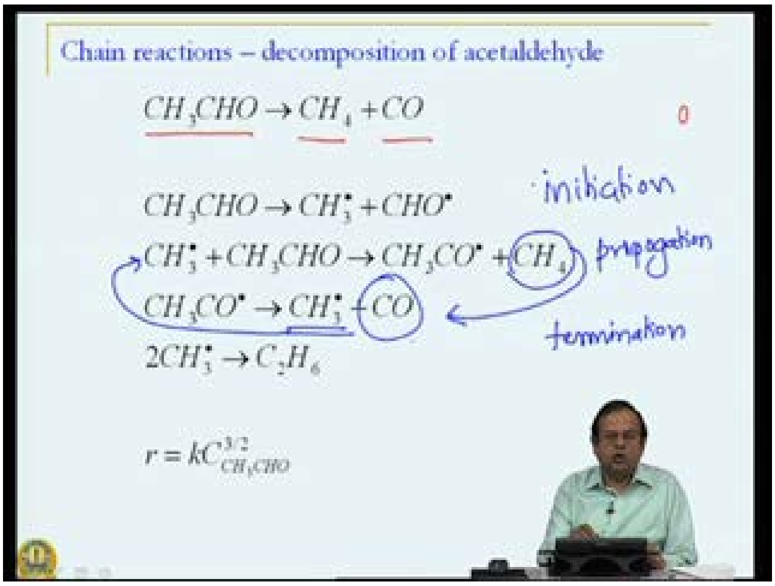

Chain reactions – decomposition of acetaldehyde

$CH_3CHO \to CH_4 + CO$

0

$CH_3CHO \to CH_3^\bullet + CHO^\bullet$ initiation

$CH_3^\bullet + CH_3CHO \to CH_3CO^\bullet + CH_4$ propagation

$CH_3CO^\bullet \to CH_3^\bullet + CO$

$2CH_3^\bullet \to C_2H_6$ termination

$r = kC_{CH_3CHO}^{3/2}$

So, what happens in the first step that is the beginning of the reaction is acetaldehyde breaks out to give radicals free radicals actually. It gives methyl radical and acetyl radical C H 3 and C H O. So that is a first step I will go through this sequence and then see the proper terminology for this. So, we have what we call first reaction as initiation reaction, the reason for this will become clear as we move along. So, next step what happens is this methyl radical extracts hydrogen from an acetaldehyde molecule and gives rise to first product methane and another radical C H 3 C O. This C H 3 C O breaks down to give methyl radical and the second product namely carbon monoxide.

So, once this third reaction takes place as you can see there is a feedback because the product of the third reaction namely methyl radical, goes back as a reactant in the second step further combining with acetaldehyde molecule and thereby closing the loop and these reaction in other words can sustain on it is own, because moment we have this methyl radical that is why this name initiation. So, once the reaction is initiated by formation of this methyl radical it can be propagated indefinitely in principle. Why because if one dimethyl radical will give this C H 3 C O will re again regenerate C H 3 and close the loop.

So these are what are called as propagation reactions, the name is self explanatory because these are the set of reactions which are propagating by themselves. Now, if this last reaction was not there then imagine what would happen just presence of one methyl radical is enough to keep this process going cycles indefinitely and rate of such reaction will be extremely fast or the reaction will end only when the entire acetaldehyde has been broken down. That means always hundred percent conversions but the experience tells that that is not the case.

That is acetaldehyde decomposition does not end only when acetaldehyde is exhausted and it does not happen at an infinitely fast rate, which implies that there must be some other reaction, which is taking away the important constituent, which keeps this reaction propagating namely these methyl radical. So what happens as shown in the fourth reaction is this methyl radical combined with another methyl radical to give rise to ethane. So, this now if there is a source of methyl radical in the initiation step, the last step is a sink because in this methyl radicals are getting consumed or and therefore, this reaction is referred to as termination reaction.

So this is a characteristic of a typical chain reaction. So what do we have here four steps in general; initiation, propagation, termination. Propagation need not be only two step process it could be several steps but the key point is that something at a later stage feedback feeds back into an earlier step in a reaction. Now there are several things to be noted, I mentioned earlier that in a reaction sequence all products have to be explained. So that is that is clear that we have methane as one product, carbon monoxide as other product.

But, there is also a side step side product namely ethane and it does not show up as a overall reaction and that is also an characteristic of a chain reaction that there will be some products, which are insignificant and therefore, are not counted as major products of a reaction. Why is it insignificant because had this reaction been significant then we would have formation of ethyl radical and it is combination with another methyl radical and reaction terminating instantaneously that means almost zero rate. But that is not that is not the case. So, it is clear that termination reaction rate is fairly small compared to propagation reaction step. So, now let us try to see how we go from this particular mechanism to deriving the kinetics.

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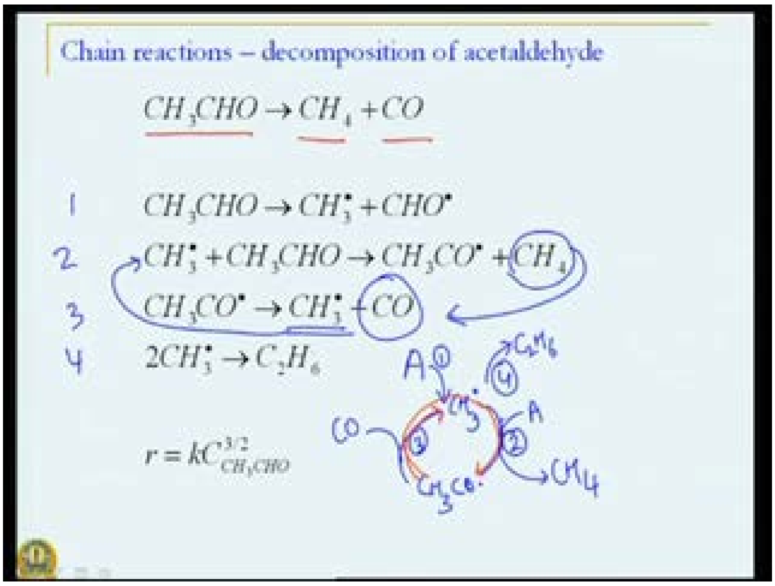

Chain reactions – decomposition of acetaldehyde

$CH_3CHO \rightarrow CH_4 + CO$

1 $CH_3CHO \rightarrow CH_3^{\bullet} + CHO^{\bullet}$

2 $CH_3^{\bullet} + CH_3CHO \rightarrow CH_3CO^{\bullet} + CH_4$

3 $CH_3CO^{\bullet} \rightarrow CH_3^{\bullet} + CO$

4 $2CH_3^{\bullet} \rightarrow C_2H_6$

$r = kC_{CH_3CHO}^{3/2}$

But before we do that let us rewrite this in a slightly different form, so that we see the cyclic nature of this reaction. So, what I am going to do is I am going to write the same reaction in a slightly different form. So, I start with acetaldehyde and I am going to call it A. This acetaldehyde as so let me number these reactions as 1 2 3 and 4. So the first reaction gives rise to a methyl radical, so that is my reaction one. This methyl radical combines with another acetaldehyde and gives rise to C H 3 C O liberating the first product methane, so that is my reaction two.

This radical C H 3 C O decomposes to regenerate C H 3 and the other product C O, so that is my reaction three and two methyl radicals combined with each other giving rise to ethane, that is my reaction four. Now you will appreciate the cyclic nature if you focus on once initiation has happened, that step one has taken place the cycle can continue forever. Till such time that termination takes place and that is the importance of termination reaction. So even though we say that propagation reactions are faster but termination reaction is an important role to play. So let us try to determine the kinetics of this particular process.

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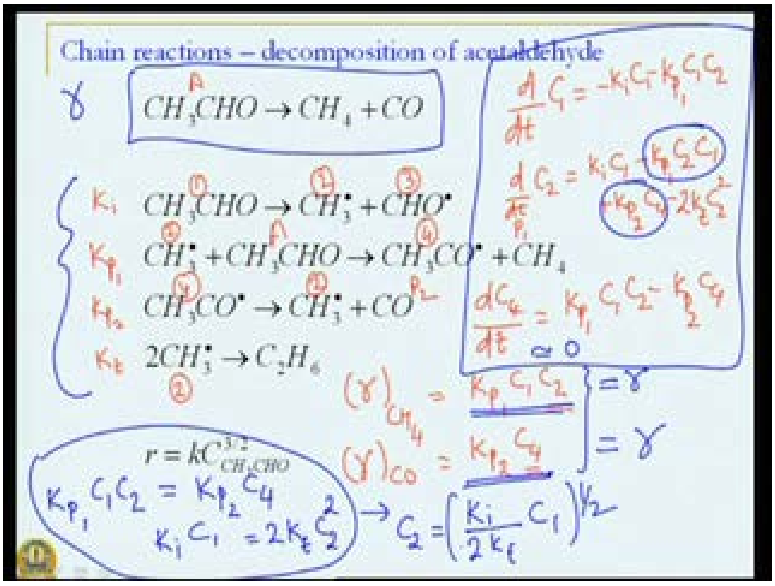

Chain reactions – decomposition of acetaldehyde

γ $\boxed{CH_3\overset{A}{C}HO \rightarrow CH_4 + CO}$

k_i $CH_3CHO \rightarrow CH_3^{\bullet} + CHO^{\bullet}$

k_{p_1} $CH_3^{\bullet} + CH_3CHO \rightarrow CH_3CO^{\bullet} + CH_4$

k_{p_2} $CH_3CO^{\bullet} \rightarrow CH_3^{\bullet} + CO$

k_t $2CH_3^{\bullet} \rightarrow C_2H_6$

$r = kC_{CH_3CHO}^{3/2}$

$\frac{d}{dt}C_1 = -k_iC_1 - k_{p_1}C_1C_2$

$\frac{d}{dt}C_2 = k_iC_1 - k_{p_1}C_2C_1 + k_{p_2}C_4 - 2k_tC_2^2$

$\frac{dC_4}{dt} = k_{p_1}C_1C_2 - k_{p_2}C_4 \simeq 0$

$(\gamma)_{CH_4} = k_{p_1}C_1C_2 \; \} = \gamma$

$(\gamma)_{CO} = k_{p_2}C_4 \;] = \gamma$

$k_{p_1}C_1C_2 = k_{p_2}C_4$

$k_iC_1 = 2k_tC_2^2 \rightarrow C_2 = \left(\frac{k_i}{2k_t}C_1\right)^{1/2}$

So the best way of doing this is let us write down the mass balances. So, assuming that this reaction is taking place this reaction is taking place in a close system. I am going to write mass balance of this particular system and to keep discussion little simple, I am just going to label this species 1 2 3, this as A so A, this is already 2, this is 4, this is product p 1. This is again species 4, so this is 2, this is 4, this is giving rise to 2 and product p 2 and this is this is again 2 giving rise to some products. So I have labeled my species 1 to 4, which are the key species in this reaction. So C 1, C 2, C 3, C 4 is going to be the concentrations of these four species. So let us write down the balance on acetaldehyde first and this reactions we are going to call 1 2 3 4, 1 2 1 2 3 4.

So, we will just simply write reactant rate constants as k 1, k 2, k 3, k 4 for these four reactions or let us still better let us call this initiation rate constant k i this propagation step one k p 1, this as k p 2 and this as k t. So let us write down the mass balance equations as minus k i into C A or C 1 because we call this methanol as acetaldehyde is one. So let us call this as species one to avoid any confusion. So, what we are saying is that we will call the acetaldehyde species one to be consist so this C 1 is k i into C 1 minus k p 1 from the second reaction into C 1 into C 2.

Similarly, d dt of C 2 will be k i into C 1 coming from the first reaction getting consumed in the second reaction. Once again getting consumed or getting formed in the third reaction and getting consumed in the fourth reaction and for four reactions, since two molecules are involved we will write the rate as 2 k t into C 2 square. Remember this is an elementary reaction so the order of this reaction is same as it is molecularity. So we have C 2 square and we have two molecules two radicals methyl radicals combining and hence we write the reaction as with the stoichiometric coefficient minus 2.

So what does that mean k t into C H C 2 square is the rate of these reaction and therefore, we write this. Let us write the same thing for C 4. Now it is getting formed in the second reaction so and getting consumed in the third reaction, so we have C 4. Now, what is the rate of methane formation? As per this is k p 1 C 1 C 2. What is the rate of C O formation? So, as per as per third reaction now if you look at the kinetics expressions, it involves two species C 2 and C 4, which are radicals and their concentration is difficult to determine.

So what are we going to do? We are going to use quasi steady state approximation. Why how do we justify quasi steady state? We say that these radicals are highly active and so movement they are formed they participate in the reaction in a fairly quickly and therefore, their concentrations are very small and dc to dt or there dynamics is also very small and so we have quasi steady state. So before we invoke quasi steady state approximation, let me recap we have the overall reaction we have the overall reaction, which we wrote in terms of its constituent reactions.

So the mechanism of these reaction and we want to invoke certain approximations or make certain assumptions. In this particular case, we make the assumption that these methyl radical C H 3 and C H 3 C O radicals are highly reactive and therefore, there dynamics is very slow or they form they get formed they get consume form consume, so very fast dynamics. So quasi steady state is a reasonable assumption for the species so in order to invoke quasi steady state we write the mass balance equations, which is what we have written over here.

The next step is to therefore, invoke now quasi steady state approximation. So we will invoke it for species 2 and 4. So, let us start with species 4. So, there we see that k p 1 C 1 C 2 that is if we said dc 4 dt is close to zero because quasi steady state k p 1 C 1 C 2 is k p 2 C 4. So, that is the first result why are we doing this because we have our rate expressions, we have our rate expressions, which are in terms of C 2 and C 4 concentrations and we do not know what these concentrations are so we want to eliminate them. So that everything is in terms of C 1 because that is the only reactant over here and p 1 and p 2 but they are not participating or there is no feedback, so in this particular case not reversible reaction. So we want to eliminate C 2 and C 4 in terms of in terms of …

So dc 4 dt gave us gave us this particular. Now what is the significance of this? If you remember for our overall reaction overall reaction, we will have certain rate as we have been defining earlier and r C H 4 or the rate of formation of methane must be the stoichoimetric coefficient times this r. So, r C H 4 must be r similarly, r C O 2 must be also r, so this is r this also is r and this approximation tells us that indeed that is the correct case that is k p 1 C 1 C 2 is same that is k p 1 C 1 C 2 is same as k p 2 C 4. That means both these are equal and we call that as r. So, that is a good sign that we are not we our assumption is a good assumption. Then we invoke the same assumption for dc to dt balance or balance for species two and you will notice because of this quasi steady state approximation for species 4, the second term and the fourth term or third term cancel each other and we are left with k i C 1 is 2 k t into C 2 square from this rate expression.

What does this what does this mean? This means that I now have concentration of C 2 in terms of C 1 and that is what we have been we have been looking for. So concentration of C 2 that is the radical in terms of species whose concentration we can measure. So, let us revisit overall reaction mechanism, mass balances, quasi steady state approximation and the simplification of that.

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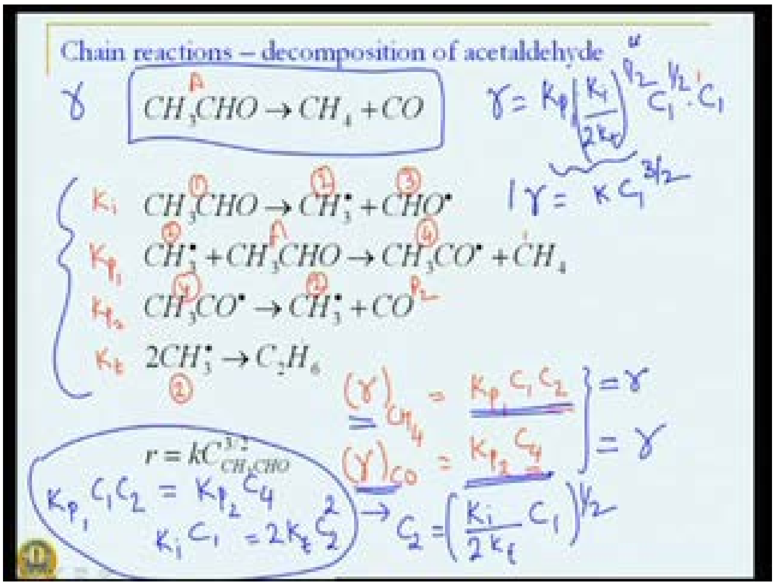

Chain reactions – decomposition of acetaldehyde

r $\boxed{\overset{A}{CH_3}CHO \rightarrow CH_4 + CO}$ $r = k_{p}\left(\frac{k_i}{2k_t}\right)^{1/2} C_1^{1/2} \cdot C_1$

$r = k C_1^{3/2}$

k_i $CH_3\overset{(1)}{C}HO \rightarrow \overset{(2)}{CH_3^\bullet} + \overset{(3)}{CHO^\bullet}$

k_{p_1} $\overset{(2)}{CH_3^\bullet} + \overset{A}{CH_3}CHO \rightarrow \overset{(4)}{CH_3CO^\bullet} + CH_4$

k_{p_2} $\overset{(4)}{CH_3CO^\bullet} \rightarrow \overset{(2)}{CH_3^\bullet} + CO$

k_t $2\underset{(2)}{CH_3^\bullet} \rightarrow C_2H_6$

$(r)_{CH_4} = k_{p_1} C_1 C_2 \} = r$

$(r)_{CO} = k_{p_2} C_4 \} = r$

$r = kC_{CH_3CHO}^{3/2}$

$k_{p_1} C_1 C_2 = k_{p_2} C_4$

$k_i C_1 = 2k_t C_2^2 \rightarrow C_2 = \left(\frac{k_i}{2k_t} C_1\right)^{1/2}$

So, now let us look at what happens as a consequence of this and to do that I am going to this is becoming too crowded. Now so let us remove some of the old part of the discussion.

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And take it from the last point, and therefore then say that my rate of this reaction, which is r C H 4 r C O over here, C 1 C 2, so that is k p 1 into k i by 2 k t raise to half C 1 raise to half into C 1. So, this is our substituted for C2 now, and the net result is that we now have r as some constant k C 1 raise to 3 by 2, which is what experimentally observed rate. So we now therefore, complete this discussion. So we have the desired rate, this particular example illustrates several aspects. If you go back to our rate expression we said that these first and third reactions are slower and so on.

So does it mean that their rates or rate constants do not matter? No, it does matter. In fact if you look at the rate expression the kinetic constant k is actually has propagation constant k p 1 k i and 2 k t. That is if we look at this particular expression. So rate constant of initiation and termination do matter. So that is point one. Point two if we look at this approximation for approximation for C 2 over here, we see that the initiation rate that is rate of this first reaction equals the rate of termination reaction the fourth reaction and this also is a typical of a chain reaction. That is reaction one is equal to reaction four, the rates of these reactions. So that is one example.

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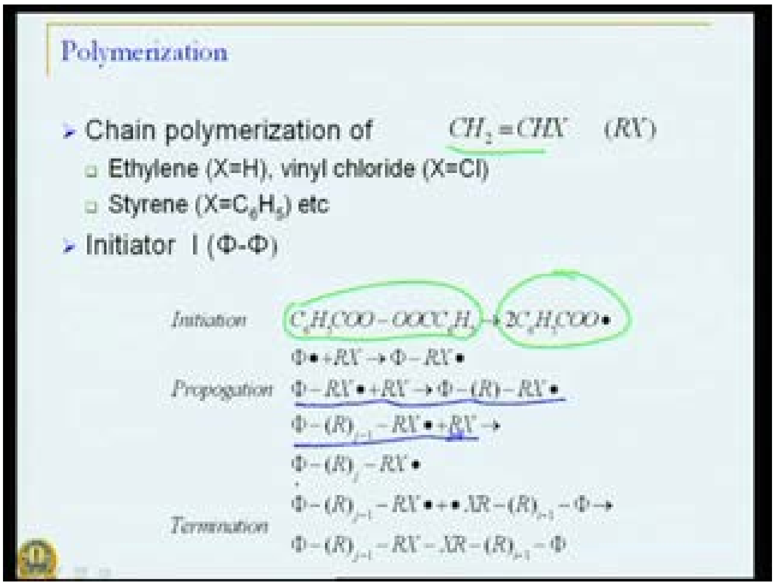

Polymerization

- Chain polymerization of $CH_2=CHX$ (RX)
  - Ethylene (X=H), vinyl chloride (X=Cl)
  - Styrene ($X=C_6H_5$) etc
- Initiator I (Φ-Φ)

Initiation $C_6H_5COO-OOCC_6H_5 \rightarrow 2C_6H_5COO\bullet$

$\Phi\bullet + RX \rightarrow \Phi - RX\bullet$

Propogation $\Phi - RX\bullet + RX \rightarrow \Phi-(R)-RX\bullet$

$\Phi-(R)_{j-1}-RX\bullet + RX \rightarrow$

$\Phi-(R)_j-RX\bullet$

Termination $\Phi-(R)_{j-1}-RX\bullet + \bullet XR-(R)_{k-1}-\Phi \rightarrow$

$\Phi-(R)_{j-1}-RX-XR-(R)_{k-1}-\Phi$

I will quickly go through second example polymerization reaction and particularly chain polymerization, because as you would know the polymerization reactions are of several types, condensation polymerization, addition polymerization and so on. But we will look at only one such example here that is chain polymerization, which is also a chain reaction mechanism. So in particular we are looking at ethyl, the polymers whose monomer can be represented as C H double bond C H X. So if X is hydrogen we have ethylene and polyethylene, if X is chlorine we have vinyl chloride and polyvinyl chloride P V C, if it is styrene C 6 H 5, we have polystyrene.

So all these polyethylene, polyvinyl chloride, polystyrene and several others can be represented polymerization reactions by looking at monomer C H 2 double bond C H X and initiator for such polymerization reaction there are several it can be even light energy. But there can be chemicals also like benzoyl peroxide benzoyl peroxide, which is shown over here. So the first step is benzoyl peroxide gives rise to benzyl radicals and this benzyl radical binds with R X, I am going to call this C H 2 C double bond C H as R and X as the appropriate side group, there is H or chlorine or C 6 H 5 and so on. So we have phi joining with R X giving rise to another radical phi R X dot then this phi R X dot in a propagation reaction.

So we have propagation now, phi R X dot binds with R X gives rise to phi R R X radical and these reactions continue. So for example, this particular radical addition of R X gives rise to phi R j R X. So, these are all propagation reactions and then we have termination reaction phi R j minus 1 X combining with another radical so having I monomeric units and j monomeric units combined to give phi polymer with I plus j monomeric units.

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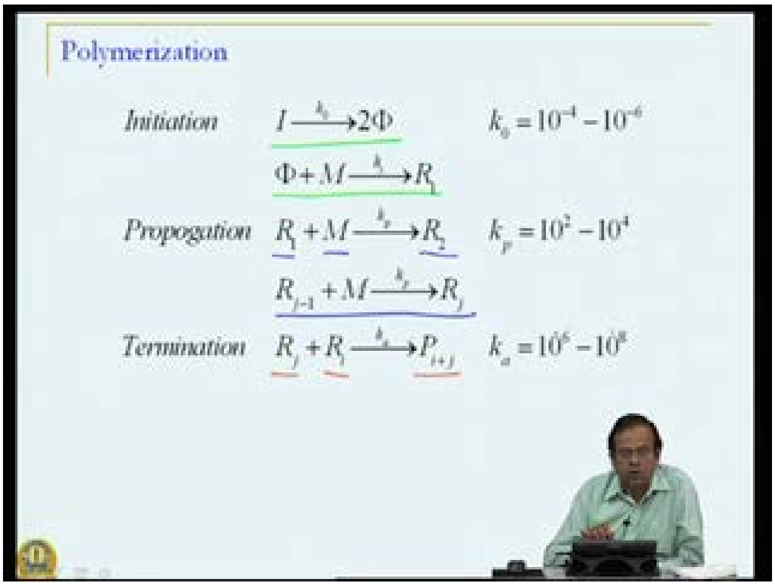

Polymerization

Initiation $I \xrightarrow{k_0} 2\Phi$ $k_0 = 10^{-4} - 10^{-6}$

$\Phi + M \xrightarrow{k_i} R_1$

Propogation $R_1 + M \xrightarrow{k_p} R_2$ $k_p = 10^{2} - 10^{4}$

$R_{j-1} + M \xrightarrow{k_p} R_j$

Termination $R_j + R_i \xrightarrow{k_a} P_{i+j}$ $k_a = 10^{6} - 10^{8}$

Now the kinetics of this, we will write it as in terms of reaction scheme. So initiator giving rise to initiator giving rise to free radicals, step one free radical benzoyl peroxide combining with monomer giving rise to a live radical R 1. Then R propagation reactions that are R 1 combining with one monomer giving rise to R 2, R 2 plus M R 3. So, in general R j minus 1 plus M as R j, so these are all propagation reaction and the termination reaction R j plus R i giving rise to P i plus j.

So these are the typical rate constants of these reactions initiation and termination being fairly small this should be minus sign here fairly small compared to propagation reaction step. So how do we determine the kinetics of this polymerization same strategy. We have a mechanism and we are going to invoke quasi steady stet approximation for all these radicals R 1 R 2 R 3 R i R i R j R M. Remember, this is a infinitely long process and therefore, we have polymer chain distribution and so on.

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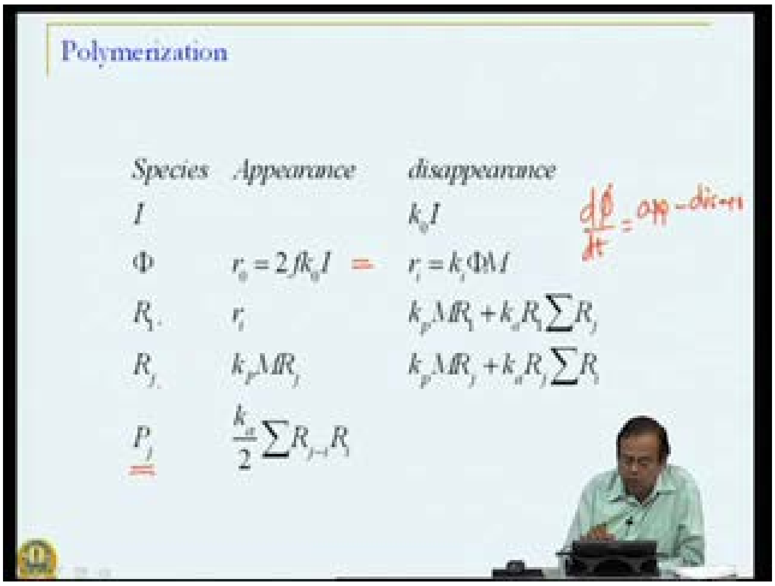

Polymerization

Species	Appearance	disappearance
I		$k_0 I$
Φ	$r_0 = 2fk_0 I$ =	$r_i = k_i \Phi M$
R_1.	r_i	$k_p M R_1 + k_d R_1 \sum R_j$
R_j.	$k_p M R_j$	$k_p M R_j + k_d R_j \sum R_i$
$\underline{\underline{P_j}}$	$\frac{k_d}{2} \sum R_{j-i} R_i$	

$\frac{d\phi}{dt} =$ app − disapp

So, let us how do we determine the kinetics in a simple manner. You can work out these details by yourself, it is writing for a given species it is appearance and disappearance rate. So, we have initiator of radical live polymer R 1 live polymer R j and the polymer P j, which is in this particular case formed from R 2 live radicals R 1 and R 2 combining. So, we now then invoke quasi steady state approximation for the species that means what does it mean that means d phi dt. For example, it is appearance rate minus disappearance rate that is true for any species rate the formation is a balance between appearance and disappearance. So for quasi steady state approximation to be invoke this must be equal, these two rates are equal and so on for all the species.

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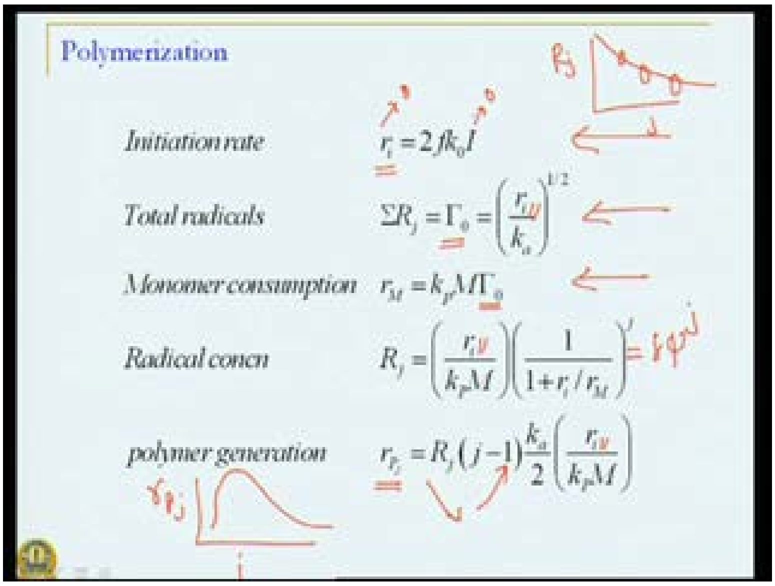

Polymerization

Initiation rate $r_i = 2fk_0 I$

Total radicals $\Sigma R_j = \Gamma_0 = \left(\frac{r_i}{k_a}\right)^{1/2}$

Monomer consumption $r_M = k_p M \Gamma_0$

Radical concn $R_j = \left(\frac{r_i}{k_p M}\right)\left(\frac{1}{1+r_i/r_M}\right)^j = \gamma\varphi^j$

polymer generation $r_{P_j} = R_j (j-1)\frac{k_a}{2}\left(\frac{r_i}{k_p M}\right)$

Now using some properties of infinite change because this is a polymer chain, we can actually simplify that by in terms of initiation rate the total radicals that is R 1 R 2 R 3 R phi R infinity is given in terms of these initiation rate r i and the initiation rate constant k a. Then monomer consumption rate this is refer to as total radicals tau zero monomer consumption rate. Radical concentration in a species R j in this particular form, which can also be written as gamma times psi raise to j and the polymer generation rate which is in terms of this R j j minus 1 into some constant.

Now, if we look at the structure of this we notice the following. The importance of initiator for example, if initiator is not there I is zero then it turns out that all these rates go to zero. That is if initiation rate is zero, then total radical concentration is zero, monomer consumption is zero, individual radical concentration is zero, polymer generation rate is zero. It also implies that if initiator concentration rate, why I am saying this because in all these rate expressions r i is there r i r i r i r i and so on.

So if initiator concentration goes to zero, that means this goes to zero, r i will go to zero and all these rates will go to zero, that is the importance of initiator. It is importance can also be felt into the following manner expressed in the following manner. If initiator concentration is small then i is small so r i is small and then all rates will be small. In other words, we have to maintain initiator concentration at a high value and furthermore it is often maintained at a constant value.

Now, if we look at these expressions once again we also notice the following these radical concentrations for example, R j as a function of j. What is j? j is the number of monomeric units one two three four and infinity it actually always falls down and that is to be expected because here R j comes from j minus 1, j minus 1 comes from j minus 2 and so on. So j minus 2 concentrations is always higher than j minus 1 is always higher than j. So, it is monotonically decreasing.

Now if you look at the rate of polymer polymerization we find that R j function is continuously decreasing as function of j, j minus 1 is continuously increasing. Hence the product of the two, if you plot it as R P j as a function of j it always goes through a maxima. And that is that distribution of the polymer that we find.

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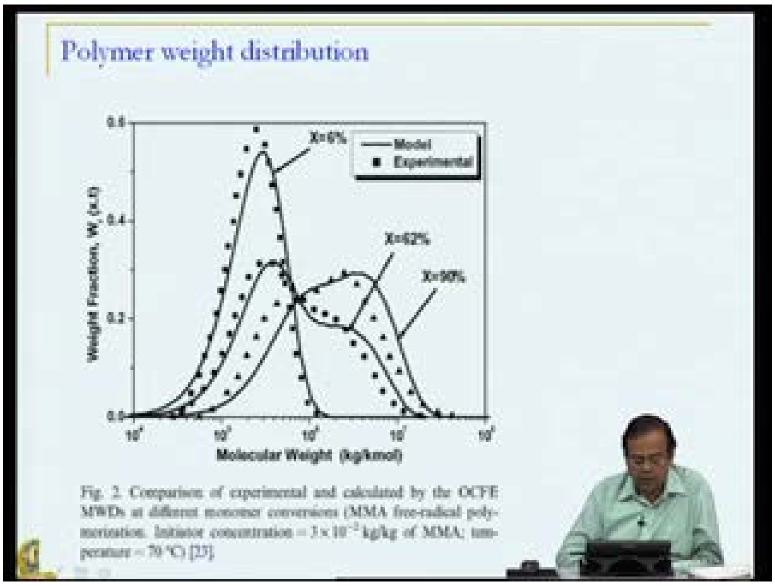

Polymer weight distribution

Fig. 2. Comparison of experimental and calculated by the OCFE MWDs at different monomer conversions (MMA free-radical polymerization. Initiator concentration = 3×10^{-2} kg/kg of MMA; temperature = 70 °C) [23].

The weight fraction of the jth component as a function of j or its molecular weight, we always see that there is a unimodel distribution, and our kinetics can explain that.

So with this, we come to the end of this particular session, and here today we saw two examples that of chain reactions and polymerization reaction, and how we use quasi steady state approximation to determine the kinetics. In the next session, we are going to look at catalytic reactions, and the kinetic rate expressions of catalytic reactions. Thank you.