Bioreactor Design and Analysis
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Lecture - 39
Non-Ideal Reactors: Design and Analysis – Part 2

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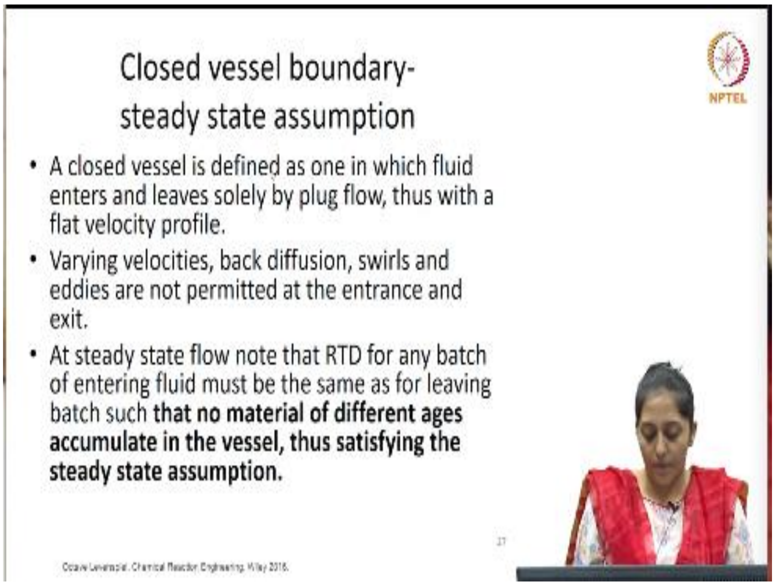

Closed vessel boundary-steady state assumption

- A closed vessel is defined as one in which fluid enters and leaves solely by plug flow, thus with a flat velocity profile.
- Varying velocities, back diffusion, swirls and eddies are not permitted at the entrance and exit.
- At steady state flow note that RTD for any batch of entering fluid must be the same as for leaving batch such **that no material of different ages accumulate in the vessel, thus satisfying the steady state assumption.**

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

Welcome back students. So, yesterday we were discussing about the non-ideality in reactors, where we first discussed about non-ideal reactors. So, the 2 major type of reactors which we generally come across while designing in is the plug flow reactor or the mixed reactor. Where the plug flow reactor is similar to the batch kinetics and mixed flow reactor, the example is the continuous stirred tank reactor.

So, then we saw how to characterised the non-ideality in the reactor systems. So, we then spoke about residence time distribution and then how to find the residence time distribution. We spoke about the tracer experiments where different kinds of inputs can be given and at the exit, the profile is noted, how the tracer is coming out from the reactor with time. So, we discussed specially the 2 types of input. One was the pulse input and the other was a step input.

Then where we came across the F curve and how E curve is related to F curve. Now, we will talk about the steady state assumption of the closed vessel boundary. So, a closed vessel is defined as one in which the fluid enters and leaves solely by plug flow, thus with a flat velocity profile, which means there is no velocity gradient. Now, varying velocities or back diffusion, swirls and Eddies they are not permitted at the entrance or at the exit.

Now, at steady state, please note that the residence time distribution for any batch of entering fluid must be the same as for the leaving batch such that no material of different ages get accumulated in the vessel, thus satisfying the steady state assumption.

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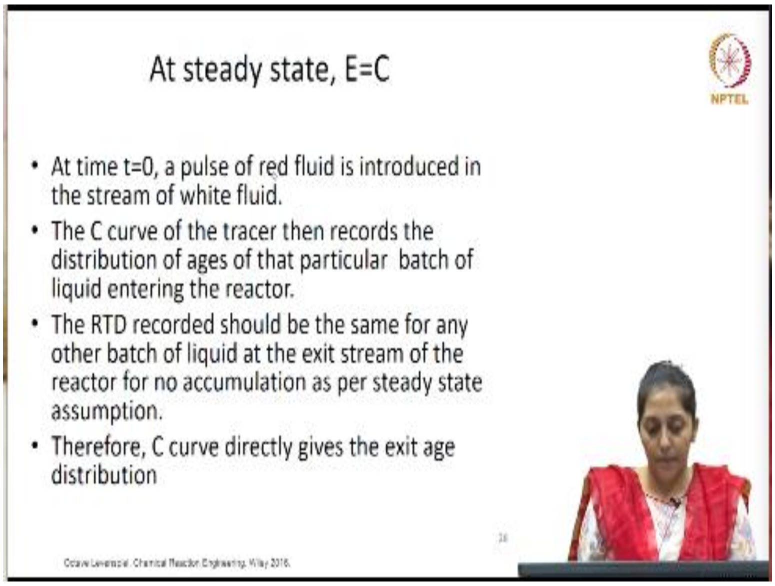

At steady state, E=C

- At time t=0, a pulse of red fluid is introduced in the stream of white fluid.
- The C curve of the tracer then records the distribution of ages of that particular batch of liquid entering the reactor.
- The RTD recorded should be the same for any other batch of liquid at the exit stream of the reactor for no accumulation as per steady state assumption.
- Therefore, C curve directly gives the exit age distribution

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

So, at t is equals to 0, if a pulse of red fluid is introduced in the stream of a white fluid being entered in the reactor. The C curve of the tracer, then would record the distribution of ages of that particular batch of liquid entering the reactor. So, the RTD recorded, it should be the same for any other batch of the liquid at the exit stream of the reactor, but no accumulation as per steady state assumption.

So, your C curve can then directly give the exit age distribution. So, this is the steady state assumption under which your E becomes equal to C.

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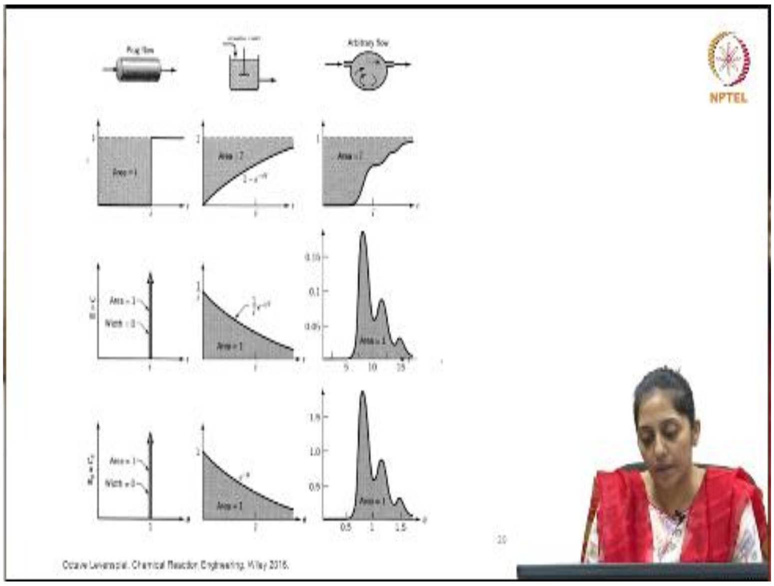

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

So, if you see on the slide, where the first picture shows a plug flow setup, so, the second is your mixed flow and the third is your arbitrary flow. Now, for a plug flow here, they have shown as step input. So, in case of a step input the exit if it is a plug flow system, will also be a step change after the residence time spent inside the vessel. Then for a mixed flow, the curve would look like where it is shown as the F curve, the value is changing from 0 to 1, it will be exponentially increasing.

So, then for a plug flow, the pulse will be coming out of the reactor after the residence time shown here as t bar. Now, for a similar impulse the concentration profile or where the unit is, so, it is a unit impulse. So, then E becomes equal to C and the exit will be an exponentially decreasing curve. If you convert E in terms of theta, then E theta will also be equal to C theta in case of a unit impulse.

And similarly, your exponential function will also get converted into the dimensionless form of theta. Now, if it is an arbitrary flow, then what you observe may not be an exponential increase, but can be with many peaks. Similarly, for an impulse, unit impulse input at the exit for an arbitrary flow, you may observe a lag as shown in the picture here. And with subsequent peaks of decreased amplitude can be observed coming out from the reactor, where the total area can be 1.

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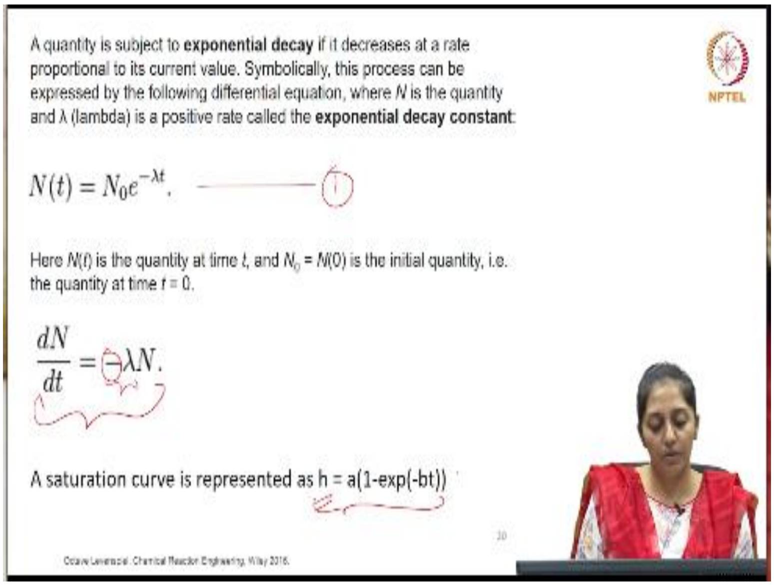

A quantity is subject to **exponential decay** if it decreases at a rate proportional to its current value. Symbolically, this process can be expressed by the following differential equation, where *N* is the quantity and λ (lambda) is a positive rate called the **exponential decay constant**:

$$N(t) = N_0 e^{-\lambda t}. \longrightarrow ①$$

Here *N*(*t*) is the quantity at time *t*, and N_0 = *N*(0) is the initial quantity, i.e. the quantity at time *t* = 0.

$$\underbrace{\frac{dN}{dt} = -\lambda N.}$$

A saturation curve is represented as h = a(1-exp(-bt))

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Now, a quantity is subject to exponential decay if it decreases at a rate proportional to its current value. Symbolically, this process can be expressed by the equation shown here, let us call it as equation 1. This differential equation, where the N is the quantity; lambda is the positive rate called as exponential decay constant. Your N t will be the quantity at time t; N 0 is the initial quantity which is at time t.

So, effectively, the rate at which the N is changing is proportional to N and lambda is your rate constant and because decay, so, therefore, the negative sign. On a saturation curve will be represented mathematically as shown here, h is equal to a 1 – e to the power of minus bt. So, a, b are constants and this is an exponential function with respect to time, so, a saturation curve.

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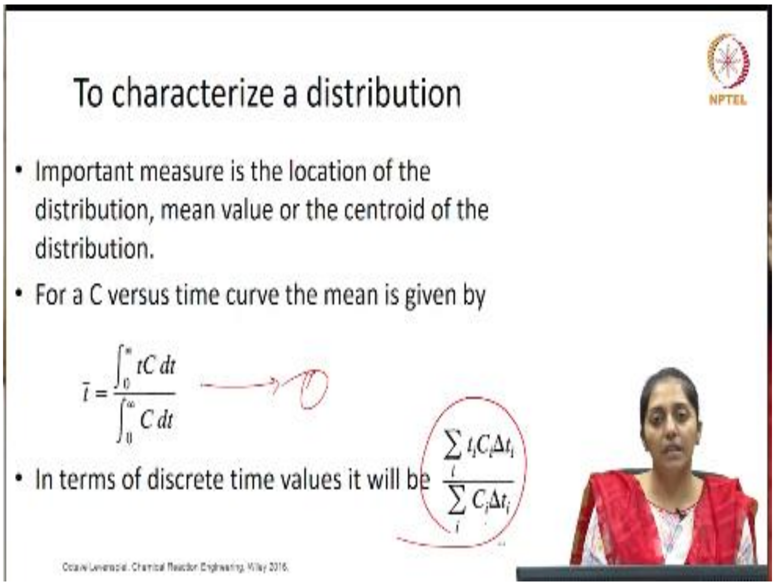

To characterize a distribution

- Important measure is the location of the distribution, mean value or the centroid of the distribution.
- For a C versus time curve the mean is given by

$$\bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} \longrightarrow ①$$

- In terms of discrete time values it will be $\dfrac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i}$

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

Now, to characterise a distribution, what is important to be measured is the location of the distribution, mean value of the distribution or the same thing is called as the centroid of the distribution. Now, for a C versus time curve, the mean can be given as shown here or in terms of discrete time values, it can be shown here in the second line. So, this is how statistically you can define mean value of time in a C versus t curve.

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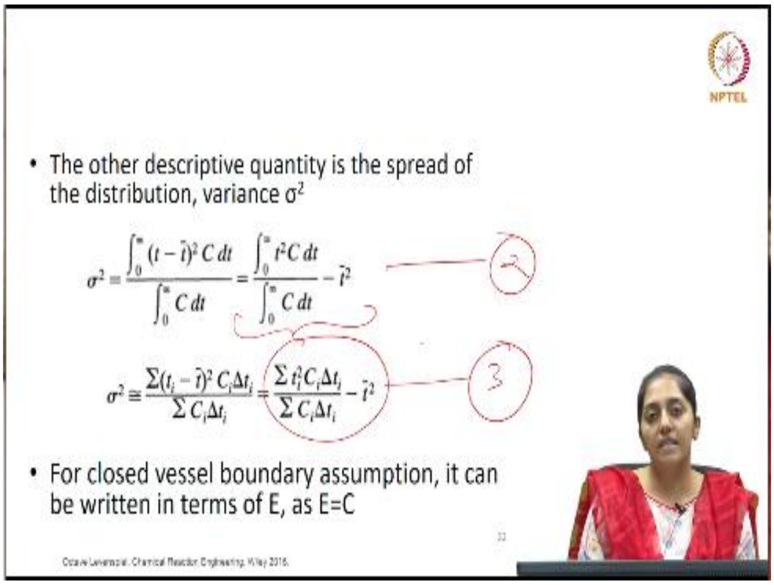

- The other descriptive quantity is the spread of the distribution, variance σ^2

$$\sigma^2 = \frac{\int_0^\infty (t-\bar{t})^2 C\,dt}{\int_0^\infty C\,dt} = \frac{\int_0^\infty t^2 C\,dt}{\int_0^\infty C\,dt} - \bar{t}^2 \quad \text{②}$$

$$\sigma^2 \cong \frac{\sum (t_i-\bar{t})^2 C_i \Delta t_i}{\sum C_i \Delta t_i} = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \quad \text{③}$$

- For closed vessel boundary assumption, it can be written in terms of E, as E=C

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

Now, the other descriptive quantity is the spread of the distribution which we call as variance. Now, variance is mathematically represented as the function shown here, let us call it as equation 2. And in discrete time intervals, it can be represented as shown in the second line. Now, for closed vessel boundaries at steady state your E is equal to C.

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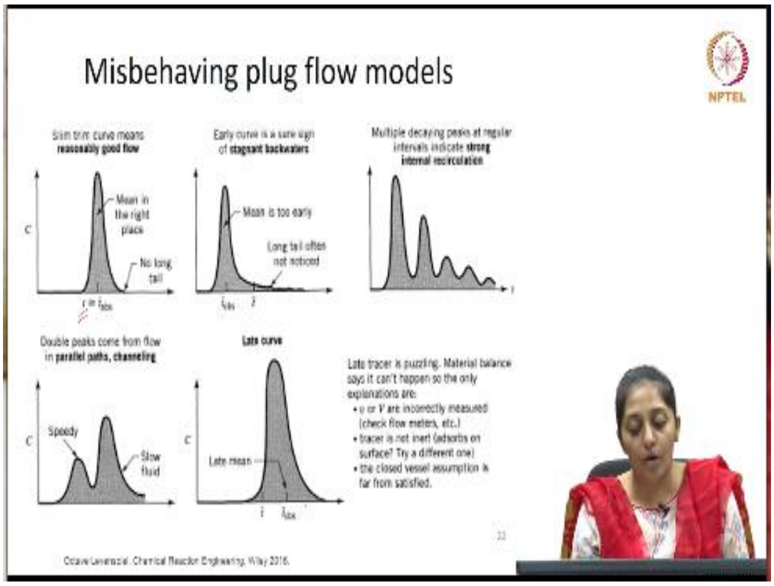

Misbehaving plug flow models

Slim trim curve means **reasonably good flow**

Early curve is a sure sign of **stagnant backwaters**

Multiple decaying peaks at regular intervals indicate **strong internal recirculation**

Double peaks come from flow in **parallel paths, channeling**

Late curve

Late tracer is puzzling. Material balance says it can't happen so the only explanations are:
- v or V are incorrectly measured (check flow meters, etc.)
- tracer is not inert (adsorbs on surface? Try a different one)
- the closed vessel assumption is far from satisfied.

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So, how do we practically find out misbehaving plug flow systems or those which are deviating from ideality? Now, if you see at the exit in a concentration versus time plot, something coming out after certain amount of time and the mean of the peak which is observed is found to be greater than the theoretical residence time. So, this shows reasonably good flow, it is a sharp peak and the mean residence time is equal to the mean residence, theoretical mean residence time.

So, this t bar is the mean residence time calculated from the C versus t data, t bar observed and t bar would be your theoretical mean residence time. So, if both are nearly same and you see a sharp peak in a plug flow system, coming out with a time mean residence time equal to that of the theoretical residence time, then it shows a reasonably good flow, so, no long tail if you see on the picture.

Now, if there are stagnant backwaters, then your observed mean residence time would come much earlier than the theoretical mean residence time and you will see a long tail at the exit of the material or of the tracer. Then in the third scenario, if you see a lot many peaks of decreased amplitude, then this shows strong internal recirculation of the medium. This gives an indication of that behaviour.

Now, if you see only 2 major peaks coming at the exit. So, the earlier one can be speedy and the later one can be slow, where you are the peak can be for 1 is less than the mean residence time; for the other is greater than the mean residence time. So, the one can be speedy liquid flow and the other fluid elements can demonstrate slow fluid movement. So, this indicates parallel paths inside the reactor or channelling.

Now, if you observe a very late curve exit of the material tracer from the reactor with the mean residence time observed being greater than the theoretical residence time, then this indicates either the volumetric flow rate or the volume have not been measured properly or the tracer may not be inert, might be getting absorbed or the close vessel boundary assumption is not getting satisfied.

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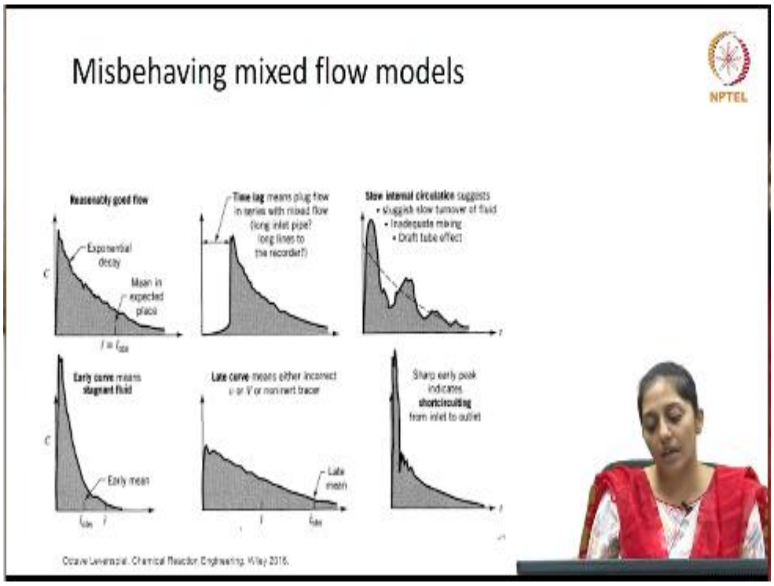

Misbehaving mixed flow models

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Similarly, for mix flow models, how to find deviation from ideality? Now, for an ideal or reasonably good flow in a mixed flow model for a pulse input, the concentration of the tracer will show an exponential detail. And your mean residence time observed would be equal to the theoretical residence time of the reactor. Now, if you observe that there is a lag and then you observe a sudden rise in the concentration with subsequent exponential detail in the C versus t curve.

Then this would mean that either there is a very long inlet pipe which indicates long lines for recording. So, either at the exit or at the entry, there are long pipe. So, there is a lag due to this path covered by the fluid elements at the exit or the entry. Then if you observed peaks more than one peaks coming out at some intervals with decreased intensity, then this would mean inadequate mixing or maybe the draft tube effect the internal recirculation.

If your mean residence time observed is found to be early than the theoretical mean residence time, this would mean stagnant zones in the reactor, because of which the path being covered effectively has been reduced. So, most of the liquid particles are spending less time than the theoretical residence time. Now, on the contrary, if there is a late curve which means your mean residence time observed is found to be later, much later than the theoretical residence time, this would indicate either, incorrect measurement of the volumetric flow rate or the volume of the reactor or the tracer is not inert.

Now, very sharp early peek, this might indicate short circuiting from inlet to the outlet and then suddenly dies down. So, this can be due to the result of short circuiting.

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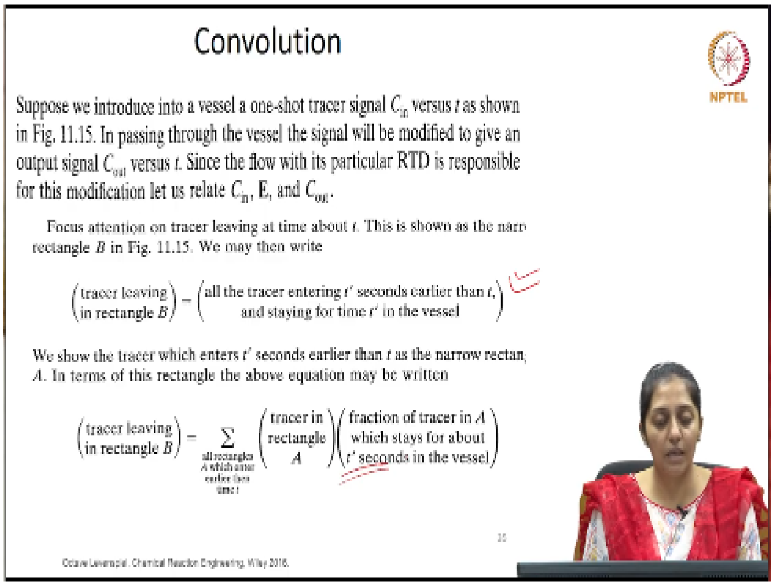

Convolution

Suppose we introduce into a vessel a one-shot tracer signal C_{in} versus t as shown in Fig. 11.15. In passing through the vessel the signal will be modified to give an output signal C_{out} versus t. Since the flow with its particular RTD is responsible for this modification let us relate C_{in}, **E**, and C_{out}.

Focus attention on tracer leaving at time about t. This is shown as the narr rectangle B in Fig. 11.15. We may then write

$$\begin{pmatrix}\text{tracer leaving}\\ \text{in rectangle } B\end{pmatrix} = \begin{pmatrix}\text{all the tracer entering } t' \text{ seconds earlier than } t,\\ \text{and staying for time } t' \text{ in the vessel}\end{pmatrix}$$

We show the tracer which enters t' seconds earlier than t as the narrow rectan A. In terms of this rectangle the above equation may be written

$$\begin{pmatrix}\text{tracer leaving}\\ \text{in rectangle } B\end{pmatrix} = \sum_{\substack{\text{all rectangles}\\ A \text{ which enter}\\ \text{earlier than}\\ \text{time } t}} \begin{pmatrix}\text{tracer in}\\ \text{rectangle}\\ A\end{pmatrix}\begin{pmatrix}\text{fraction of tracer in } A\\ \text{which stays for about}\\ t' \text{ seconds in the vessel}\end{pmatrix}$$

Octave Levenspiel, Chemical Reaction Engineering, Wiley 2016.

Now, whatever we have been spoken or we have derived up till now has been for a non-reactive system. Now, how can we relate the residence time distribution or this non-ideality, how will it impact the reaction or the performance of the reactor? Let us see and characterise that. Now, in order to characterise that we need to determine how the concentration of the inlet and the concentration at the outlet are related to the mean residence time distribution.

So, that in case of a non-ideality one can take into account, what will be the actual reaction kinetics and the performance? So, in order to derive that let us first see, how C in and C out can be related with the residence time distribution or the E value. Now, suppose, we introduce in a vessel one short tracer, let the signal be C in and this tracer is not a pulse tracer, but it is an entire profile of C in versus t. So, this is a curve signal.

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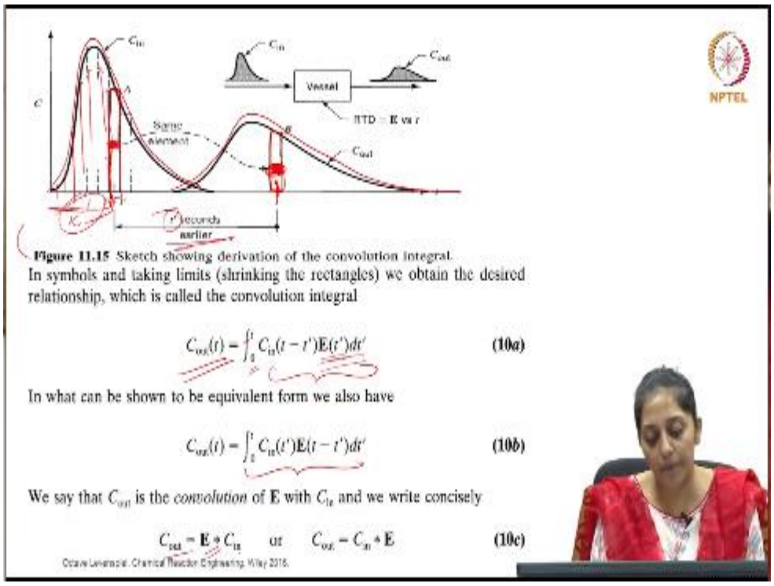

Figure 11.15 Sketch showing derivation of the convolution integral.

In symbols and taking limits (shrinking the rectangles) we obtain the desired relationship, which is called the convolution integral

$$C_{out}(t) = \int_0^t C_{in}(t - t')\mathbf{E}(t')dt' \quad \textbf{(10a)}$$

In what can be shown to be equivalent form we also have

$$C_{out}(t) = \int_0^t C_{in}(t')\mathbf{E}(t - t')dt' \quad \textbf{(10b)}$$

We say that C_{out} is the *convolution* of **E** with C_{in} and we write concisely

$$C_{out} = \mathbf{E} * C_{in} \quad \text{or} \quad C_{out} = C_{in} * \mathbf{E} \quad \textbf{(10c)}$$

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

Now, you can see it on the slide here. So, this portion is your C in. Now, while passing through the vessel, this signal may get modified to get the C out signal. So, let us assume, we were able to see this profile at the exit. Now, since the flow with its particular residence time distribution is what is responsible for this modification of the curve of C in and C out. Let us try to connect it with the RTD. Now, focus your attention on the tracer which is leaving at time t, so, which is shown here.

So, this is the fluid element marked as B which is leaving the reactor at time t. So, the tracer in this rectangle B will be equal to so, let us see this, so, gray box. So, the amount of tracer in this rectangle B, how do we determine? So, the tracer which is leaving in this rectangle B fluid element is nothing but all the tracer entering at t prime seconds earlier than t. Now, what was t prime?

t prime is nothing but the corresponding element. It is the same fluid element which is in the inlet now being called as A. And this grey box was your tracer element which is leaving here in the fluid element B and this gap is t seconds earlier. So, I will repeat, all the tracer entering t prime seconds earlier than t and staying for t prime in the vessel. So, whatever tracer we measure here at time t is nothing.

But, all the tracer which must have entered the reactor before t prime seconds and which must have stayed in the reactor for the t prime seconds. Now, we show that the tracer which enters t prime seconds earlier than t as a narrow rectangle A, this was the same element at the before t prime seconds. Now, in terms of this rectangle, the above correlation can then be written as.

Let us see, tracer leaving in rectangle B is equal to summation of all the rectangles A which have entered earlier than time t.

So, which means similar such all rectangles before time t. Now, in terms all the rectangle A is which enter earlier than time t, the summation of all such rectangles having what? The tracer in all these rectangles multiplied by the fraction of the tracer in each of these rectangles, which stays for about t prime seconds in the vessel. So, not all the tracer here is spending only t prime seconds in the reactor.

So, among all these rectangles, the fluid elements, we need to find the fraction of those tracers which have spent t prime second inside the reactor. So, this means what? That the concentration at the output at time t is the concentration of the fluid elements before t prime entering the vessel residence time distribution, this is nothing but E t prime is the fraction of the tracer in the fluid element which stays for about t prime seconds in the vessel. So, this is nothing but E t prime as per the definition of the E curve.

So, the fraction of the fluid element which is stain for the time t prime, this is E t prime dt. Now, here the integral will be all those elements up till the time t. So, the limit for integration would be 0 to t. So, we need to consider all the elements which have been entering and before time t. Now, with the law of convolution, this integral can be rewritten in the form of 0 to t C in t prime E t – t prime dt prime. So, your C out becomes nothing but the exit age distribution multiplied by C in.

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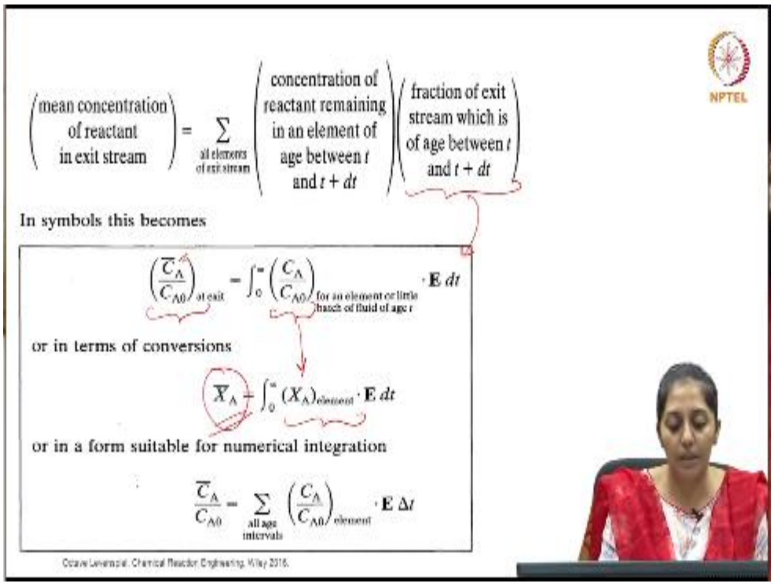

$$\begin{pmatrix}\text{mean concentration}\\ \text{of reactant}\\ \text{in exit stream}\end{pmatrix} = \sum_{\substack{\text{all elements}\\ \text{of exit stream}}} \begin{pmatrix}\text{concentration of}\\ \text{reactant remaining}\\ \text{in an element of}\\ \text{age between } t\\ \text{and } t+dt\end{pmatrix} \underbrace{\begin{pmatrix}\text{fraction of exit}\\ \text{stream which is}\\ \text{of age between } t\\ \text{and } t+dt\end{pmatrix}}$$

In symbols this becomes

$$\underbrace{\left(\frac{\overline{C}_A}{C_{A0}}\right)_{\text{at exit}}} = \int_0^\infty \underbrace{\left(\frac{C_A}{C_{A0}}\right)}_{\text{for an element or little batch of fluid of age } t} \cdot \mathbf{E}\,dt$$

or in terms of conversions

$$\overline{X}_A = \int_0^\infty \underbrace{(X_A)_{\text{element}}} \cdot \mathbf{E}\,dt$$

or in a form suitable for numerical integration

$$\frac{\overline{C}_A}{C_{A0}} = \sum_{\substack{\text{all age}\\ \text{intervals}}} \left(\frac{C_A}{C_{A0}}\right)_{\text{element}} \cdot \mathbf{E}\,\Delta t$$

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Now, let us say, it is reacting. So, mean concentration of the reactant in the exit stream will be equal to all the elements of the exit stream and the summation of all such elements. And summation of what? The concentration of the reactant leaving in an element of age between t and t + dt. And the fraction of the exit stream which is of age between t and t + dt. So, first we need to find out the fraction of those exit stream, which are of the age between t and t + dt.

And multiply it with the concentration of the reactant remaining in any element between the age t + t dt, t and t + dt. So, now, in terms of symbols and the mathematical form C A prime by C A 0. So, this is at the exit fraction of conversion. So, this becomes your conversion which is called as X A, it is 0 to infinity; all the elements of the exit stream so, we are having the limits as 0 to infinity.

Now, for an element or a batch of fluid of age t, the second part of the summation is nothing but your E dt and C A by C A 0 is the concentration of the reactants at present fraction versus the initial concentration. So, this is your theoretical X A multiplied by theoretical conversion multiplied by E dt with (()) (22:49) 0 to infinity will give you the actual conversion.

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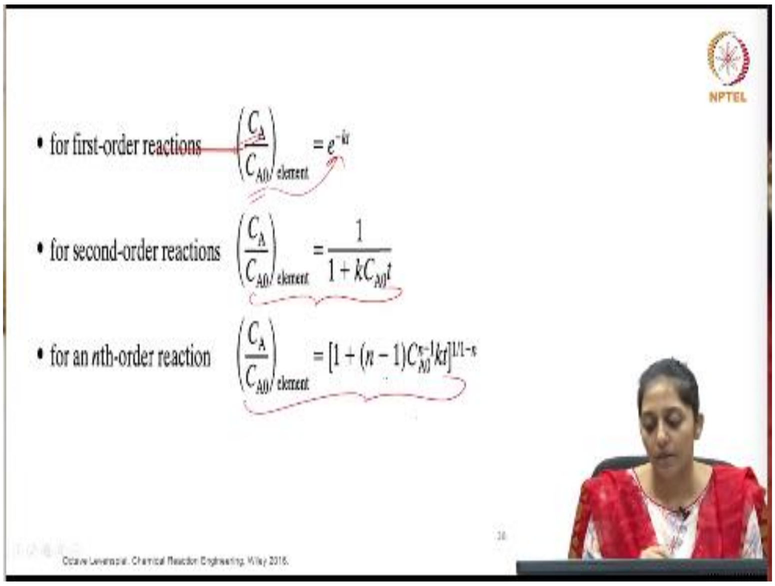

- for first-order reactions $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = e^{-kt}$
- for second-order reactions $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = \frac{1}{1+kC_{A0}t}$
- for an nth-order reaction $\left(\frac{C_A}{C_{A0}}\right)_{\text{element}} = [1+(n-1)C_{A0}^{n-1}kt]^{1/1-n}$

Octave Levenspiel, Chemical Reactor Engineering, Wiley 2016.

Now, for the first order reactions, we know that the product is related to the initial or the final concentration is related to initial concentration by an exponentially decreasing function in case of reactions, C A is the reactant. For the second order, it will take this form. And for an nth order, let us say it is taking this form.