Process design decisions and project economics

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Module - 02

Flowsheet Synthesis

(Conceptual Design of a Chemical Process)

Lecture - 10

Recycle Structure of Flowsheet (part IV) and Tutorial (part I)

Welcome we are now looking at the Flowsheet Synthesis, the Recycle Structure of the Flowsheet. In the previous lecture we dealt with the equilibrium limited processes or processes with irreversible reactions, and then we saw a how we can estimate the equilibrium conversion, and then identify the dominant design variables, that can help us take the convergent to maximum.

So, as to have as little recycle flow as possible, then we also saw some other examples in which other means are used for shifting equilibrium to favorable site such as, a continuous withdrawal of one of the products or addition of innards etcetera. And then we also saw the basic design of a compressor. Because compressor is a major piece of equipment that adds to the process once, we use a gas recycle and purchase string, we shall see in this lecture some aspects of reactor design.

This lecture I am not going to go into great details of reactor design because we do have a separate module on reactor design. We shall see some basic aspects of operation of reactor or let us say how to feed the reactants to the reactor, so as to increase the selectivity and yield of the desired product as well as to suppress, the undesired products and the reversible by products. In the initial stage the kinetic model for the reactor may not be available, because in the initial stage the most of the data comes from chemist who measures the cross conversion of the reactant limiting reactant and he tries to optimize the reaction at the point of maximum yield.

Therefore, we have to waste our material balance calculations on the basis of product distribution correlation a chemist does develop this kind of correlations in terms of temperature pressure conversion. And so what kind of reactor we should use for our process. For the initial designs, it is much useful to assume that we use the same type of reactor in the plant as used by the chemist in the laboratory, who generate the data. And then we have to waste the reactor size on the reaction half life measured by the chemist reaction half life is essentially.

The time that is required for about 63.2 percentage conversion of the limiting reactor, if the reactor is adiabatic we have to base the design on the isothermal temperature, which is the average of inlet and outlet temperature or the average of inlet and outlet rate constant.

In the previous lecture, when we dealt with reactor heat effects, we saw the basic decision of operation of reactor in either isothermal mode or the adiabatic mode. Assuming that all heat of the reaction is absorbed by the reactor contents, after absorption of all the heat, if the temperature of the reactor contents does not go beyond the limit. Then we can very easily go for the adiabatic operation, this kind of analysis is quite crude though in most of the cases the reactor cost is not as important as the product distribution aspects and therefore, we have to look at the sensitivities until we can justify the additional work or the kinetic model, that we need to develop for the rigorous reactor design. Now, as far as the cost estimation is concerned, you can very easily use the correlations develop for pressure vessel for estimation of the reactors. Now let us see some basic design guidelines for the reactor.

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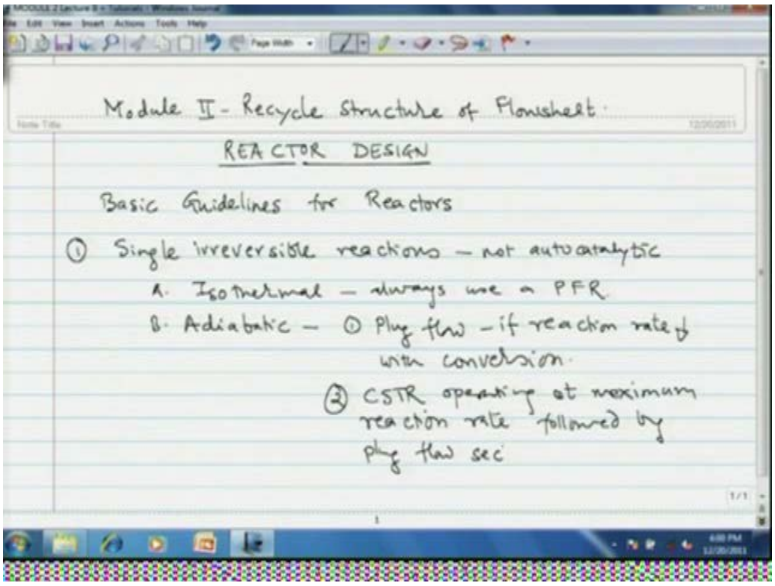

Module II - Recycle Structure of Flowsheet.

REACTOR DESIGN

Basic Guidelines for Reactors

① Single irreversible reactions - not autocatalytic
  A. Isothermal - always use a PFR
  B. Adiabatic - ① Plug flow - if reaction rate $\downarrow$ with conversion.
    ② CSTR operating at maximum reaction rate followed by plug flow sec

Some of these things, you have already seen in the chemical reaction engineering course. So, this will be repetition depending on what kind of reactions are occurring in the reactor you have to base the choice of the reactor.

In the simplest case, where you have single irreversible reactions which are not autocatalytic, if the reaction is isothermal with not much heat liberated or absorbed you can always use Pluck Flow Reactor PFR. If the reaction has rate has significant heat effects then go for adiabatic mode, pluck with pluck flow, if reaction rate decreases with conversion that means, the amount of heat that is liberated goes down. And the reactor load reactor heat load goes down.

Reactor reaction rate decreases with conversion or you can use a CSTR operating at maximum reaction rate, where the rate of heat liberation will also be maximum. So, the heat load will be maximum followed by the pluck flow reaction, pluck flow section once the rate of reaction slows down.

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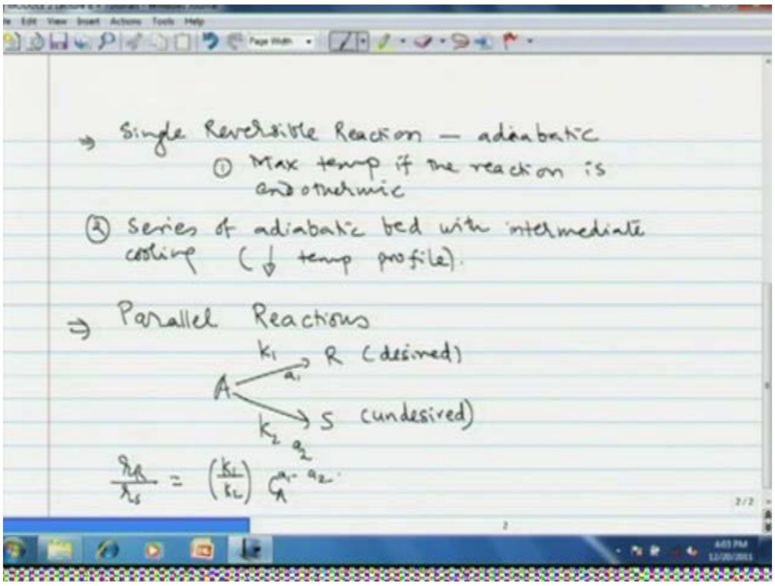

⇒ Single Reversible Reaction — adiabatic

① Max temp if the reaction is endothermic

② Series of adiabatic bed with intermediate cooling (↓ temp profile).

⇒ Parallel Reactions

$$A \xrightarrow[a_1]{k_1} R \text{ (desired)}$$

$$A \xrightarrow[a_2]{k_2} S \text{ (undesired)}$$

$$\frac{r_R}{r_S} = \left(\frac{k_1}{k_2}\right) C_A^{a_1 - a_2}$$

If you have single reversible reaction, operating in adiabatic mode use maximum temperature, if the reaction is endothermic. So, that you have maximum equilibrium conversion or alternatively, if the reaction is exothermic. Then you have to use a series of adiabatic beds with intermediate cooling. So, as to enhance the equilibrium conversion by applying intermediate cooling, you are essentially working with reducing temperature profile. Now, these are the guidelines in perhaps the luckiest situation, when you have a single reaction with the reversible or irreversible, but in most of the cases you will have multiple reactions.

Now let us consider a case of parallel reactions and the reaction, that we take is a goes to R, which is desired product and A goes to S, which is undesired product the rate constant for A to R is K 1 and rate constant for A to S is K 2. The order of reaction is a 1 and a 2 made, now the if you take the ratio of the two reactions, A goes to R and A goes to S plus, then we get K 1 by k 2 into C A raise to a 1 minus a 2. Now depending on the relative values of the rate constants as well as the order of reactions, we have to choose the proper concentrations of the two reactants.

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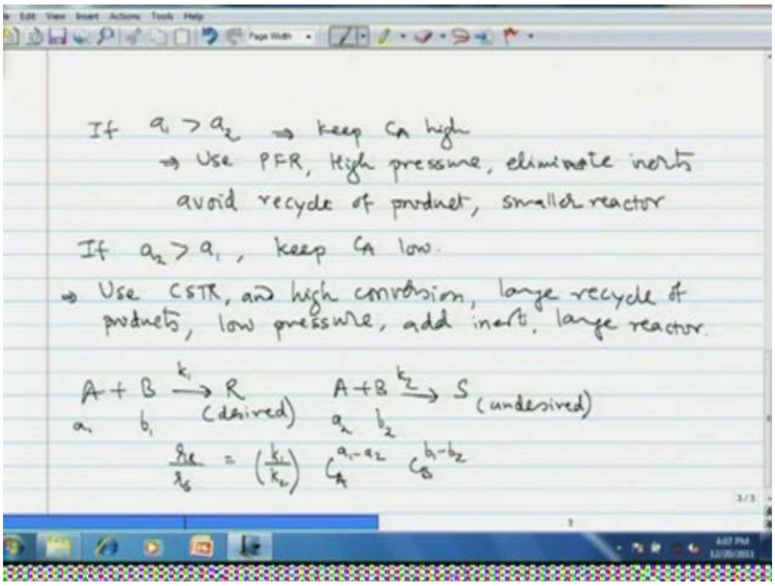

If $a_1 > a_2$ ⇒ keep C_A high

⇒ Use PFR, High pressure, eliminate inerts avoid recycle of product, smaller reactor

If $a_2 > a_1$, keep C_A low.

⇒ Use CSTR, and high conversion, large recycle of products, low pressure, add inert, large reactor.

$$\underset{a_1}{A} + \underset{b_1}{B} \xrightarrow{k_1} \underset{\text{(desired)}}{R} \qquad \underset{a_2}{A} + \underset{b_2}{B} \xrightarrow{k_2} S \text{ (undesired)}$$

$$\frac{r_R}{r_S} = \left(\frac{k_1}{k_2}\right) C_A^{a_1-a_2} \, C_B^{b_1-b_2}$$

If a 1 is greater than a 2, we have to keep the concentration of a high, so that we favor the desirable product. Now how we can achieve it, you can use a pluck flow reactor or use high pressure. If it is gas reaction try to eliminate the innards, which we decrease the partial pressure of your reactions or you avoid recycle of products, which would again lower the partial pressure or you can use as smaller reactor. So, as to have higher concentration of the reactants, this is when a 1 is greater than a 2.

Now, incase a 2 is greater than a 1 or a 1 is less than a 2, then to favor formation or R we have to keep C A low the concentration of limiting reactant, A has to kept low. Now how we can do that, we use CSTR, so that the concentration goes down of all the reactant.

And high conversion which means, the residence time in the reactor is also high, than you can decrease the partial pressure or concentration of the limiting reactant by large recycles of product. Then you can use low pressure or as I mentioned in the previous lecture, you can add some innards, which will reduce the partial pressure and lastly use a large reactor. That will reduce the effective concentration of the limiting reactant, so that is about the single parallel reaction with a single reactant.

Suppose, you have several reactants like, we have a reaction A plus B goes to R and we have a reaction A plus B goes to S; again R is a desired product and S is the undesired or waste product. Now, in this case let us say the rate constants are K 1 and K 2 and now, we have to take into consideration the order of the reaction with respect to both reactants.

Let us say the order of reaction, first reaction with respect to A is a 1 with respect to B is b 1. And then for the second reaction the order with respect to A is a 2 and order with respect to B is b 2. Now, if we take the ratio of the rates of the two reactions, similar way as we did earlier, then we get K 1 by K 2 into C A raise to a 1 minus a 2, C B raise to b 1 minus b 2. Now here we have more alternatives depending on relative values of relative numerical values of a 1 and a 2, b 1 and b 2.

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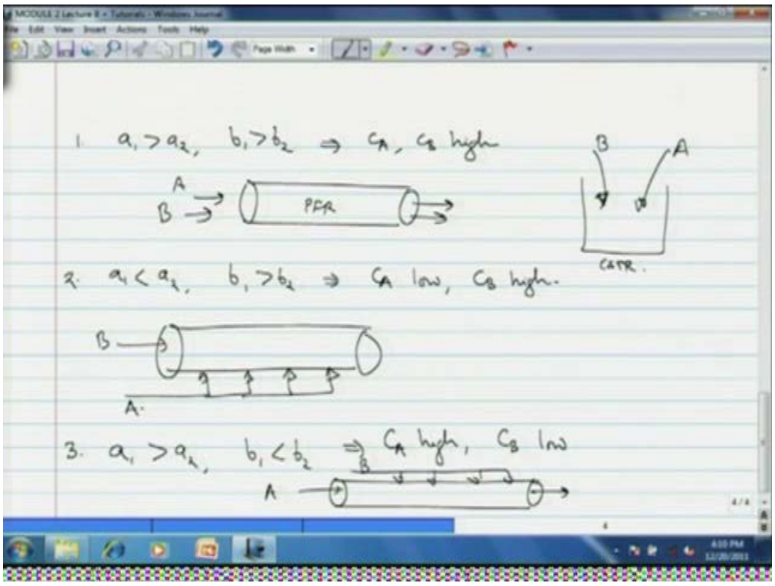

1. $a_1 > a_2$, $b_1 > b_2 \Rightarrow C_A, C_B$ high

2. $a_1 < a_2$, $b_1 > b_2 \Rightarrow C_A$ low, C_B high.

3. $a_1 > a_2$, $b_1 < b_2 \Rightarrow C_A$ high, C_B low

Let us say a 1 is greater than a 2 and b 1 is greater than b 2. Now in this situation we have to keep both C A and C P high, we can again use this same strategies as we state earlier that you can use pluck flow reactor, where both A and B are added at the same time. Let us see how pluck flow reactor and then both A and B are added at the same time, that will keep that, will give you maximum of the desired product or if you have a CSTR. Then you add all of A and all of B together that means, the net concentration is high in case of a CSTR.

Now, second possibility if a1 is less than a 2 and b 1 is greater than b 2. Now in this case we have to keep C A low, but C P high, now how we can achieve this a simple way to have this is to have a pluck flow reactor in which B enters at the inlet and A is added at various locations.

So, that at any particular location in the reactor the concentration of A is low in the third situation, where we have a1greater than a 2, but b 1 less than b 2, we had to go for high

C A and low C B. You can exactly reverse the strategy used earlier and instead of B entering at the PFR inlet, A enters at inlet and then B is added at different locations. So, that at any particular location, the net concentration of B is less.

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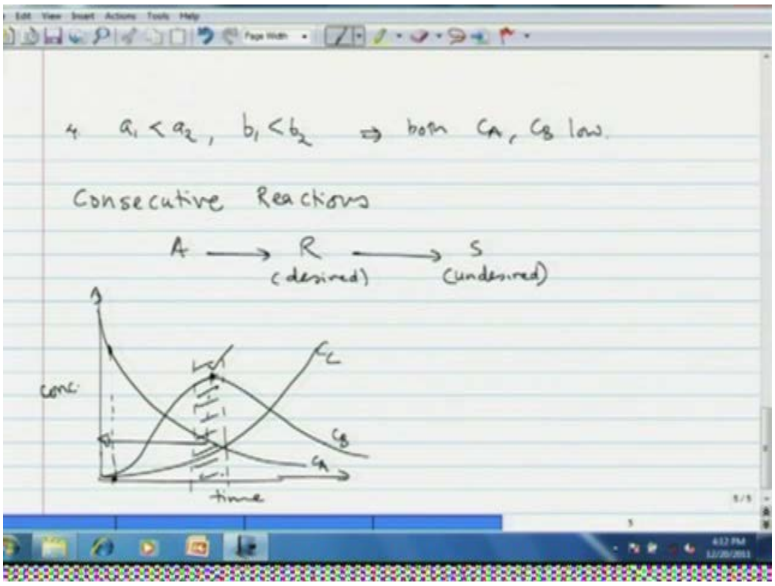

4. $a_1 < a_2$, $b_1 < b_2$ $\Rightarrow$ both C_A, C_B low.

Consecutive Reactions

$$A \longrightarrow \underset{\text{(desired)}}{R} \longrightarrow \underset{\text{(undesired)}}{S}$$

And finally the case where, a 1 is less than a 2 and b 1 is less than b 2. Now in this case we have to keep both C A and C B low. Now you can have this by using a CSTR, but very slow addition of A and B into it, so that at any point of time throughout the progress of the reaction the net concentrations are small.

This is as far as the parallel reactions from the reactions, you may also have consecutive reactions, like A goes to R, which is a desired product, which then gets converted to S which is undesired product you might recall that in a previous lecture we have dealt with such kind of system.

The typical concentration profile in this particular case, would look like this concentration of a continuously decreases with time concentration of B, the intermediate product shows a maxima and concentration of C continuously increases with time as the reaction proceeds. Now in case of a chemist we would like to give you maximum data in this range. The shaded range the yield of desired product is maxima however, as we have seen.

The point of maximum yield may not be the point of most optimum operation, because by the time we reach the maximum concentration of the desired product. A Large amount of reactant is already converted as is shown and if the value addition from A to B is marginal, which is the case for many petrochemical processes.

We would not like to have conversion of a, which is a valuable reactant into the waste product, therefore although the point of maximum yield. May be this the point of optimum operation could be at much lower conversion, which would suppress the formation of the undesired product. Now, in this case of course, we are going to have large recycle flow, but that is still affordable compared to the loss of reactant to the base product. So, this is as far as the consecutive reactions are concerned. So, in this case we have to solve the equations that we are going to do in the tutorial and see as what is the optimum time for maximum yield and so on. So, this point we leave here by with this qualitative discussion.

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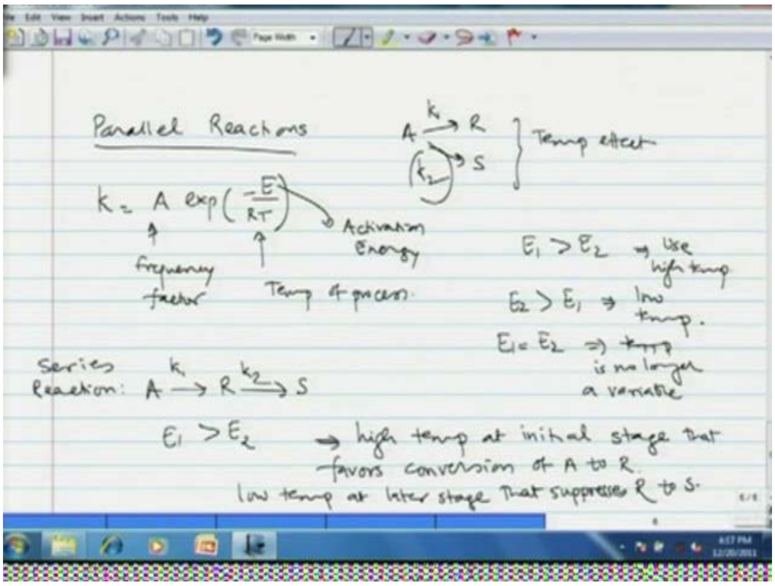

Parallel Reactions

$A \xrightarrow{k_1} R$, $A \xrightarrow{k_2} S$ } Temp effect

$k = A \exp\left(\frac{-E}{RT}\right)$

A: frequency factor

E: Activation Energy

T: Temp of process.

$E_1 > E_2 \Rightarrow$ use high temp

$E_2 > E_1 \Rightarrow$ low temp.

$E_1 = E_2 \Rightarrow$ temp is no longer a variable

Series Reaction: $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

$E_1 > E_2$ → high temp at initial stage that favors conversion of A to R.
low temp at later stage that suppresses R to S.

In some cases the temperature effect comes into picture, like let us say you have a parallel reactions as earlier A goes to R and a goes to S. Now how we can shift the product distribution by shifting temperature let us say the rate constants of reaction are K 1 and K 2 K 1 for the desired process and K 2 for a undesired product.

Now, any constant can be written in this way, A is the frequency factor the equation E is the activation energy, R is the gas constant and T is the temperature of the process. Now if E 1 is greater than E 2, if the activation energy for a to R reaction is higher than activation energy for A to S reaction. Use of high temperature will favor the desired product, because due to high E1 the rate will increase faster with temperature than compared to the second reaction.

However, if E 2 is greater than E 1 the reverse we prefer low temperature. So, that the rate constant of the undesired reaction is suppressed. In the case, where even is equal to E 2, then temperature is no longer a variable because shift of temperature to any value will modify the rate of the both the reactions to the same extents. So, that K 1 by K 2 a ratio of rate constants remains the same. So, that point we have noted if E 1 equal to E 2 temperature is no longer a variable.

Now, this is for the parallel reaction let us say we have series reactions, then how we can use temperature for shifting the equilibrium, if E1 is greater than E2, then we have to use higher temperature at the initial stage of the reaction, that will favor conversion of A to R, but lower temperature in the later stage of the reaction which will suppress conversion of R to S. That point you note higher temperature at initial stage or initial time that favors conversion of A to R and low temperature at later stage, that suppresses R to S.

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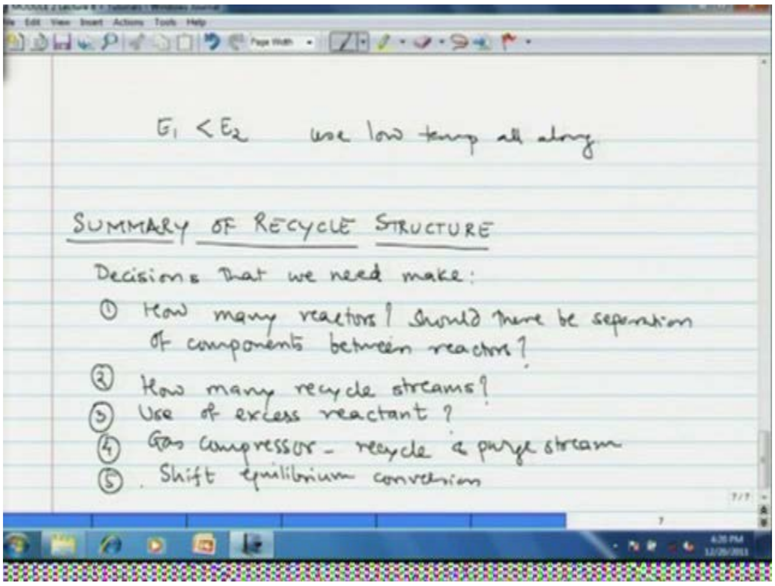

$E_1 < E_2$ use low temp all along

SUMMARY OF RECYCLE STRUCTURE

Decisions that we need make:

① How many reactors? Should there be separation of components between reactors?
② How many recycle streams?
③ Use of excess reactant ?
④ Gas compressor - recycle & purge stream
⑤ Shift equilibrium conversion

On the other hand if E1 is less than E 2, then we have to use low temperature all along. So, that the conversion of A to R is favored, but R to S is suppressed. So, these are some of the basic guidelines, that we can have for the reactor configuration or reactor design as

I said we have a module on reactor reactors after this. So, we are going to treat this topic with greater detail in that particular module. So, this essentially finishes our discussion on flow sheet synthesis, I would like to summarize what we have seen in the recycle structure of flow sheet.

Before we proceed for tutorial session summary of recycle structure, we have essentially seen the questions or the decisions. That we need to make to fix the recycle structure of the flow sheet affix the cost of operation significantly, because the recycle structure decides the separation system and also the cost of recycling.

The decisions that we need it to make for deciding the recycle structure, the flow sheet is how many reactors, then should there be separation of any component between the reactors, then the next question that we dealt with was how many recycles streams. If two components which are essentially in the same phase liquid or solid or gas are being recycled at the same point of the process. There is no point in separating them they can go in the same stream.

So, that is the logic behind the number of recycle streams. Then use of excess reactant so, as to convert. So, as to force conversion of the limiting reactant to completion or to shift the equilibrium and then the recycle of the unconverted reactant the gas compressor recycle and purge stream. Then we saw the equilibrium limited process or the processes with equilibrium reactions and then we saw how to shift the equilibrium conversion for the favorable product. And finally, we saw some basic guidelines of reactor operation

So, this completes the module 2 of this course the theory part and now we shall see some problems based on the theory, that we learnt. We have essentially seen the three stages of the flow sheet synthesis. The first stage was to decide whether to go for a batch processor continuous process, then the next was the input output structure of the flow sheet and then the recycle structure of the flow sheet that very stages of the flow sheet synthesis. We identified certain aspects of the process which affect the flow sheet design.

The first aspect that we identified was that of the selectivity rarely, you will find the process in which a single reaction occurs rarely, you will find a process in which the there is only a single product. There are always large number of products, some are desired, some are undesired. There are always multiple reactions and therefore, the selectivity is a very important aspect of the process design. Now, we shall see some problems on estimation of selectivity as a function of design variables.

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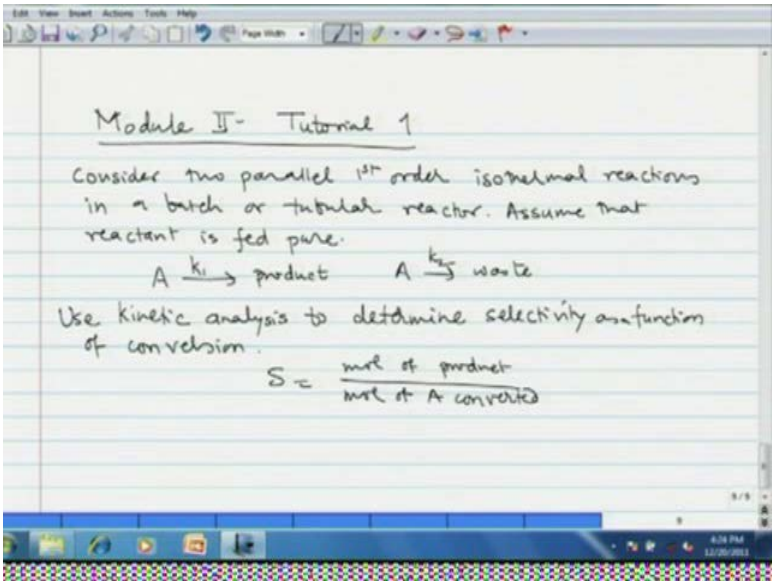

Module II - Tutorial 1

Consider two parallel 1st order isothermal reactions in a batch or tubular reactor. Assume that reactant is fed pure.

$A \xrightarrow{k_1} \text{product} \qquad A \xrightarrow{k_2} \text{waste}$

Use kinetic analysis to determine selectivity as a function of conversion.

$$S = \frac{\text{mol of product}}{\text{mol of A converted}}$$

Now, let us see a simple problem, I am writing now, the problem definition consider two parallel first order isothermal reactions in a batch or tubular reactor and we assume that the react the reactant that is fed is pure. The reactions are A goes to product, the desired product and A goes to waste the undesired product. The rate constants are K 1 and K 2 and we have to use kinetic analysis to determine the selectivity as a function of conversion. So, the selectivity S is defined as mols of product divided by mols of A converted.

I already mentioned to you different definitions of selectivity. So, before you use data in literature you have to make sure as how selectivity is defined selectivity can also be defined in an alternate way that mols of desired product divided by mols of the of undesired product for. But however, in the present situation, we are defining selectivity as mols of the product divided by mols of A converted. Now, let us start the analysis.

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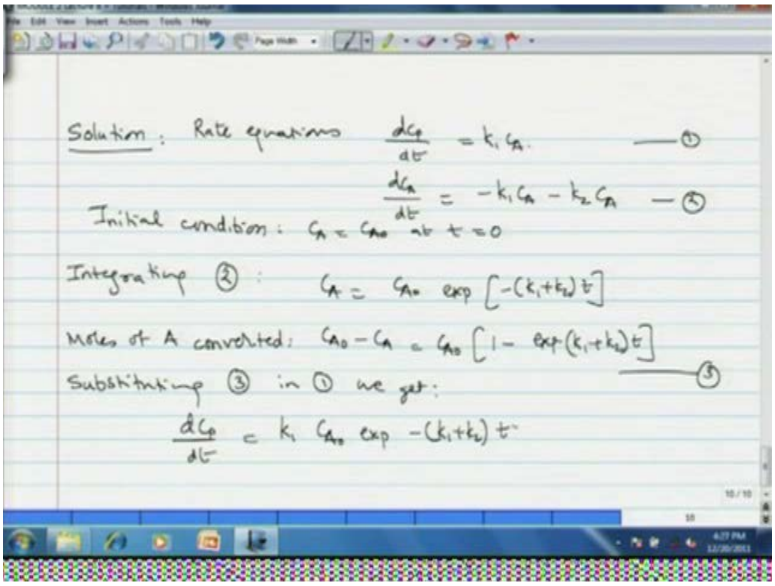

Solution: Rate equations $\frac{dC_P}{dt} = k_1 C_A$ — ①

$\frac{dC_A}{dt} = -k_1 C_A - k_2 C_A$ — ②

Initial condition: $C_A = C_{A0}$ at $t = 0$

Integrating ②: $C_A = C_{A0} \exp\left[-(k_1+k_2)t\right]$

Moles of A converted: $C_{A0} - C_A = C_{A0}\left[1 - \exp(k_1+k_2)t\right]$ — ③

Substituting ③ in ① we get:

$$\frac{dC_P}{dt} = k_1 C_{A0} \exp -(k_1+k_2)t$$

Let us write the rate equations d c p by d t, where p denotes the desired product is equal to K 1 into C A d c a by d t is equal to minus K 1 into C A minus K 2 into C A, because A is getting consumed through two reactions. So, you had two expressions the initial condition is C A equal to C A naught at t equal to 0. So, well you can integrate, the equation second equation first and then put that solution in the first equation. So, integrating two equation two, we get C A equal to C A naught exponential minus K 1 plus K 2 into t.

Now, mols of a converted are C A naught into C A naught minus C A. Therefore, ca naught into 1 minus exponential minus K1 plus K2 into t and now we substitute this expression we number this as 3. So, substituting 3 in 1 we get d c p by d t equal to K 1 into C A naught into exponential minus K 1 plus K 2 into t.

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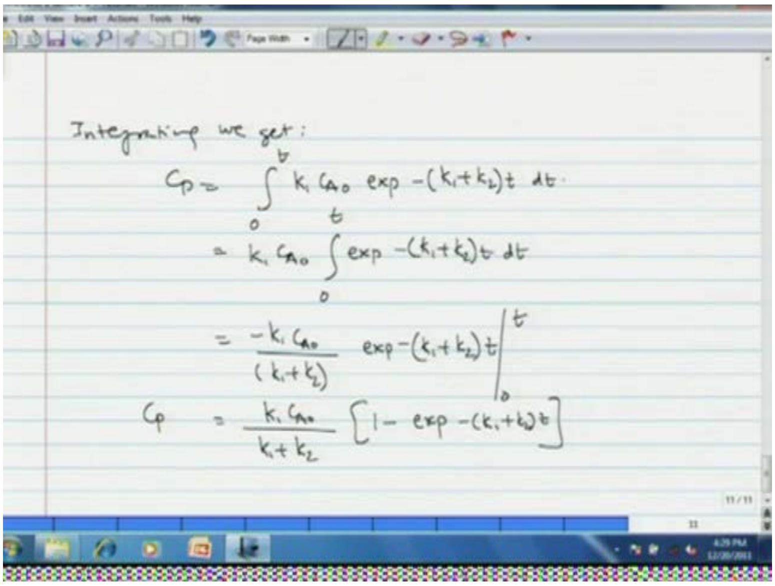

Integrating we get:

$$C_p = \int_0^t k_1 C_{A0} \exp -(k_1+k_2)t \, dt$$

$$= k_1 C_{A0} \int_0^t \exp -(k_1+k_2)t \, dt$$

$$= \frac{-k_1 C_{A0}}{(k_1+k_2)} \exp -(k_1+k_2)t \Big|_0^t$$

$$C_p = \frac{k_1 C_{A0}}{k_1+k_2} \left[1 - \exp -(k_1+k_2)t\right]$$

And now integrate C p is equal to integral K 1 into C A naught exponential minus K1 plus K2 into t d t. So, the integration limits are 0 to t, we take K1 C A naught outside 0 to t exponential minus K 1 plus K2 into t d t. The integral is 1 by K 1 plus K 2 exponential minus K 1 plus K 2 into t with limits 0 to t and done, K 1 into CA naught divided by K1 plus K 2 into 1 minus exponential K 2 into t. So, these are the number of mols of product that are of the concentration of the desired product.

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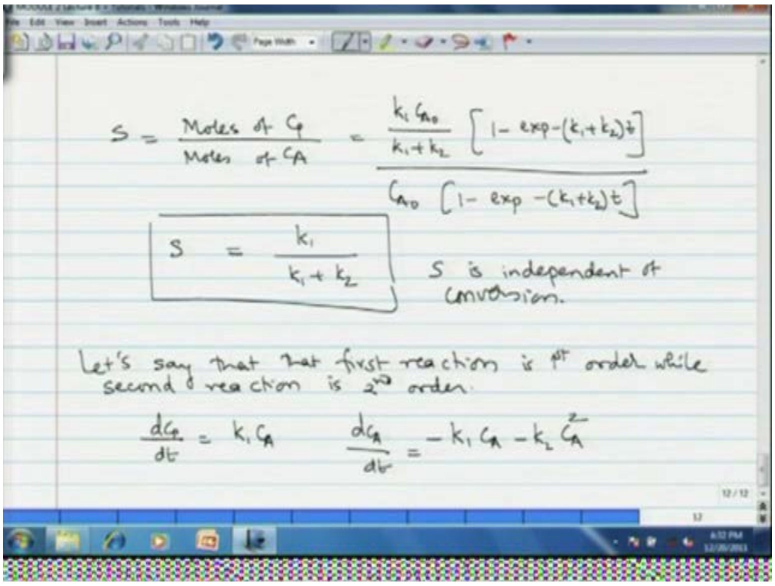

$$S = \frac{\text{Moles of } C_p}{\text{Moles of } C_A} = \frac{\frac{k_1 C_{A0}}{k_1+k_2}\left[1-\exp -(k_1+k_2)t\right]}{C_{A0}\left[1-\exp -(k_1+k_2)t\right]}$$

$$\boxed{S = \frac{k_1}{k_1+k_2}}$$

S is independent of conversion.

Let's say that that first reaction is 1st order while second reaction is 2nd order.

$$\frac{dC_p}{dt} = k_1 C_A \qquad \frac{dC_A}{dt} = -k_1 C_A - k_2 C_A^2$$

We have to substitute this in the definition of selectivity S is equal to mols of C p divided by mols of A or C A, that is K 1 into C A naught divided by K 1 plus K 2 into 1 minus exponential minus K1 plus K 2 into t divided by C A naught into 1 minus exponential minus K 1 plus K 2 into t. Now this simplifies to S is equal K 1 plus K 1 divided by K 1 plus k 2. This result is rather peculiar because you do not see here the conversion S is independent of conversion that point you note. So, the selectivity throughout reaction remains the same, now let us see slight modification of this problem.

Now, let us say that the first reaction is first order as earlier, but the second reaction is second order and let us see how selectivity gets modified, we again start with the rate expressions d c p by d t is equal to K 1 into C A. However, d c a by d t is now minus K 1 into C A minus K 2 into C A square because the contraction is second order.

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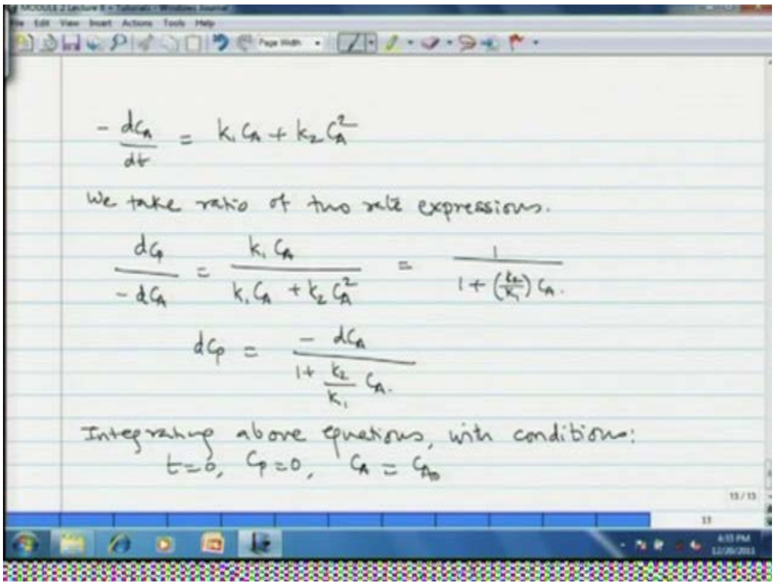

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A^2$$

We take ratio of two rate expressions.

$$\frac{dC_p}{-dC_A} = \frac{k_1 C_A}{k_1 C_A + k_2 C_A^2} = \frac{1}{1+\left(\frac{k_2}{k_1}\right) C_A}.$$

$$dC_p = \frac{-dC_A}{1+\frac{k_2}{k_1} C_A}.$$

Integrating above equations, with conditions:

$t=0,\ C_p=0,\ C_A = C_{A0}$

Now, minus d c a by d t is equal to K 1 into C A plus K 2 into C A squared, now what we do is that we take the ratio of the two rate expression. So, d c p divided by minus d c a is equal to K 1 into C A divided by K 1 into C A plus K2 into C A squared or rearranging this, we get 1 divided by 1 plus K 2 by K 1 into C A, then we separate variables. So, we have an equation to integrate and we have two initial conditions at t equal to 0 C p equal to 0 and C A equal to C A naught.

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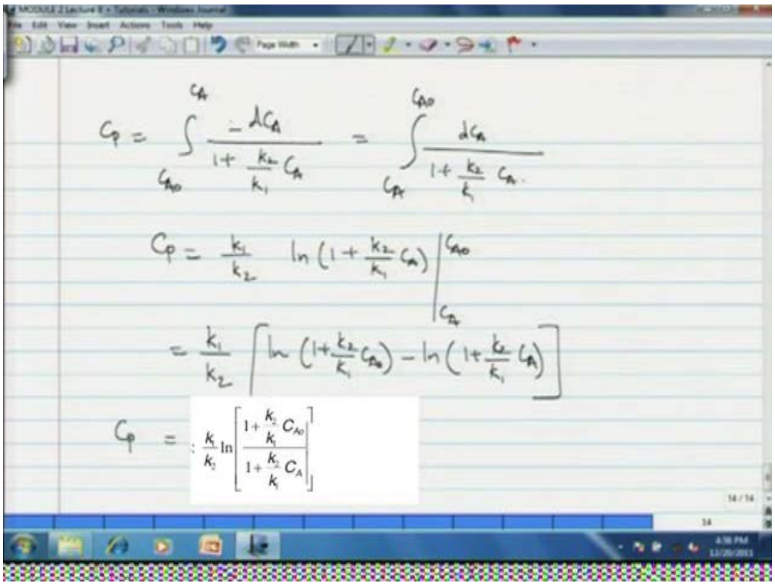

$$C_p = \int_{C_{A0}}^{C_A} \frac{-dC_A}{1+\frac{k_2}{k_1}C_A} = \int_{C_A}^{C_{A0}} \frac{dC_A}{1+\frac{k_2}{k_1}C_A}.$$

$$C_p = \frac{k_1}{k_2} \ln\left(1+\frac{k_2}{k_1}C_A\right)\Bigg|_{C_A}^{C_{A0}}$$

$$= \frac{k_1}{k_2}\left[\ln\left(1+\frac{k_2}{k_1}C_{A0}\right) - \ln\left(1+\frac{k_2}{k_1}C_A\right)\right]$$

$$C_p = \frac{k_1}{k_2}\ln\left[\frac{1+\frac{k_2}{k_1}C_{A0}}{1+\frac{k_2}{k_1}C_A}\right]$$

So, then we have the integrated expression, C p is K 1 by K 2 into l n 1 plus K 2 by K 1 into C A. The limits are C A naught to C A, but we have observed the negative sign here to reverse. The limits and then what we get is the final integral.

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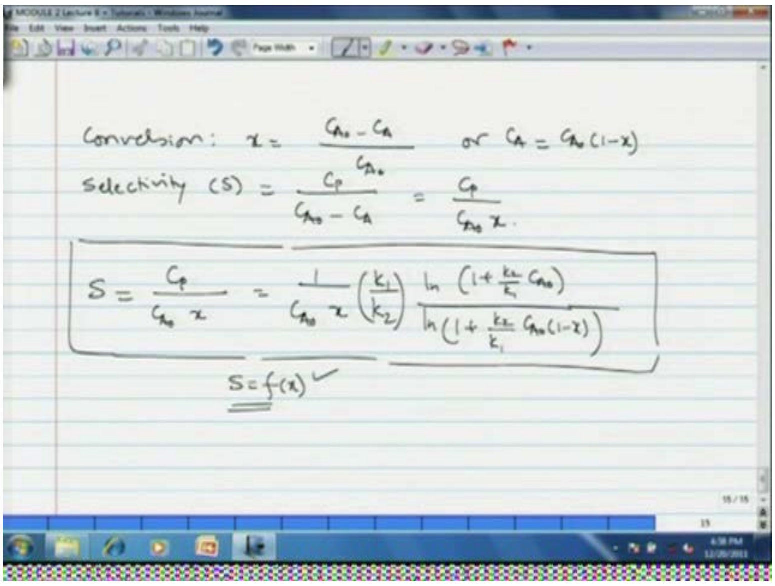

Conversion: $x = \frac{C_{A0}-C_A}{C_{A0}}$ or $C_A = C_{A0}(1-x)$

Selectivity $(S) = \frac{C_p}{C_{A0}-C_A} = \frac{C_p}{C_{A0}\,x}.$

$$\boxed{S = \frac{C_p}{C_{A0}\,x} = \frac{1}{C_{A0}\,x}\left(\frac{k_1}{k_2}\right)\frac{\ln\left(1+\frac{k_2}{k_1}C_{A0}\right)}{\ln\left(1+\frac{k_2}{k_1}C_{A0}(1-x)\right)}}$$

$$\underline{\underline{S = f(x)}}\ \checkmark$$

Now let us substitute both C A and C P in the definition of selectivity but before that we defined conversion x as C A naught minus C A initial concentration of a minus concentration at any time t divided by initial concentration or in, other words C A equal to C A naught into i minus x.

So, the selectivity S is defined as C p divided by C A naught minus C A rise in concentration of product p divided by the reduction in concentration of A. Now if you multiply this concentrations by volume will get number mols. So, this is initially same as number of mols of product p form divided by mols of A converted.

So, this is C p into C A naught into x and then we substitute all that we have we substitute C p, we substitute for C, S is equal to C p divided by C A naught into x. So, 1 divided by C A naught into x into K 1 by K 2 ln 1 plus K2 by K 1 into CA naught divided by l n 1 plus K 2 by i k 1. Now instead of C A, here we put ca naught to 1 minus x and this goes the result, now here you will find thus selectivity is the function of conversion, which was in the earlier case here, you see x on the right hand side.

So, here the selectivity changes with the conversion, so we have to find the optimum residence time in the reactor. So, as to have the maximum production of the desired product. Now, this was the determination of selectivity in parallel reactions, now let us try to see the same thing in consecutive reactions.

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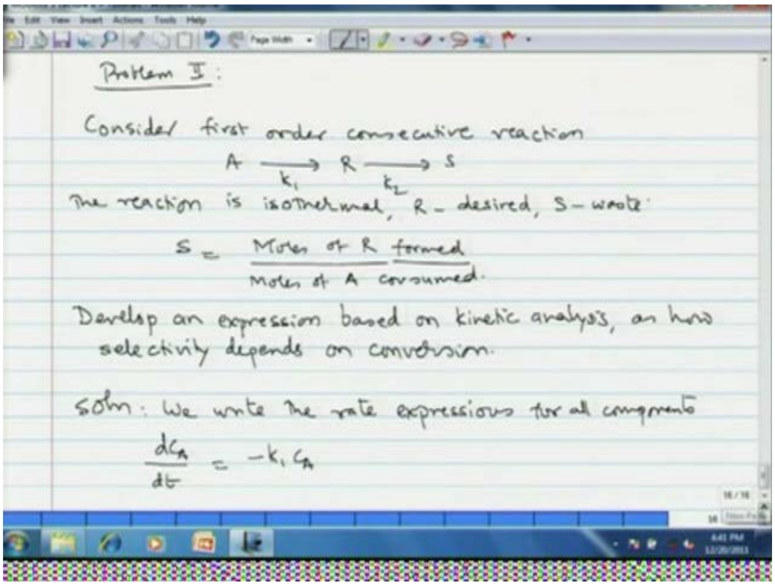

Problem II :

Consider first order consecutive reaction

$$A \xrightarrow[k_1]{} R \xrightarrow[k_2]{} S$$

The reaction is isothermal, R - desired, S - waste

$$S = \frac{\text{Moles of R formed}}{\text{Moles of A consumed}}$$

Develop an expression based on kinetic analysis, on how selectivity depends on conversion.

soln : We write the rate expressions for all components

$$\frac{dC_A}{dt} = -k_1 C_A$$

Consider this is problem two, consider first order consecutive reaction A goes to R goes to S with constants given K 2 the reaction is isothermal, R is a desired product and S is the waste product. Now again selectivity is defined as mols of R, which is desired product divided by mols of A, mols of R form divided by mols of A consumed and our task is to develop an expression based on kinetic analysis as how selectivity depends on conversion.

Now our approach is exactly the same as earlier, we have to first write the rate equations for all the three components rate expressions for all components d c a by d t is equal to minus K 1 into C A, we assume all reactions to first order.

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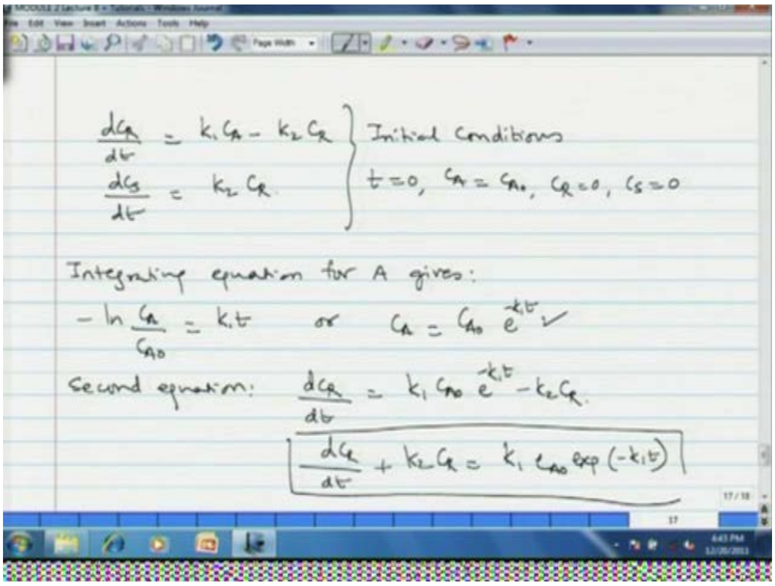

$$\left.\begin{aligned}\frac{dC_R}{dt} &= k_1 C_A - k_2 C_R\\ \frac{dC_S}{dt} &= k_2 C_R\end{aligned}\right\}$$

Initial conditions

$t = 0,\ C_A = C_{A0},\ C_R = 0,\ C_S = 0$

Integrating equation for A gives:

$$-\ln\frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0}\, e^{-k_1 t}\ \checkmark$$

Second equation: $\dfrac{dC_R}{dt} = k_1 C_{A0}\, e^{-k_1 t} - k_2 C_R$

$$\boxed{\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} \exp(-k_1 t)}$$

We also assume that whole process of isothermal, so effects towards d c r by d t is equal to K1 into C A minus K 2 into C R and then d c s by d t is equal to K 2 into C R. Then initial conditions are at t equal to 0, C A equal to C A naught C R equal to 0 and C S is equal to 0. Now integrating equation rate expression for A, gives minus ln C A by C A naught equal to K 1 t or C A equal to C A naught e to the power minus K 1.

Now, the second equation, that is a equation for R, now we substitute this particular expression for C A there. So, what we have is this if we rearrange then what we have is this. Now, if we see what type of differential equation is this expression for C R.

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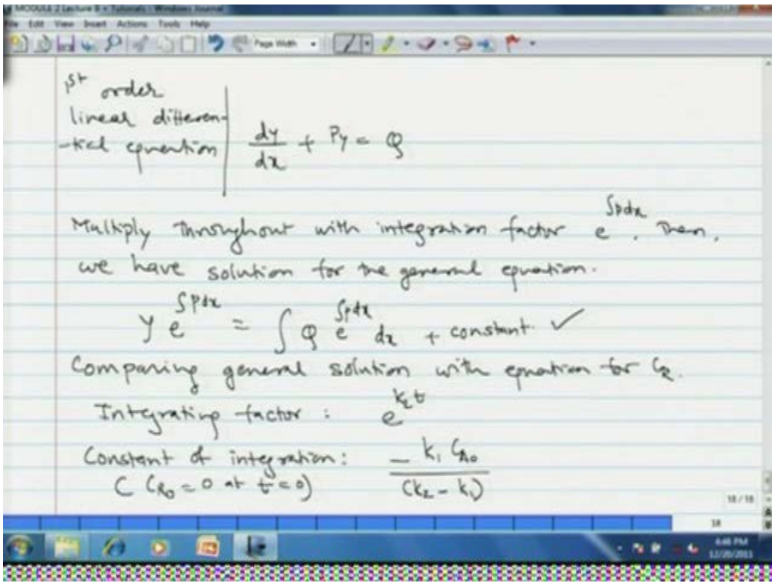

1st order linear differential equation $\frac{dy}{dx} + Py = Q$

Multiply throughout with integration factor $e^{\int P dx}$. Then, we have solution for the general equation.

$$y e^{\int P dx} = \int Q e^{\int P dx} dx + \text{constant} ✓$$

Comparing general solution with equation for C_R.

Integrating factor : $e^{k_2 t}$

Constant of integration: $\frac{-k_1 C_{A0}}{(k_2 - k_1)}$

C ($C_{R0} = 0$ at $t = 0$)

Then, we find that the expression in very much similar the differential equation in the form d y by d x plus P y is equal to Q. This is linear differential equation in the general from and what we have is very similar. Now what we do is that we multiply throughout with integration factor to the power integral P d x and then we have a solution for the above general equation as y into integral e to the power integral, P d x is equal to l q into e to the power integral P d x into d x plus constant.

So, this is the solution of general form of this particular equation. Now if we compare this general solution to the equation, we have for CR comparing general solution with equation for C R, we will find that the integrating factor is e to the power K2 into t, which is similar to e to the power P d x. And then the constant of integration with condition C r naught equal to 0 at t equal to 0. The initial condition the constant of integration is minus K 1 into C R naught divided by K 2 minus K 1.

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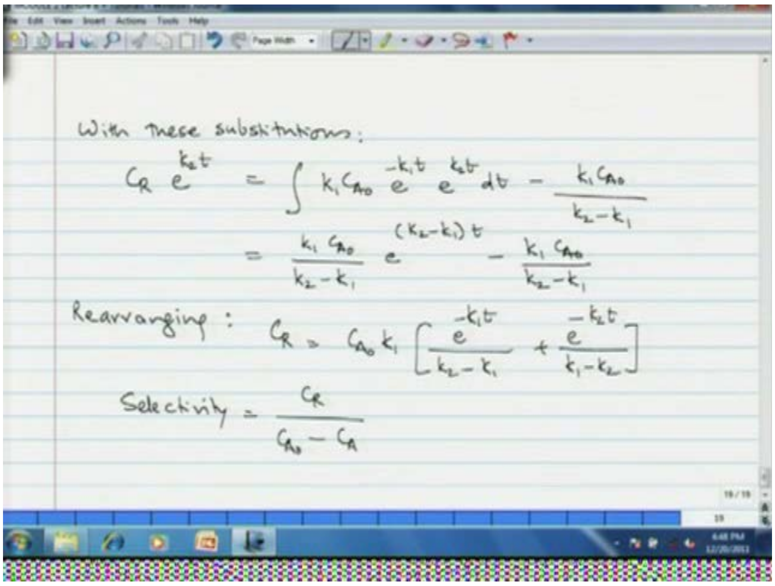

With these substitutions:

$$C_R e^{k_2 t} = \int k_1 C_{A0} e^{-k_1 t} e^{k_2 t} dt - \frac{k_1 C_{A0}}{k_2 - k_1}$$

$$= \frac{k_1 C_{A0}}{k_2 - k_1} e^{(k_2 - k_1) t} - \frac{k_1 C_{A0}}{k_2 - k_1}$$

Rearranging : $C_R = C_{A0} k_1 \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right]$

$$\text{Selectivity} = \frac{C_R}{C_{A0} - C_A}$$

With this substitutions, we get the expression C R into e to the power K 2 t is equal to integral K 1 into C A naught into e to the power minus k1t into e to the power k 2 t into d t minus third integration constant k 1 C A naught divided by K 2 minus K 1 or plus integration constant, which is minus K 1 C A naught divided by K 2 minus K 1. Now you can easily simplify this, I am going to skip the intermediate algebra, you can easily work it out. But I am going to view the final expression and then if you rearrange this, you will get expression for C R in terms of K 1 K 2 and C A naught. Now this selectivity is defined in the similar way number of mols of desired product from divided by number of mols of A converted so, C R divided by C A naught minus C A.

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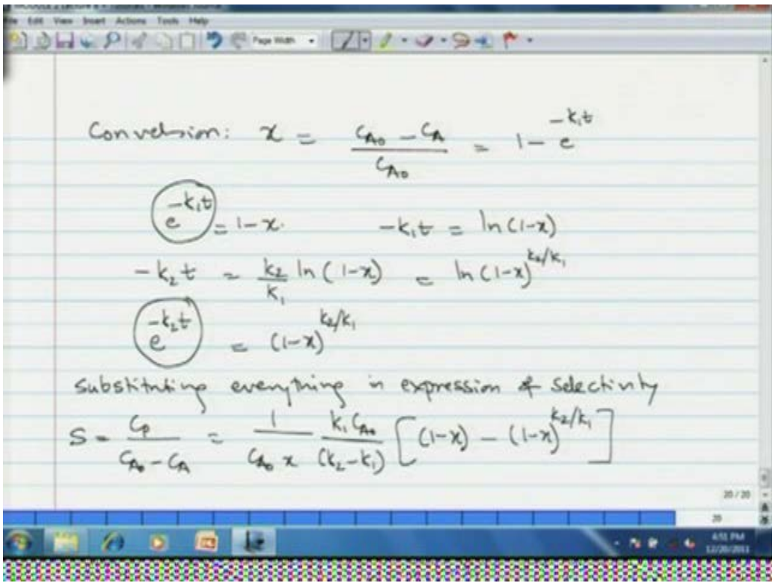

Conversion: $x = \frac{C_{A0} - C_A}{C_{A0}} = 1 - e^{-k_1 t}$

$\boxed{e^{-k_1 t}} = 1 - x \qquad -k_1 t = \ln(1-x)$

$-k_2 t = \frac{k_2}{k_1} \ln(1-x) = \ln(1-x)^{k_2/k_1}$

$\boxed{e^{-k_2 t}} = (1-x)^{k_2/k_1}$

Substituting everything in expression of selectivity

$S = \frac{C_P}{C_{A0} - C_A} = \frac{1}{C_{A0}\, x} \frac{k_1 C_{A0}}{(k_2 - k_1)} \left[(1-x) - (1-x)^{k_2/k_1} \right]$

Now, we defined the conversion x as C A naught minus C A divided by C A naught and then using, the solution for the first equation that is equation for C A differential equation for C A, we get x equal to 1 minus e to the power e to the power minus K 1 t. Now e to the power minus K1t then becomes equal to 1 minus x then minus K1t becomes equal to l n 1 minus x then similarly by multiplying both sides by K 2, you get this is all mathematical jugglery, you can very easily compute it. And therefore, e to the power minus K2t is equal to 1 minus x is to K 2 by K 1.

So, what we have done is that essentially, we have tried to get the expressions for two exponentials e to the power minus K 1 t and e to the power minus K 2 t, in terms of conversion x. And now we substitute all expressions substituting everything in expression of selectivity S is equal to C p divided by C A naught minus C A is equal to 1 divided by C A naught into x into K 1 C A naught divided by K 2 minus K 1 into 1 minus x minus 1 minus x raise to K 2 by K 1.

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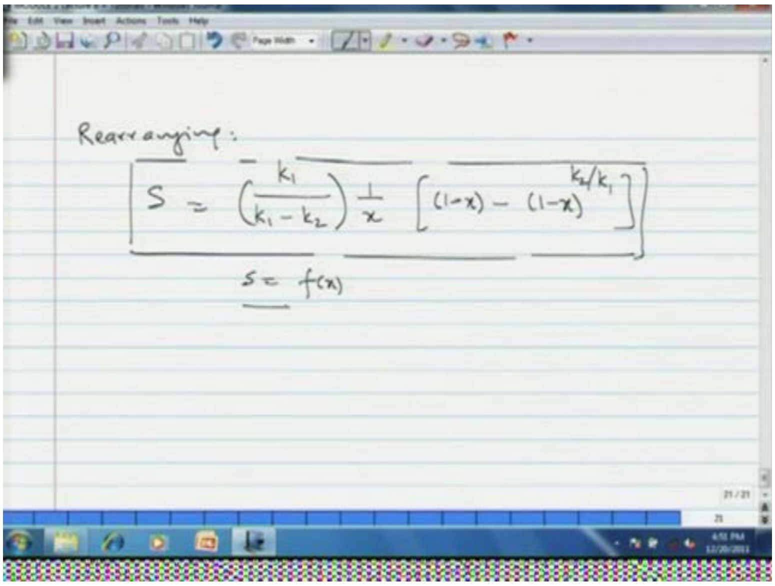

Rearranging:

$$\boxed{S = \left(\frac{k_1}{k_1 - k_2}\right)\frac{1}{x}\left[(1-x) - (1-x)^{k_2/k_1}\right]}$$

$$\underline{s} = f(x)$$

So, rearranging we have final expression for selectivity S as K 1 divided by K 1 minus K 2 divided by x into 1, 1 minus x minus 1 minus x raise to K 2 by K 1 and that completes our exercise. So, here also you see that selectivity is a function of x.