Chemical Reaction Engineering

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Lecture No. #10

Complex Reactions – Yield and Selectivity

Friends, let us continue our discussion on complex reactions and to recap, we saw in the last class various examples; where reactions do not occur as simply one step process; but typically complex reactions involve large number of reactants, large number of products, large number of reactions which connect reactant to products.

In the process, there are lot of intermediates in the reactions, that appear and we are now concerned about, how do we determine the kinetics of such processes? So, that is our ultimate objective; that how do we determine the rate at which reactants are going to product or rate at which products are being formed; when we have such large systems to deal with.

What we are started with is construct very simple complex reactions, such as we considered last time parallel reactions, series reactions and so on. And we are we are, we were looking at parallel reactions; and what happens when you have more than 1 reaction. You you usually have conversion is not in sufficient criteria for design of reactors.

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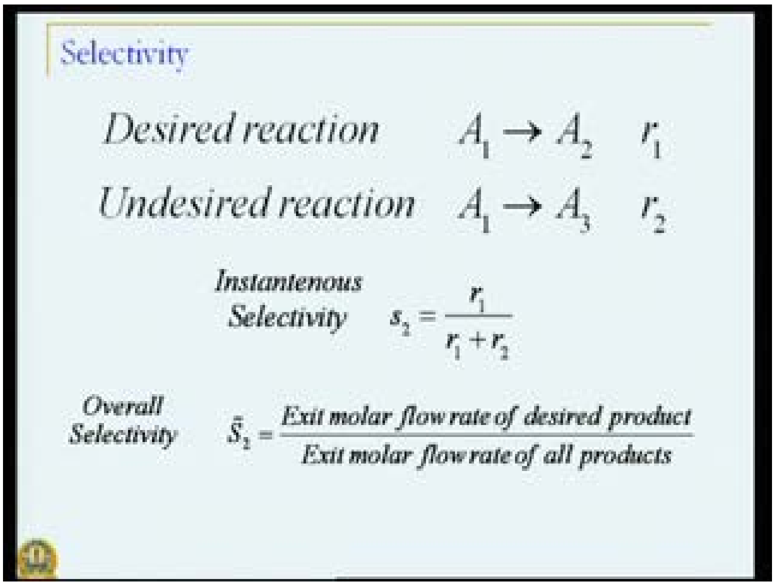

Selectivity

Desired reaction $A_1 \rightarrow A_2$ r_1

Undesired reaction $A_1 \rightarrow A_3$ r_2

Instantenous Selectivity $s_2 = \frac{r_1}{r_1 + r_2}$

Overall Selectivity $\bar{S}_2 = \frac{\text{Exit molar flow rate of desired product}}{\text{Exit molar flow rate of all products}}$

Because, let us go back to our example, and let us say that we have these desired reaction A 1 going to A 2, which is accompanied by an undesired reaction A 1 going to A 3; then conversion of A 1 alone is not sufficient for design of reactor, because it does not tell us anything about, how much of that A 1 is going to actually A 2, because that is what we want as a product.

So, we have to define, what we term as selectivity and in the last class we defined two different kinds of selectivity s, one instantaneous selectivity small S 2, which is a ratio of, rate of the desired reaction to the total rate of consumption of A 1; that is both in desired as well as undesired reaction, so r 1 by r 1 plus r 2.

We also defined overall selectivity for example, if you have a plug flow reactor, then overall selectivity is the exit molar flow rate of the desired product to exit molar flow rate of the total products, that are that are coming in. Let us now, see how these two quantities are related to each other and how the design of reactor now gets influenced by idea, such as selectivity.

So, let us work this same problem, but now let us say that, we have we have a plug flow reactor we have a plug flow reactor in which these two reactions, A 1 going to A 2 at a rate r 1 and A 1 going to A 3 at a rate r 2 are taking place; and our first reaction and the product is a desired product A 2, but there is a unfortunately and undesired product also coming into into the picture.

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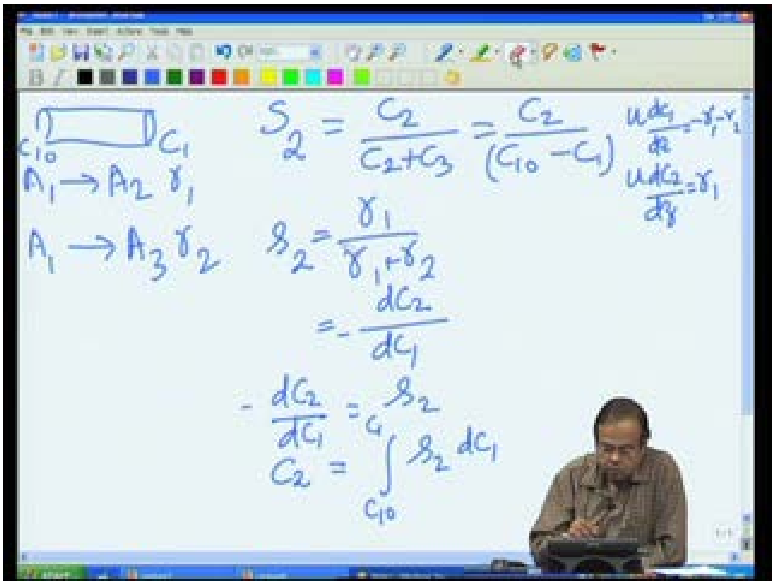

C_{10} C_1

$A_1 \rightarrow A_2 \quad r_1$

$A_1 \rightarrow A_3 \quad r_2$

$$S_2 = \frac{C_2}{C_2+C_3} = \frac{C_2}{(C_{10}-C_1)}$$

$$u\frac{dC_1}{dz} = -r_1-r_2$$

$$u\frac{dC_2}{dz} = r_1$$

$$s_2 = \frac{r_1}{r_1+r_2} = -\frac{dC_2}{dC_1}$$

$$-\frac{dC_2}{dC_1} = s_2$$

$$C_2 = \int_{C_{10}}^{C_1} s_2 \, dC_1$$

So, we make another assumption, that volumetric flow rate is constant. So, the selectivity capital S 2, which is defined in terms of molar flow rates will also, now can be defined in terms of concentrations. Because, it is a volumetric flow rate, we have assumed constant for sake of this illustration.

Now, we also have stoichiometry and we know that, for every mole of A 1 that is consumed A 2 is formed, same is the case with A 3, so the concentration of species 2 and 3 put together, must be same as that of A 1 that has got consumed. So, if C 1 0 is the concentration here at the inlet and C 1 is the concentration in the exit, then C 1 0 minus C 1 must be C 2 plus C 3.

Once again, we have made a small assumption, that there is no A 2 and A 3 at the inlet of the reactor or at the entry point, that is a reasonable assumption, because normally you would not want to feed the reactor with the product itself, because where do we get that product. So, this is our overall selectivity and now, let us try to see, how this selectivity, overall selectivity is related to the point selectivity.

So, our point selectivity as we defined earlier, was r 1 by r 1 plus r 2, which if we use our mass balance equations for example, u d C 1 d z as the consumption of species 1, so that is minus r 1 minus r 2 and u d C 2 d z is r 1. Our normal plug flow reactor mass balance is this point selectivity which is r 1 by r 1 plus r 2 is nothing but d C 2 by d C 1 minus. So, that is our point selectivity which is which is S 2.

So, now I can write d C 2 by d C 1, which is S 2 minus d C 1, d C 2 by d C 1 is S 2 and then I can therefore, write C 2 as integral C 1 0 to C 1, S 2 d C 1 and therefore, write let me, therefore, write C 2 by C 1 0 minus C 1 is 1 over C 1 0 minus C 1 integral S 2 d C 1, C 1 0 to C 1, see this is nothing but my overall selectivity, so my overall selectivity is related to my instantaneous selectivity small s 2. This is what happens in a plug flow reactor.

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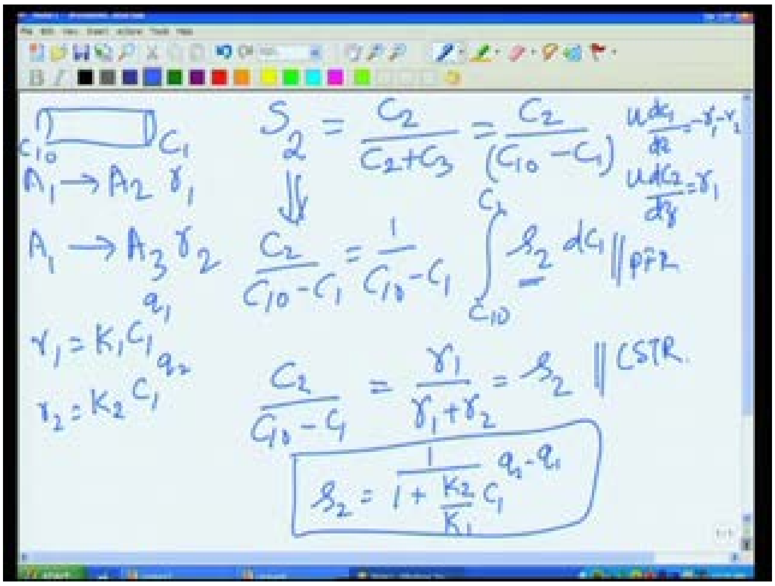

$$C_{10} \quad C_1$$

$$A_1 \rightarrow A_2 \quad r_1$$

$$A_1 \rightarrow A_3 \quad r_2$$

$$r_1 = K_1 C_1^{q_1}$$

$$r_2 = K_2 C_1^{q_2}$$

$$S_2 = \frac{C_2}{C_2 + C_3} = \frac{C_2}{(C_{10} - C_1)}$$

$$u\frac{dC_1}{dz} = -r_1 - r_2$$

$$u\frac{dC_2}{dz} = r_1$$

$$\Downarrow$$

$$\frac{C_2}{C_{10} - C_1} = \frac{1}{C_{10} - C_1} \int_{C_{10}}^{C_1} \underline{s_2} \, dC_1 \quad \| \text{PFR}$$

$$\frac{C_2}{C_{10} - C_1} = \frac{r_1}{r_1 + r_2} = s_2 \quad \| \text{CSTR}$$

$$\boxed{s_2 = \frac{1}{1 + \frac{K_2}{K_1} C_1^{q_2 - q_1}}}$$

What happens in a CSTR? You can a once again write the mass balances for species C 1 and C 2; and rearrange rearrange the equations and we will get C 2 by C 1 0 minus C 1 as r 1 by r 1 plus r 2 are nothing but S 2. We will get equal to S 2, so we have this equation for plug flow reactor, we have this equation for CSTR; and question naturally we would like to now ask is which of this 2 reactors give you better selectivity, to answer that question we need, what are these r 1s and r 2 s.

So, let us say my r 1 is K 1 C 1 raise to q 1, power law kinetics with order q 1 and for second reaction; it is K 2 C 1 raise to q 2, again and power law power law kinetics. So, with this 2 rate rate equations, I can now write selectivity, point selectivity S 2 which is, which is r 1 by r 1 plus r 2, so if I do little bit of manipulation, I will get this value as, 1 by 1 plus K 2 by K 1 C 1 raise to q 2 minus q 1. So, this is my point selectivity, I know it changes as concentration C 1 changes; and these are the two design equations, which tell me, what is a selectivity in a plug flow reactor and what is a selectivity in a CSTR.

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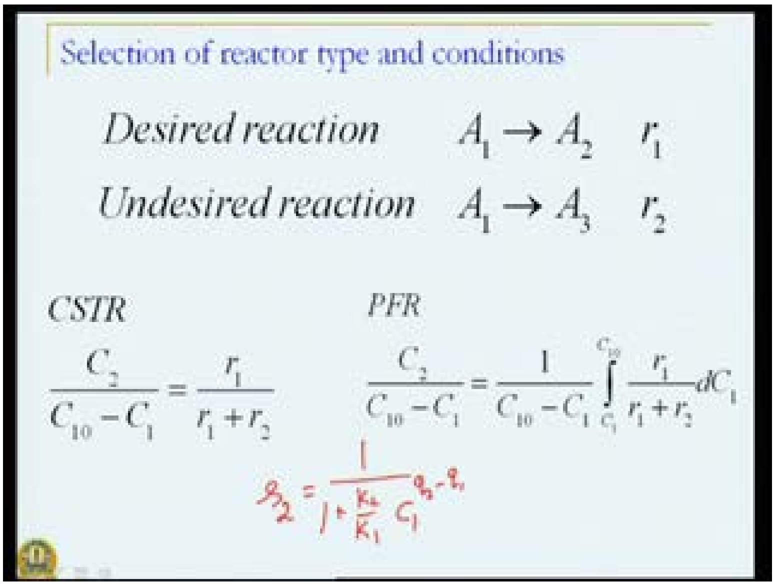

Selection of reactor type and conditions

Desired reaction $A_1 \rightarrow A_2$ r_1

Undesired reaction $A_1 \rightarrow A_3$ r_2

CSTR

$$\frac{C_2}{C_{10}-C_1} = \frac{r_1}{r_1+r_2}$$

PFR

$$\frac{C_2}{C_{10}-C_1} = \frac{1}{C_{10}-C_1}\int_{C_1}^{C_{10}} \frac{r_1}{r_1+r_2} dC_1$$

$$s_2 = \frac{1}{1+\frac{K_2}{K_1} C_1^{q_2-q_1}}$$

So, now let us look at, how the system behaves for different different scenarios. So, we have this, once again same reiterating the same idea, that for CSTR this is my selectivity, for plug flow reactor this is my selectivity; and we just now, just now wrote that selectivity s 2 is 1 over 1 plus K 2 by K 1 C 1 raise to q 2 minus q 1, if r 1 and r 2 are expressed as power law kinetics having orders q 1 and q 2. So, now how selectivity changes as the concentration of concentration of C 1 is changed will depend upon these values of q 2 and q 1.

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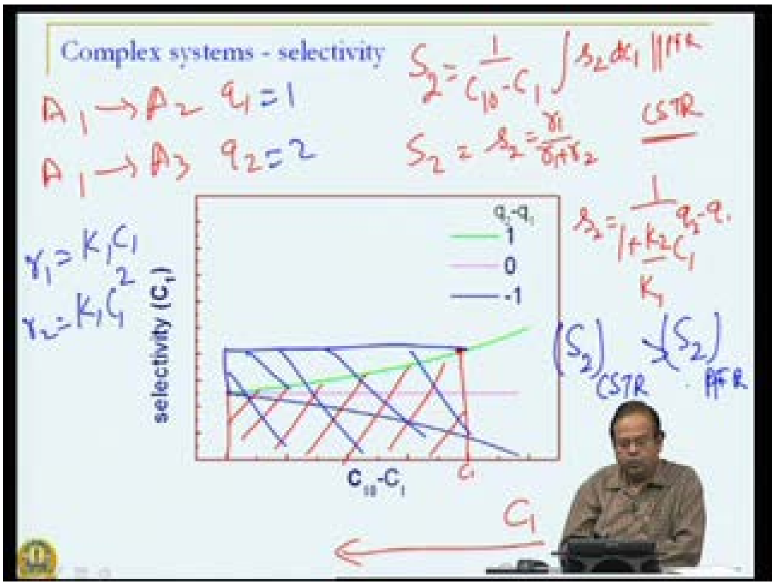

Complex systems - selectivity

$A_1 \rightarrow A_2$ $q_1 = 1$

$A_1 \rightarrow A_3$ $q_2 = 2$

$r_1 = K_1 C_1$

$r_2 = K_1 C_1^2$

$S_2 = \frac{1}{C_{10}-C_1}\int s_2 dC_1$ || PFR

$S_2 = s_2 = \frac{r_1}{r_1+r_2}$ CSTR

$s_2 = \frac{1}{1+\frac{K_2}{K_1} C_1^{q_2-q_1}}$

$(S_2)_{CSTR} \not> (S_2)_{PFR}$

So, let us let us look at, look at that behavior once again in the same plot of C 1 0 minus C 1 against selectivity. Let me, let me write the design equation once again, for plug flow reactor and S 2 equal to small s 2 or is equal to r 1 by r 1 plus r 2 for CSTR; and my selectivity is 1 by 1 plus K 2 by K 1 C 1 raise to q 2 minus q 1.

So, let us examine what happens to our selectivity, as function of concentration of C 1, but instead of looking at C 1 we are going to look at C 1 0 minus C 1. The simplest case is q 2 and q 1 are same; that means, the orders with respect to A 1 going to A 2 and A 1 going to A 3, these are the orders q 1 and q 2; if both are equal then selectivity is independent of concentration and that is represented by these violet color line, when q 2 and q 1 are q 2 and q 1 are same.

Let us consider a case, where q 2 is greater than q 1, that means the second reaction order is higher than the first reaction order; if that is the case, then q 2 minus q 1 is positive, so as C 1 increases the selectivity should decrease and C 1 increase in our case is in this direction. Because this is C 1 0 minus C 1, so C 1 increases in this direction, so as C 1 increases, we get increase in the in the, we get rather decrease in the selectivity, if q 2 minus q 1 is positive. This is the case shown with this green line, when q 2 minus q 1 is positive.

The third thing now you can expect, is if q 2 minus q 1 is negative, we should get a behavior, which is shown by this blue line over here by this blue line over here. So, now we have we have various behaviors of selectivity as a function of C 1 0 minus C 1.

Now, let us look at, what happens to a plug flow reactor? For a plug flow reactor, again the design equations are independent of the kinetics; they are the characteristic of the flow conditions and what kind of reactor we have, so for plug flow reactor, by now you would have guessed is nothing but the area under the curve, over C 1 0 minus C 1. So, let us say, if our q 2 and q 1 are same, S 2 is independent of selectivity; then the area under the curve or area of the rectangle, why are we interested in area of the rectangle? The CSTR line is nothing but the area of the rectangle and P F R is nothing but a represented by the selectivity is represented by area under the curve.

So, let us say for this particular, particular concentration C 1 whatever that value value is the selectivity for selectivity for plug flow reactor is given by this shaded curve, which is for the case of q 2 minus q 1 greater than 0, which is which is our our green line and plug flow reactor as the area under the curve. But what happens, if it is actually not selectivity, because you have to nor divide it by 1 over C 1 minus C 1 0 minus C 1, so if you if you do that, but but the area gives you the representative value.

Now, what happens for a CSTR? This is nothing but this particular value, this particular value which is actually the area under this curve, under this rectangle divided by C 1 0 minus C 1; and you can clearly see here that, if q 2 is greater than q 1 then what happens? Selectivity in a CSTR is higher than the selectivity in a plug flow reactor, which means that as far as the selectivity is concerned, CSTR is better than plug flow reactor.

But, what about conversion, so just let us put some numbers, so suppose q 1 is 1, q 2 is 2, we know that for power law kinetics with positive values of q 1 and q 2, conversion is always highest in plug flow reactor, we discussed that few sessions back; that is because the concentration is, concentration suddenly decreases in CSTR whereas, the decrease is gradual in plug flow reactor, so conversions are better in plug flow reactor, compared to compared to CSTR.

But what happens, when it comes to selectivity? The selectivity in a plug flow reactor is now worse than, the CSTR or CSTR is better than that in the plug flow reactor or what it implies is that for conversions P F R may be desirable, but that does not guarantee high selectivity, for achieving high selectivity CSTR is better than, better than plug flow reactor; and why why why is this happening? You go back to this particular, particular kinetics, see the rate of first reaction is K 1 C 1 let us say q 1 is 1 and second reaction is K 1, C 1 square, see we are looking for making more of A 2.

So, what happens in a CSTR? CSTR concentration is low compared to that in a plug flow reactor, lower concentration because it is squared in the second reaction reduces the rate more or that as compared to when the order is 1; that means, between comparing between high concentration and low concentration, the concentration has more effect on reducing the second reaction than the first reaction, why because in the second reaction concentration is squared.

So, square is always the contribution of a square is always higher than, contribution of a linear term, so that applies to reduction also, so reduction is higher in the rate is higher for the undesired reaction, in a, and whenever there is a reduction, higher reduction in undesired reaction rate; that means, that is desirable. So, CSTR has lower rates of certain reaction, compared to their counterparts in a plug flow reactor; and as a result the selectivity in a CSTR is better than, that in the plug flow reactor.

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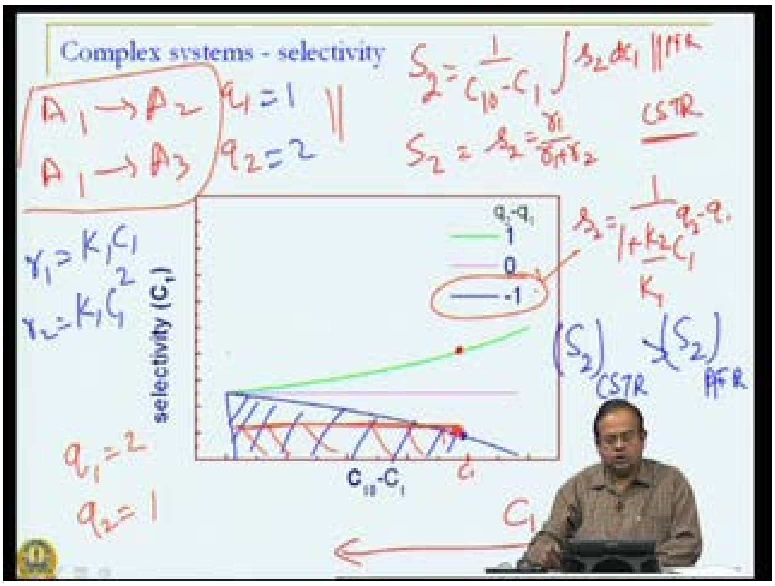

Complex systems - selectivity

Now, we can we can we can argue in a similar manner, what must be happening for, for q 2 minus q 1 negative. Once again, so for the same concentration area under the curve now, for a plug flow reactor is higher than the area of the rectangle, somewhere over here, area of this rectangle which is for CSTR; that means, for this particular case, CSTR selectivity is lower compared to plug flow selectivity; that means, both from the point of view of conversion and selectivity, plug flow reactor is better than stirred tank reactor for this particular case, when q 1, q 2 minus q 1 is a negative quantity.

So, for example, a situation where q 1 is 2 q 2 is 1; and you can now argue it along the same lines as we saw for this particular example, because 1 is square other is linear term, so which one will give you higher rate of favorable reaction. So, this particular example, tells us that, how reactor design criteria s change, when you have complex reactions.

Remember we considered a very simple prototype of a complex reaction, we did not have more than 3 species, only 2 reactions, but with that alone it is sufficient to illustrate, that things are not straight forward anymore, there has to be a compromise between conversion and selectivity, when it comes to such, such reactor behaviors.

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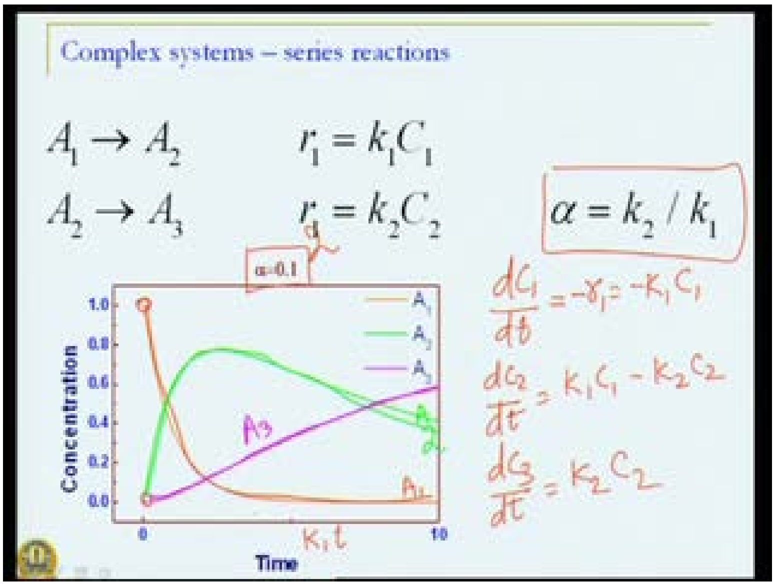

Complex systems – series reactions

$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$

$A_2 \rightarrow A_3 \qquad r_2 = k_2 C_2$

$\boxed{\alpha = k_2 / k_1}$

$$\frac{dC_1}{dt} = -r_1 = -K_1 C_1$$

$$\frac{dC_2}{dt} = K_1 C_1 - K_2 C_2$$

$$\frac{dC_3}{dt} = K_2 C_2$$

Let us, let us continue our discussion with such simple prototypes, but this time let us take example of a series reaction, so we have 2 reactions A 1 going to A 2 and A 2 going to A 3, both proceeding at rates r 1 and r 2; this this should read as r 2, rates r 1 and r 2, r 1 is K 1 C 1, r 2 is K 2 C 2; and we would let us for sake of argument for this discussion, let us say that we are conducting these reaction in a in a batch reactor. If we are conducting these reaction in a batch reactor, then we can write the mass balance equations for the batch reactor, which we had seen earlier, again assuming constant density as minus r 1 or minus K 1 C 1, d c 2 d t as K 1 C 1 minus K 2 C 2 and d c 3 d t as K 2 C 2, so these are our mass balance equations for our batch reactor.

Now, let us see how does this reaction progresses in a batch reactor, so to do that, we are going to say that, we started these reaction with some quantity of A 1 to begin with, so what we are seeing here in this particular plot, is time axis on the x and y axis represents concentration of 3 different species red or orange is A 1, green is A 2 and violet color is A 3.

So, we started this reaction with some quantity of A 1 and nothing of A 2 and A 3. To monitor the progress of these reaction, we measure it is concentrations and what you see pictorially in this in this particular graph is the simulation of these equations, simulation of these equations for value of ratio of K 2 by K 1, now it turns out that, if you make these equations dimensionless, then time can be represented as K 1 t. So, this is actually not real time, but some K 1 K 1 into t. So, if you if you dimension make these equations dimensionless a ratio, appears in the mass balance equations of K 2 and K 1 and we call that ratio as alpha; and this example or this particular graph is for value of alpha equal to 0.1.

We will do it for different values of alpha little later on, but at this point, let us look at what happens, when we have when we have value of alpha equal to 0.1. So, what we are seeing here, is A 1 is going to A 2, so A 1 is continuously decreasing as time increases, so we have we have continuous decrease in decrease in A 1, so this is my A 1. What happens to A 2? A 1 goes to A 2, so initially A 2 builds up initially A 2 builds up, but A 2 is also going to A 3, for this series reaction, so after sometime the rate of generation of A 2, fall short of rate of consumption of A 2 and therefore, there is a net consumption and A 2 starts going down, so this is what happens with A 2.

What happens with A 3? You can expect as soon as A 1 is formed, A 2 A 2 is formed, A 2 is going to A 3, so there is a gradual build up of A 3, as the reaction proceeds, so this is my this is my A 3. And that that behavior explains how these reactions proceed in the in the…

Now, let us let us bring in a more realistic situation, where we say that A 1 going to A 2 going to A 3 is my reaction, but my main product or desired product is A 2; and A 2 going to A 3 is an undesired reaction, I do not want it, but it is inheritable, that it it it happens in the reactor, so now, what we will do is the same representation of concentration versus time, we will now try to see what happens to A 2, buildup of A 2 as A 1 is getting converted or in other words, we will now see the same behavior, but instead of time, this time on x axis we have conversion of A 1 conversion of A 1 and on y axis we have yield of A 2, so we are looking at yield of A 2, versus conversion of A 1.

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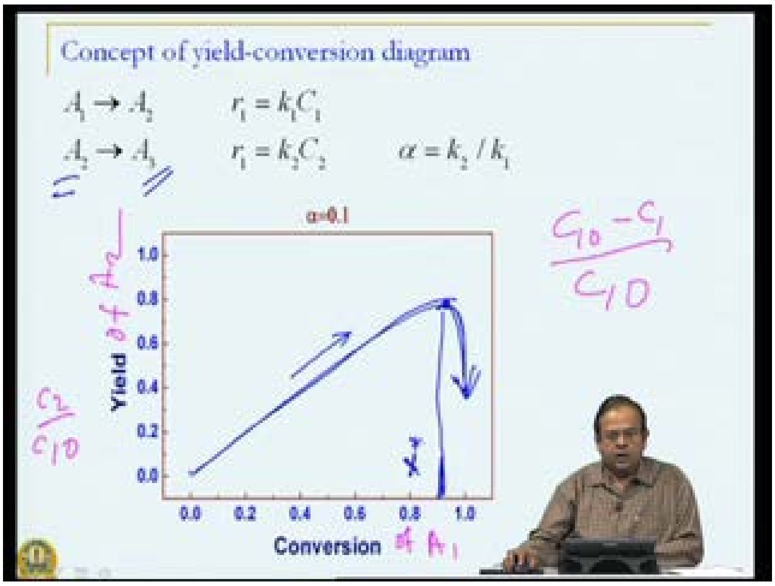

Concept of yield-conversion diagram

$A_1 \to A_2 \qquad r_1 = k_1 C_1$

$A_2 \to A_3 \qquad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$

$\frac{C_{10} - C_1}{C_{10}}$

$\frac{C_2}{C_{10}}$

How do we define yield? Suppose, we are doing a batch reaction, this is nothing but C 2 by C 1 0; and how do we define conversion, we had done this earlier, we have defined conversion as C 1 0 minus C 1 divided by C 1 0. So, we are looking at this two behavior; and what do we what do we see here, as conversion is increasing the yield is also increasing, so that means, as more and more of A 1 is getting converted, we are getting more and more of A 2.

But this increase is halted at certain value of conversion, let us say this particular value, where it reaches the peak and any conversion of A 1 beyond this value, the yield of A 2 actually decreases A 2 actually decreases from here to here. So, it is increasing from here from 0 conversion to this particular value, let us say some value of conversion x star; and beyond that value it is decreasing, why is why is that happening? If you recall, the behavior of the system from the previous plot A 1 is getting continuously converted to A 2. So, the conversion of A 1 is continuously increasing, but what is happening as a result of more and more A 2 accumulating in the system, is that more and more A 2 is now going to A 3, A 2 is going to A 3.

So, beyond this critical point, instead of A 2 accumulating in the system, it actually is now consumed and we are seeing formation of more and more of A 3. So, if this is kind of kind of system that we have with us; then it does not make any sense to go to design reactors for more than critical conversions such as this x star.

Let me relate this to, what we we saw by way of example, few slides back, that is we earlier we consider this example of hydrogenation of oil; and we saw this behavior what happens by way of conversion versus yield. This particular behavior is very similar to, what we just now saw when we considered when we considered the reaction, a simple simple kind of reaction such as A 1 going to A 2 going to A 3, that means, that hydrogenation of unsaturated oils must have somewhere in the reaction scheme, reactions of the type A 1 going to A 2 going to A 3, so which results into this kind of kind of conversion.

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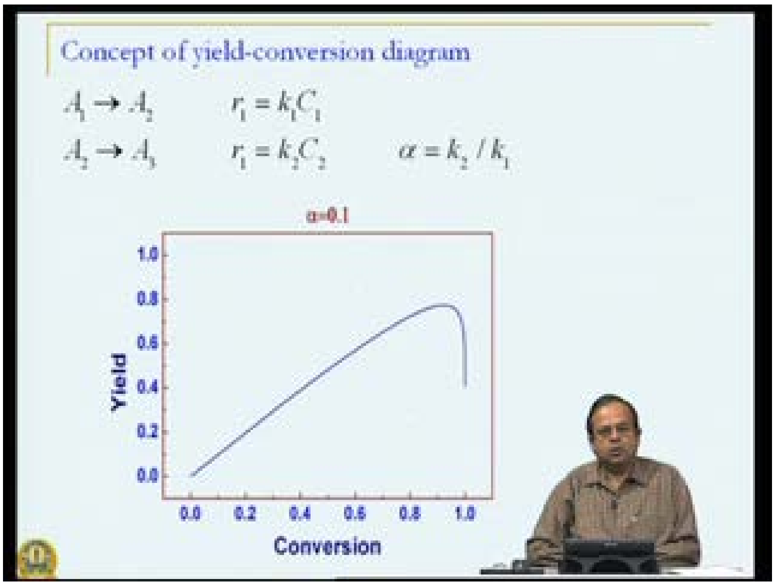

Concept of yield-conversion diagram

$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$

$A_2 \rightarrow A_3 \qquad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$

So, two lessons we learnt, when it comes to complex reactions, lesson number one that, when we have complex reactions, conversion is not the only criteria for design, we have to worry about yields selectivity s and so on. And when it comes to designing for selectivity; it is not necessary that, plug flow reactor will always be better than, a stirred tank reactor or in other words, the choice of reactor for maximizing selectivity is not necessarily same as choice of reactor for maximizing the conversion.

So, there is a balance that need to be then sort, what do we prefer more, the selectivity or conversion. And if you recall my first first session, we are more and more concerned about not making undesirable product, so it means that, we are more and more worried about selectively making the product or enhancing the selectivity, rather than the conversion.

The second lesson that we that we learnt from this particular example is that, maximizing conversion is not always the criteria, because maximum conversion often gives lower yields compared to restricted restricted conversion over here.

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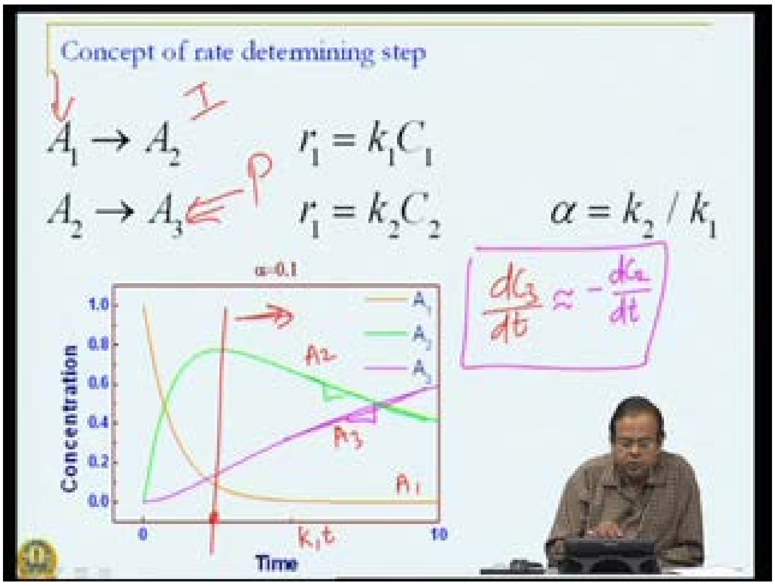

Concept of rate determining step

$A_1 \rightarrow A_2$ I $\quad r_1 = k_1 C_1$

$A_2 \rightarrow A_3 \Leftarrow$ P $\quad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$

$$\boxed{\frac{dC_3}{dt} \approx -\frac{dC_2}{dt}}$$

Let us consider this same example of A 1 going to A 2 going to A 3; and illustrates another concept which is often used, when we try to analyze complex complex reactions; and this is the concept of rate determining step, what is this what is this concept? This concept is very simple, we use this all the time in our in our, we see this or we experience this; you imagine a relay team, they are participating in 4 by 100 Olympic team or Olympic event let us say or let us say commonwealth event which is going to be shortly held in India.

Now, we know that, a performance of the relay team is determined by the weakest runner in this team; it is not determined by the fastest runner, the fastest runner may try to improve his or her performance by running even faster, but that is not going to improve the team performance, what is going to improve the team performance is if the slowest of the runners or of the teammates improves his or her performance and that, will improve the performance of the team, we know this. In fact, we should know this more so if you drive in India. You are often seeing people driving very fast, whenever they see an empty road, but they do not realize that fasting, driving faster on an empty road is not going to improve your time to go from point a to point b, because the bottleneck is somewhere else, the traffic jam is somewhere else; so, you will end up going taking the same amount of time, even if you try to go very fast on a empty road.

The point I am trying to make is that, it is the slowest step which always determines the performance of any process, when there are more than one process, when there is more than one runner, when there are more than one road we have to travel, the empty road does not determine the traveling time.

Let us, go back to our reaction kinetics and see how this applies to our reaction kinetics; and we will see this with an example, so let us let us go back to this, A 1 going to A 2, A 2 going to A 3; we are looking at the batch reactor and same dimensionless time, same dimensionless time K 1 t and concentrations of A 1 A 2 and A 2 and A 3. But this time, I am going to look at this system in a slightly different way; I am going to look at this system saying that, A 1 is my main reactant and A 3 is my main product, main product that I am interested in; and A 2 is in some intermediate which is appearing in these reaction scheme; because we said that complex reactions start from reactants, end up in products, but there are lot of intermediates in between.

So, now let us treat A 2 as an intermediate; and we are now interested in looking at, what is the rate of formation of this product what is the rate of formation of this product? So, we are looking at d C 3 d t, since it is a batch reactor that directly tells me the rate of formation of this product. So, let us look at the same results, we saw these results few minutes back, for alpha value that is the ratio of K 2 by K 1 to be 0.1, let us look at A 1, A 2, A 3. So, we saw these earlier, so A 1, A 2, A 3.

We see that, A 1 decreases, A 2 first increases and then decreases and A 3 is continuously decreasing. Now, if you look at this figure more closely; and if we look at particularly, what is happening after this particular time, sometime over here, let us not worry about what happens from the start of the reaction up to this time, but for for the time for which A 2 is A 2, the product is appearing in the reaction, quite significantly.

So, we are looking at this part of this this particular part of this curve and what do we see; we see that the rate of appearance of A 2 that is, this violet line over here. The rate is almost similar, to the rate of disappearance of A 2, that is this slope is in magnitude same as this slope only the signs are different; or in other words d C 3 d t is almost equal to minus d C 2 d t, because A 2 is consuming, so we have to put a minus sign there, so this is this is what happens when alpha is 0.1.

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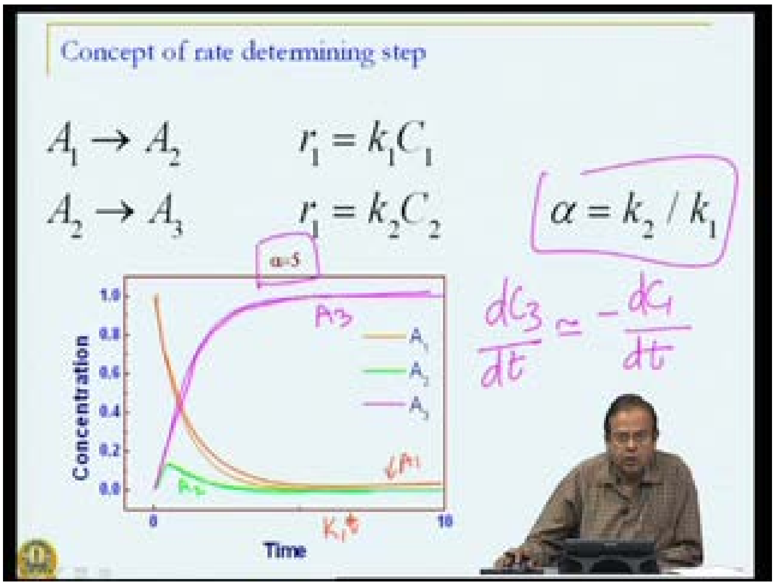

Concept of rate determining step

$A_1 \rightarrow A_2 \qquad r_1 = k_1 C_1$

$A_2 \rightarrow A_3 \qquad r_1 = k_2 C_2$

$\boxed{\alpha = k_2 / k_1}$

$\frac{dC_3}{dt} \simeq -\frac{dC_1}{dt}$

Let us, now look at what happens when alpha is 5? The same reaction, everything is same in the batch reactor, so we are now carrying out this reaction, when alpha is alpha is 5. So, once again as before A 1 is A 1 is decreasing, in fact, it is same as before, because we are looking at dimensionless time, K 1 into t.

A 2 is also initially increasing and decreasing, qualitatively same behavior as before, this is my A 2. But let us look at, what happens to, so let me go back over here, this is my A 1, this red line over here; I have A 2 and let me go back and look at what happens to A 3? A 3 is of course, qualitatively same behavior is increasing. So, whether it is alpha is 0.1 or alpha is 5, that is this ratio of K 2 by K 1 is 0.1 or 5, qualitatively behavior is same, but quantitatively there is a difference.

I think, I need not repeat myself, but write this straightaway; that in this case we see that, d C 3 d t is almost same in magnitude as d C 1 d t, but with a negative sign. So, this time, the rate of formation of C 3 is same as the rate of consumption of A 1 or C 1, when alpha is 5. In my previous example, when alpha was 0.1 d C 3 d 2 was equal to minus d C 2 d 2, so this is for alpha equal to 0.1 and let me write down, what happen when alpha is 5 alpha is 5.

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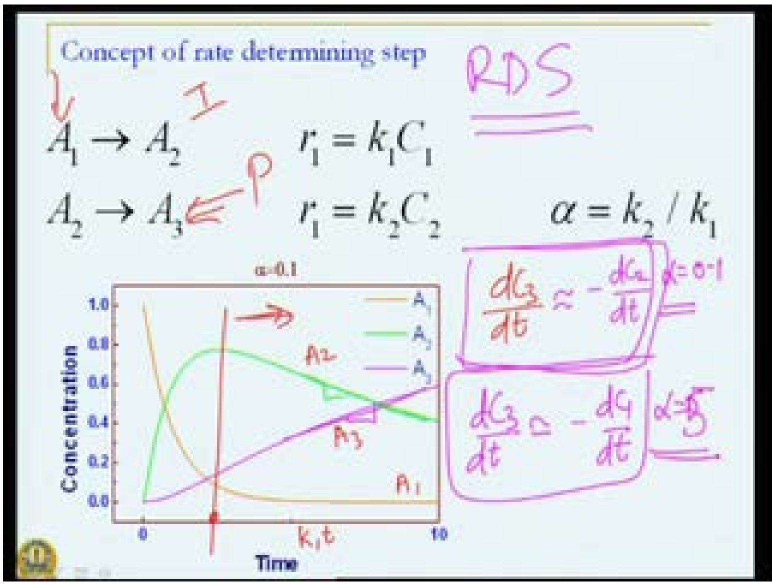

Concept of rate determining step

RDS

$A_1 \to A_2$ I $\quad r_1 = k_1 C_1$

$A_2 \to A_3$ P $\quad r_1 = k_2 C_2 \qquad \alpha = k_2 / k_1$

$\frac{dC_3}{dt} \approx -\frac{dC_2}{dt}$ $\alpha = 0.1$

$\frac{dC_3}{dt} \simeq -\frac{dC_1}{dt}$ $\alpha = 5$

Let us, examine the value of alpha, what does alpha mean? Alpha is a ratio of second reaction rate to the first reaction rate, So between these two, alpha is lower in the first case that is 0.1; that means, second reaction is substantially slower compared to the first reaction; and what happened to rate of product formation? The rate of product formation is determined by now the second reaction, because d C 3 d t is d C 2 d t; that means, rate in this particular case is determined by second reaction.

This on the contrary, when alpha is 5, the rate is determined by first reaction, what happen when alpha is 5 alpha is 5, first reaction is slower than the second reaction. So, in either case, the rate of the reaction is determined by the slower of the two reactions, if first reaction is or rather, second reaction is slow the rate of formation of A 3 is determined by the second reaction; if first reaction is slow, when alpha is 5, the rate is determined by the by the first first reaction; again the idea that, there is a rate determining step, which determines the rate of conversion to product or rate of formation of product.

This is a very useful concept and we will be using this concept time and again, when we try to analyze complex complex reactions; that is when you have large number of reactions, we will make an assumption that one of these reacting step is a slowest of all, that is my rate determining step; in fact, it is also referred to as R D S, rate determining determining step, R D S and then we will have to make certain other assumption as far as the other reactions are concerned; so, what we are saying is we have let us say 10, 15, whatever number of reactions 1 or it could be more than 1, but these 1 or more than 1 may be two steps or reactions are very slow, compared to all the other reactions.

So, we will therefore, then say that the rate of conversion of reactant to product is then determined by, the rate of this slow steps 1 or 2, whatever that may be; and then we will try to determine the kinetics of process by, further applying certain other simplifying assumptions to the remaining remaining steps; and this will be our logic, that we will follow for determining the kinetics of complex processes. What are those assumptions for remaining fast steps, we will see that in the next session, thank you.