# Lecture # 30 CHE331A

## Models for non-ideal reactors – from the RTD curves to conversions

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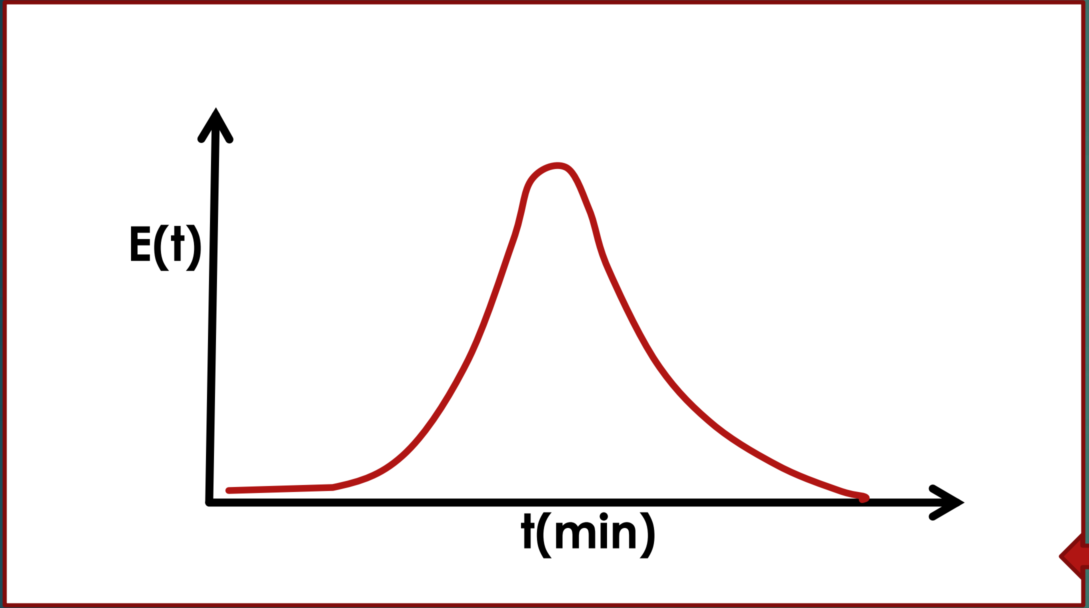
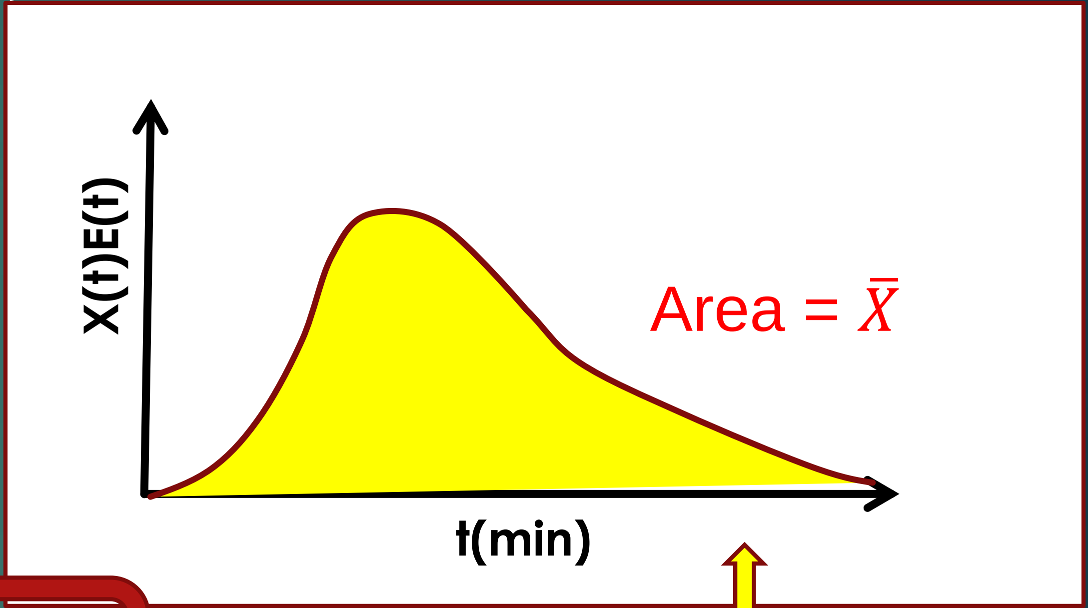
- Non-ideal reactors
  - Construction of C(t) and E(t)
  - Convolution integral & Step-input
  - Moments of the RTD and application to PFR/PBR and CSTR
  - RTD of LFR – an example of a non-ideal reactor
  - Models for real reactors

# Given a E(t), conversion can be calculated for the segregated model: PFR/PBR, CSTR, LFR and in general

- Experimentally determined *E(t)* curve from *C(t)*



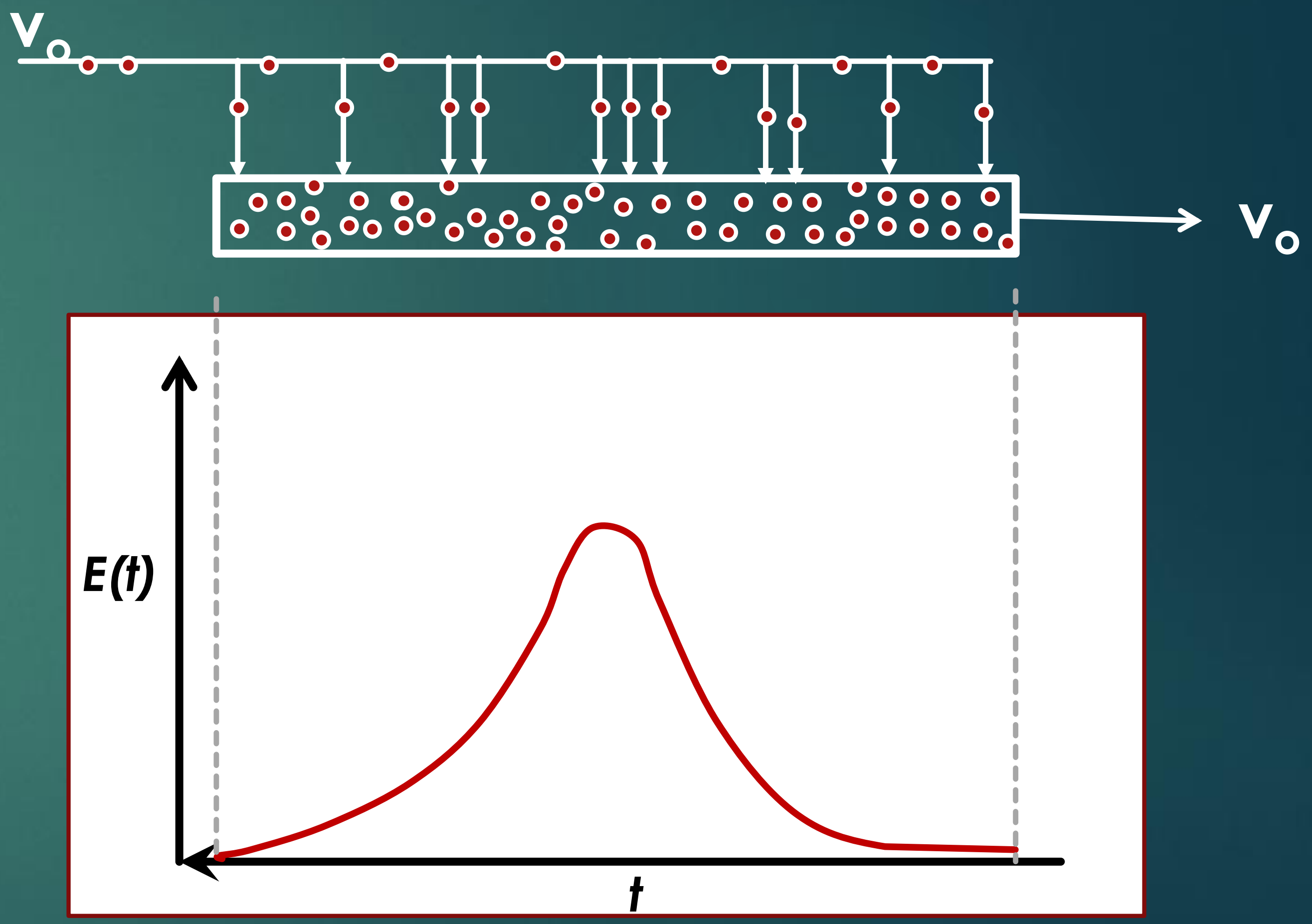

| t (min) | C(t) | E(t) $min^{-1}$ | X(t) | X(t).E(t) $min^{-1}$ |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 1 | 1 | 0.02 | 0.095 | 0.0019 |
| 2 | 5 | 0.10 | 0.181 | 0.0180 |
| | | And so on | | |

- *X(t)* determined for a batch reactor for specified kinetics

$$\bar{X} = \int_0^\infty X(t).E(t).dt$$

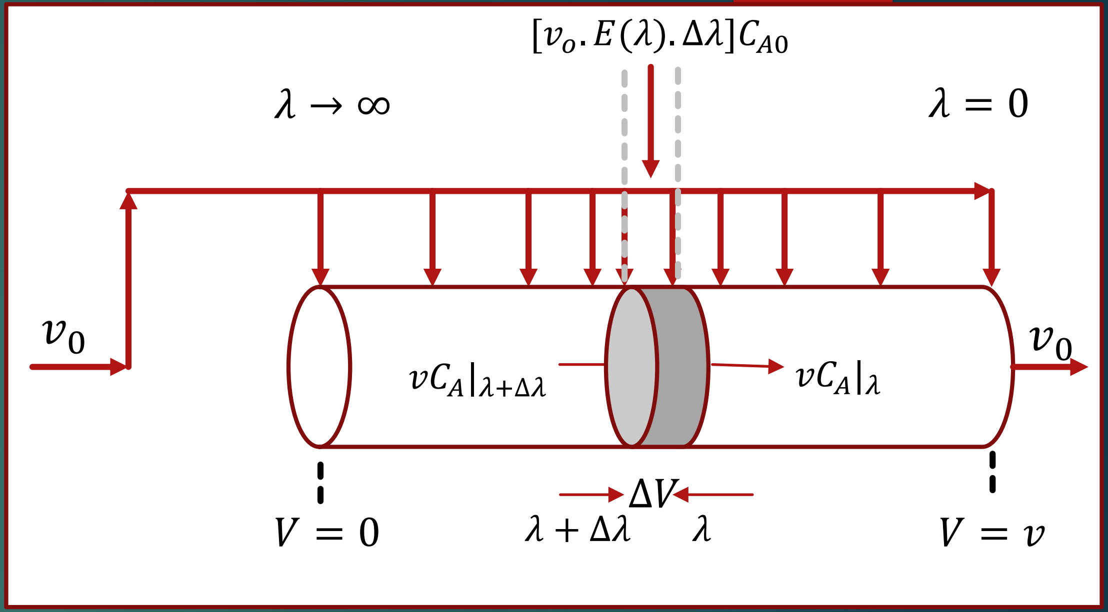
# Maximum Mixedness model – the other zero parameter model

- Fluid elements enter, as per the E(t) curve, and mix radially but not axially
- Fluid elements at the far left spend the most amount of time and those at the far right the least
- λ Is the time it takes for the fluid to move from a particular point in the reactor to the end (also called life expectancy)
- Thus, E(λ)dλ is the fraction of molecules having a life expectancy between λ and λ+dλ




Note the t-axis direction

# Mole balance for the elemental volume, $\Delta V$




- Balance in the elemental volume
- $v_\lambda = v_{\lambda+\Delta\lambda} + v_o.E(\lambda).\Delta\lambda \quad \Rightarrow \quad \frac{dv_\lambda}{d\lambda} = -v_0 E(\lambda)$
- Integrating with $v_\lambda = 0 \; at \; \lambda = \infty$
- $v_\lambda = v_0 \int_\lambda^\infty E(\lambda).d\lambda = v_0[1 - F(\lambda)]$
- Thus, the volume of fluid with life expectancy between λ and λ+dλ is

$$\Delta V = v_0[1 - F(\lambda)]\Delta\lambda$$

- rate of generation of species A in this volume is: $\quad r_A \Delta V = r_A v_0[1 - F(\lambda)]\Delta\lambda$
- Thus mole balance in the elemental volume is:

$$v_0\{[1 - F(\lambda)]C_A\}|_{\lambda+\Delta\lambda} + v_0 C_{A0} E(\lambda)\Delta\lambda - v_0\{[1 - F(\lambda)]C_A\}|_\lambda + r_A v_0[1 - F(\lambda)]\Delta\lambda = 0$$

# The differential equation for maximum mixedness model

- $v_0\{[1-F(\lambda)]C_A\}|_{\lambda+\Delta\lambda} + v_0 C_{A0} E(\lambda)\Delta\lambda - v_0\{[1-F(\lambda)]C_A\}|_{\lambda} + r_A v_0[1-F(\lambda)]\Delta\lambda = 0$
- Dividing by $v_0\Delta\lambda$ and taking the limits of $\Delta\lambda \to 0$ we have
- $C_{A0}E(\lambda) + \frac{d}{d\lambda}\big[[1-F(\lambda)]C_A\big] + r_A[1-F(\lambda)] = 0$ remember: $C_A = C_A(\lambda)$
- Thus, $C_{A0}E(\lambda) + [1-F(\lambda)]\frac{d}{d\lambda}[C_A] - C_A E(\lambda) + r_A[1-F(\lambda)] = 0$

$$\frac{dC_A}{d\lambda} = -r_A + (C_A - C_{A0})\frac{E(\lambda)}{1-F(\lambda)}$$

- And in terms of conversion:

$$\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + X\frac{E(\lambda)}{1-F(\lambda)}$$

  - With boundary conditions of $\lambda \to \infty$ then $C_A = C_{A0}$ or $X = 0$

# Comparison between complete segregation and maximum mixedness models

- $2^{nd}$ order liquid phase reaction $2A \rightarrow B$ $\quad C_{A0} = 8\frac{mol}{dm^3};\ v_0 = 25\frac{dm^3}{min}$

  $-r_A = kC_A^2$ with $k = 0.01\frac{dm^3}{mol.min}$ at 320 K; Reactor vol $= 1000\ dm^3$

  Tracer test: $N_0 = 100\ g$ and $v = 25\frac{dm^3}{min}$

- Determine E(t) curve from C(t) curve
  - Is it a CSTR
  - However, $\frac{1}{\tau} = \frac{v_0}{V} = \frac{25}{1000} = 0.025 \neq 0.028$
- For Segregation model: $\bar{X} = \int_0^\infty X(t)E(t)dt$
- Batch reactor equation for $2^{nd}$ order reaction: $X = \frac{kC_{A0}t}{1+kC_{A0}t}$
- Numerical integration using trapezoid rule gives: $\bar{X} = \sum_0^\infty X(t)E(t)dt = 0.61$

| t (min) | C(t) | E(t) min$^{-1}$ | X(t) | X(t).E(t) min$^{-1}$ | $X(t)E(t)\Delta t$ |
|---|---|---|---|---|---|
| 0 | 112 | 0.0280 | 0 | 0 | 0 |
| 5 | 95.8 | 0.0240 | 0.286 | 0.00686 | 0.0172 |
| 10 | 82.2 | 0.0206 | 0.444 | 0.00916 | 0.0400 |
| 15 | 70.6 | 0.0177 | 0.545 | 0.00965 | 0.0470 |
| And so on | | | | | |

# Maximum mixedness the other bound for the zero parameter models

- Conversions for maximum mixedness: $\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + X\frac{E(\lambda)}{1-F(\lambda)}$ Determine: $\frac{E(\lambda)}{1-F(\lambda)}$
- Using Euler method for numerical integration: $X_{i+1} = X_i + \Delta\lambda[\frac{r_A}{C_{A0}} + X_i\frac{E(\lambda)}{1-F(\lambda)}]$
  - This starts from $\lambda = 0$, however the solution is unstable and depends on the starting value of X $\rightarrow$ integrate backwards, i.e., start from $\lambda \rightarrow \infty$
- Integrating backward: $X_{i-1} = X_i - \Delta\lambda[X_i\frac{E(\lambda_i)}{1-F(\lambda_i)} - kC_{A0}(1-X_i)^2]$
- $\lambda \rightarrow \infty$ (or at the beginning), we have X = 0
- X at ($\lambda = 0$, outlet) = 0.564 compared to 0.61

  for segregated model

| t (min) | C(t) | E(t) $min^{-1}$ | 1-F(t) | E(t)/[1-F(t)] | $\lambda$ |
|---|---|---|---|---|---|
| 0 | 112 | 0.0280 | 1.00 | 0.0280 | 0 |
| 5 | 95.8 | 0.0240 | 0.871 | 0.0276 | 5 |
| 10 | 82.2 | 0.0206 | 0.760 | 0.0271 | 10 |
| | | And so on | | | |
| 200 | 0.90 | 0.000225 | 0.003 | 0.0750 | 200 |

# Maximum mixedness model by solving the ODE

- The maximum mixedness model: $\frac{dX}{d\lambda} = \frac{r_A}{C_{A0}} + X\frac{E(\lambda)}{1-F(\lambda)}$
  - Which is to be integrated from $\lambda \to \infty$ (reactor beginning) to $\lambda = 0$ (reactor end)
  - Difficult to integrate backwards → change variable so integration is in forward direction
  - Achieved by introducing a new variable, z, such that

$$\mathrm{z} = \bar{T} - \lambda = 200 - \lambda \text{ OR } \lambda = \bar{T} - z = 200 - z$$

- Thus, $\frac{dX}{dz} = -\frac{r_A}{C_{A0}} - X\frac{E(\bar{T}-z)}{1-F(\bar{T}-z)}$
- To solve the ODE, the $E(t)$ or $F(t)$ curve are fit to polynomial(s)
  - E(t) should not be negative and F(t) should not be equal to one at the beginning
- It is then possible to integrate from z = 0 (reactor beginning) to z = 200 (reactor end)
- For the same case (Example 13-7) X = 0.56 compared to 0.61

# Comparison of ideal reactors and models and some comments

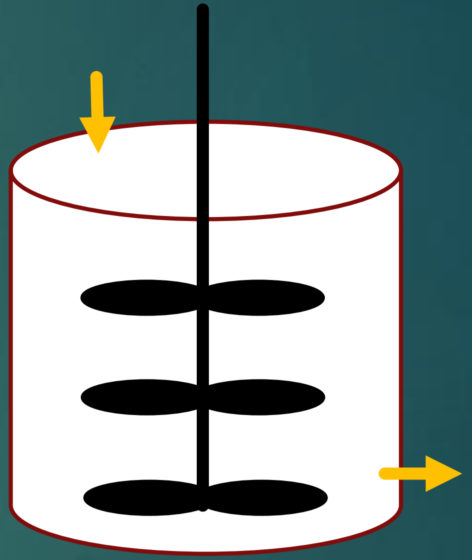
- Example 13-7 is a nice exercise on the application of segregated and maximum mixedness models in detail
  - Complete segregation: 0.61
  - Maximum mixedness: 0.56
  - For a PFR of this size: 0.76
  - For a CSTR of this size: 0.58
- Not all tank reactors are CSTRs nor are all tubular reactors PFRs
- RTD is sufficient if the reaction was 1st order; Non-1st order needs a model
- Segregation and Maximum mixedness models (zero parameter) are bounds to the real reactor

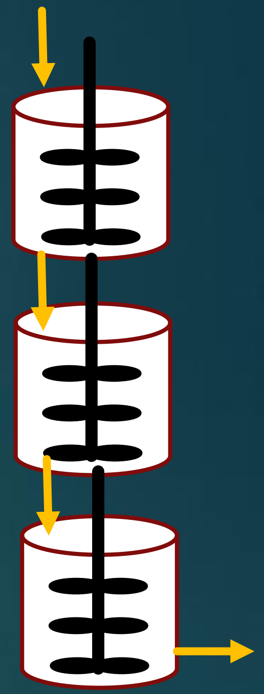
# One parameter models

- One parameter is used to describe the non-ideality of the real reactor
  - One parameter models for CSTR are dead volume, $\boldsymbol{V_D}$, or fraction of bypass, $\boldsymbol{f}$
  - One parameter models for PFR include tanks-in-series (n) and dispersion ($D_a$)
- Often the parameter is obtained by analyzing the RTD function determined by from a tracer test
- Tubular reactors may be empty or packed
  - Ideal tubular (PFR) have piston like flow, no radial velocity profile, no axial mixing and every fluid element spends the same amount of time in the reactor
  - Often plug-flow and insufficient axial-mixing usually fail in real reactors
- One approach is to model the non-ideal tubular reactor as a series of identical CSTRs (tanks-in-series); the other is to consider axial dispersion along with plug-flow

# Tanks-in-series (T-I-S) model is an one parameter model

- Analyze the RTD to determine the number of ideal tanks in series that can approximate the non-ideal tubular reactor
- For example, 3 T-I-S to represent the real reactor
  - Then generalize for n T-I-S
- Analysis of the 3 T-I-S based on pulse injected to 1st
- From the C(t) curve coming out of the 3rd reactor





$$E(t) = \frac{C_3(t).v}{\int_0^\infty C_3(t).v.dt} = \frac{C_3(t)}{\int_0^\infty C_3(t)dt}$$

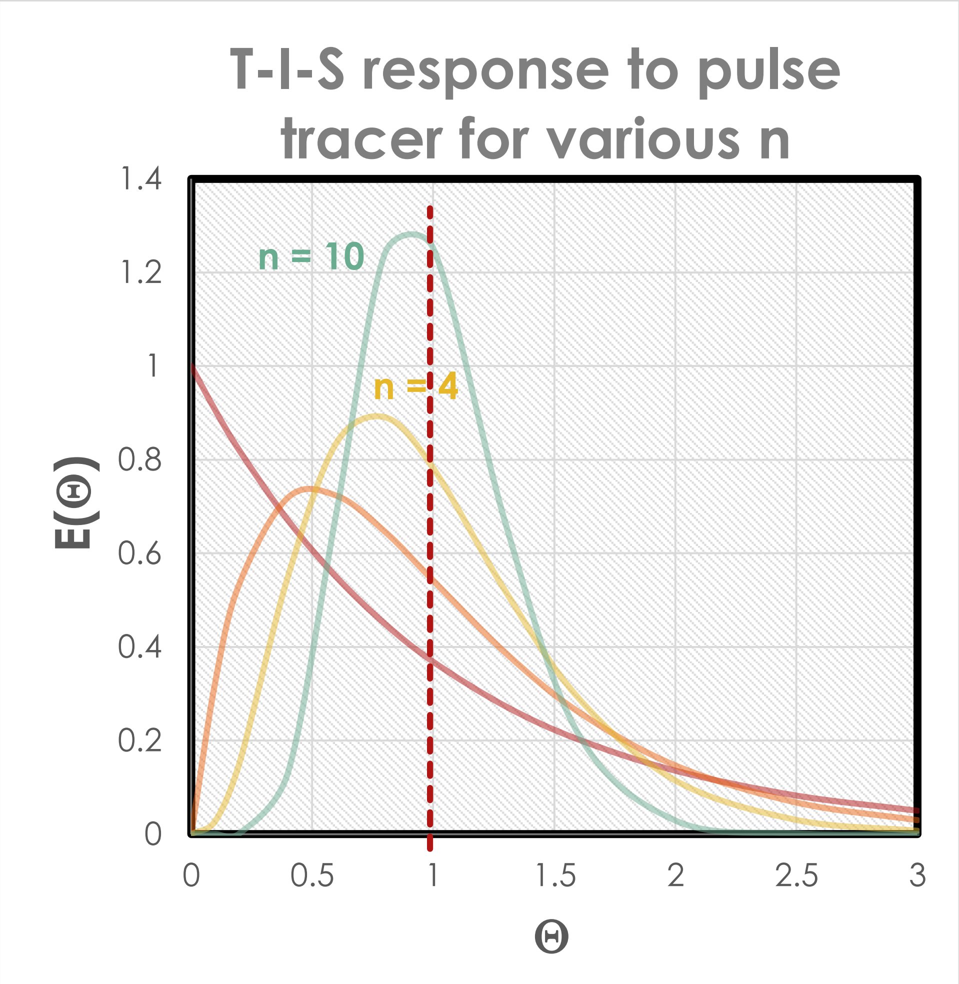
- For the 1st reactor: $C_1 = C_0 \exp(-{}^{t}/_{\tau})$ and $C_0 = \frac{N_0}{V_1} = \frac{v_0 \int_0^\infty C_3(t)dt}{V_1}$

# Material balance on tracer is useful for analysis

- For 1st reactor: $C_1 = C_0 \exp(-{}^{t}/_{\tau_1})$
- For 2nd reactor: $V_2 \frac{dC_2}{dt} = vC_1 - vC_2 \rightarrow \tau_2 \frac{dC_2}{dt} = C_0 \exp(-{}^{t}/_{\tau_1}) - C_2$
- $\frac{dC_2}{dt} + \frac{C_2}{\tau_2} = \frac{C_0}{\tau_2} \exp(-{}^{t}/_{\tau_1})$ since CSTRs are of equal vol: $\tau_1 = \tau_2 = \tau_3 = \tau_i$
- Thus, $C_2 = \frac{C_0 t}{\tau_i} \exp(-{}^{t}/_{\tau_i})$ Similarly, $C_3 = \frac{C_0 t^2}{2\tau_i^2} \exp(-{}^{t}/_{\tau_i})$
- Substituting in RTD: $E(t) = \frac{C_3(t)}{\int_0^\infty C_3(t)dt} = \frac{\frac{C_0 t^2}{2\tau_i^2} \exp(-{}^{t}/_{\tau_i})}{\int_0^\infty \frac{C_0 t^2}{2\tau_i^2} \exp(-{}^{t}/_{\tau_i}) dt} = \frac{t^2}{2\tau_i^2} \exp(-{}^{t}/_{\tau_i})$
- In general: $E(t) = \frac{t^{n-1}}{(n-1)!\tau_i^n} \exp(-{}^{t}/_{\tau_i})$ Further, $V = nV_i$
- And, $\tau_i = \frac{\tau}{n}$ where $\tau$ is for real reactor Thus, $E(\theta) = \frac{n(n\theta)^{n-1}}{(n-1)!} \exp(-n\theta)$

# RTD response depends on the number of Tanks-In-Series

- $E(\theta) = \frac{n(n\theta)^{n-1}}{(n-1)!}\exp(-n\theta)$ and $\sigma_\theta^2$ is given by
- $\sigma_\theta^2 = \frac{\sigma^2}{\tau^2} = \int_0^\infty (\theta - 1)^2 E(\theta)d\theta = \int_0^\infty \theta^2 E(\theta)d\theta - 1$
- $\sigma_\theta^2 = \int_0^\infty \theta^2 \frac{n(n\theta)^{n-1}}{(n-1)!}\exp(-n\theta)d\theta - 1$
- $\sigma_\theta^2 = \frac{(n)^n}{(n-1)!}\int_0^\infty \theta^{n+1}\exp(-n\theta)d\theta - 1$
- $\sigma_\theta^2 = \frac{(n)^n}{(n-1)!}\left[\frac{(n+1)!}{n^{n+2}}\right] - 1 = 1/n \qquad \rightarrow n = \frac{1}{\sigma_\theta^2} = \frac{\tau^2}{\sigma^2}$




- Thus, the number of reactors needed to model the real reactor as *n* ideal tanks in series can be determined from the variance of the E(Θ) vs Θ data
- Using ***n*** the conversion can be calculated for a series of CSTRs!