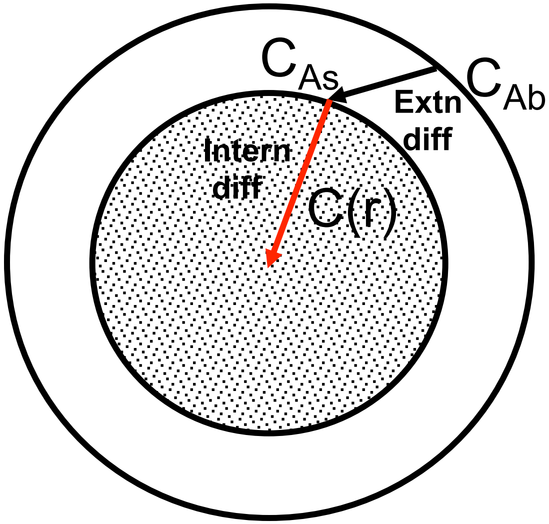
Review: Simultaneous Internal Diffusion & External Diffusion

Goal: Derive a new rate eq that accounts for *internal & external* diffusion

- $-r'_A$ is a function of reactant concentration
- Reactant conc is affected by internal & external diffusion
- Express reactant conc in terms of diffusion-related constants & variables

→Use mole balance



At steady-state: transport of reactants from bulk fluid to external catalyst surface is equal to net rate of reactant consumption in/on the pellet

Molar rate of mass transfer from bulk fluid to external surface:

$$M_A = W_{Ar}\left(a_c\right)\Delta V$$

molar flux

external surface area per unit reactor volume

reactor volume

This molar rate of mass transfer to surface is equal to net rxn rate <u>on & in </u>pellet!

$$M_A = -r''_A\left(\text{external area} + \text{ internal area}\right)$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Review: Basic Molar Balance at Spherical Pellet Surface

$$\left\{\begin{array}{c}\text{Flux:}\\ \text{bulk to}\\ \text{external}\\ \text{surface}\end{array}\right\} \text{x} \left\{\begin{array}{c}\text{External}\\ \text{S.A.}\end{array}\right\} = \left\{\begin{array}{l}\text{Actual rxn}\\ \text{rate per}\\ \text{unit total}\\ \text{S.A.}\end{array}\right\} \text{x} \left\{\begin{array}{c}\text{external +}\\ \text{internal S.A.}\end{array}\right\}$$

$$M_A = W_{Ar}\big|_{r=R} a_c \Delta V = -r''_A\left(a_c\Delta V + S_a\rho_b\Delta V\right)$$

a_c: external surface area per reactor volume (m^2/m^3)

ΔV: reactor volume (m^3) ϕ: porosity of bed (void fraction)

$-r''_A$: rate of reaction per unit surface area ($mol/m^2 \cdot s$)

$-r'_A$: mol/g cat·s $-r_A$: mol/volume·s

S_a: surface area of catalyst per unit mass of catalyst (m^2/g cat)

ρ_b: bulk density, catalyst mass/ reactor volume $\rho_b = \rho_c(1-\phi)$

per volume

$$-r'_A = -r''_A S_a \qquad -r_A = -r'_A\,\rho_c \qquad -r_A = -r''_A S_a\rho_c$$

per mass cat→

$$k'_n = k''_n S_a \qquad k_n = -k'_n\,\rho_c \qquad k_n = k''_n S_a\rho_c$$

per surface area

For a 1st order reaction, simplifies to:

$$\rightarrow M_A = W_{Ar}\big|_{r=R} a_c \rightarrow k_c\left(C_{Ab} - C_{As}\right)a_c = -r''_A S_a\rho_b \rightarrow\rightarrow -r''_A = \frac{\eta k_1 k_c a_c C_{Ab}}{k_c a_c + \eta k_1 S_a \rho_b}$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Review: Effectiveness Factors

Remember, the **internal effectiveness factor** is based on C_{As}

$$\eta = \frac{\text{actual overall rate of reaction}}{\text{rate of rxn if entire interior surface were exposed to the external surface conditions}}$$

The **overall effectiveness factor** is based on C_{Ab}:

Omega

$$\Omega = \frac{\text{actual overall rate of reaction}}{\text{rate of reaction if entire interior surface were exposed to the bulk conditions}}$$

$$\Omega = \frac{-r''_A}{-r''_{Ab}} \quad \rightarrow \Omega = \frac{\dfrac{\eta \cancel{k_1 C_{Ab}}}{1+\eta k_1 S_a \rho_b / k_c a_c}}{\cancel{k_1 C_{Ab}}} \quad \rightarrow \Omega = \frac{\eta}{1+\eta k_1 S_a \rho_b / k_c a_c}$$

$$\rightarrow \Omega\left(-r''_{Ab}\right) = -r''_A$$

Put into design eq to account for internal & external diffusion

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Review: Reaction Rate Variation vs Reactor Conditions

External diffusion $$-r'_A \propto k_c = \frac{D_{AB}}{d_p}Sh \rightarrow k_c = \frac{D_{AB}}{d_p}\left(2+0.6\left(\frac{Ud_p}{\mu/\rho}\right)^{1/2}\left(\frac{\mu/\rho}{D_{AB}}\right)^{1/3}\right)$$

Internal diffusion $$-r'_A = \eta k_r C_{As} S_a \quad \eta = \frac{3}{R^2\frac{\rho_c k_1 S_a}{D_e}}\left(R\sqrt{\frac{\rho_c k_1 S_a}{D_e}}\coth\left(R\sqrt{\frac{\rho_c k_1 S_a}{D_e}}\right)-1\right)$$

Surface reaction $-r'_A = kC_A$

Type of Limitation	Variation of Reaction Rate with:		
	Superficial velocity	**Particle size**	**Temperature**
External	$U^{1/2}$	$d_p^{-3/2}$	Linear
Internal	Independent	d_p^{-1}	Exponential
Surface reaction	Independent	Independent	Exponential

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

L22: Nonideal Flow & Reactor Design

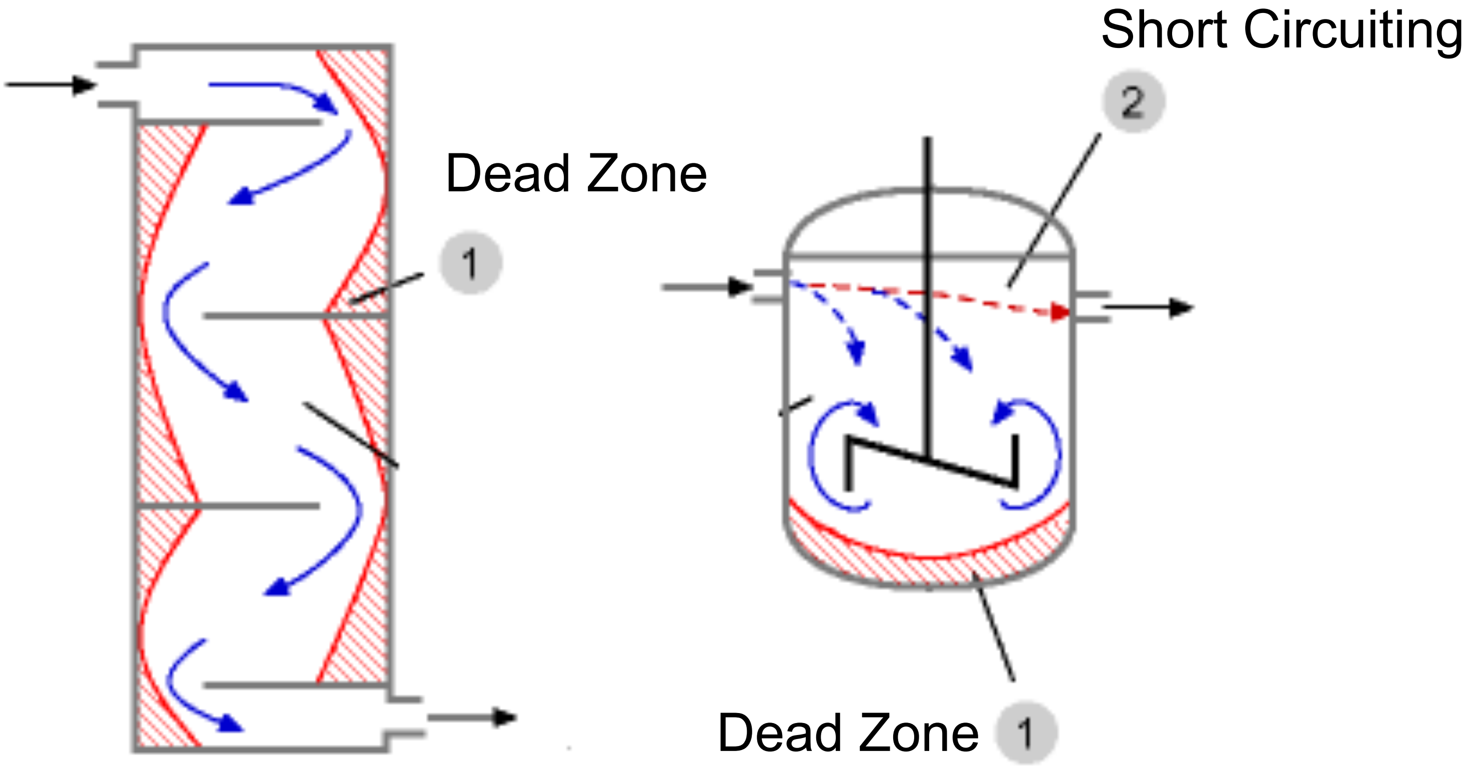
- So far, the reactors we have considered ideal flow patterns
  - Residence time of all molecules are identical
  - Perfectly mixed CSTRs & batch reactors
  - No radial diffusion in a PFR/PBR

- **Goal: mathematically describe non-ideal flow and solve design problems for reactors with nonideal flow**
  - Identify possible deviations
  - Measurement of residence time distribution
  - Models for mixing
  - Calculation of exit conversion in real reactors

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Nonideal Flow in a CSTR

- Ideal CSTR: uniform reactant concentration throughout the vessel
- Real stirred tank
  - Relatively high reactant concentration at the feed entrance
  - Relatively low concentration in the stagnant regions, called dead zones (usually corners and behind baffles)



Short Circuiting

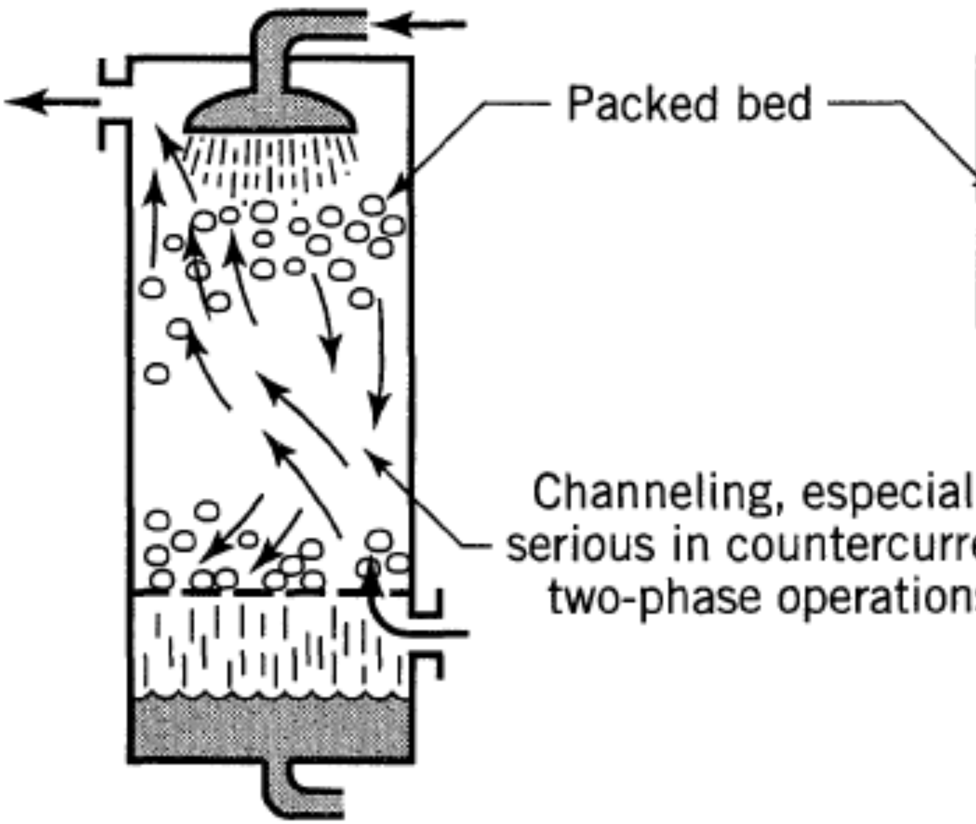
Dead Zone

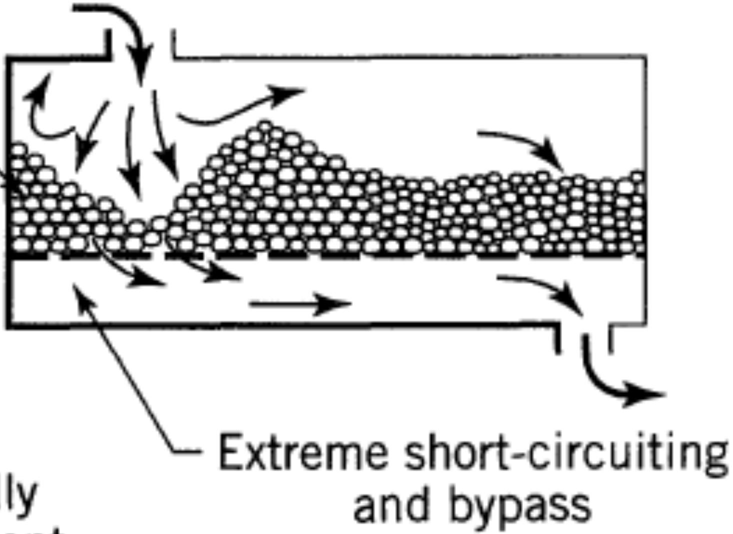
Dead Zone

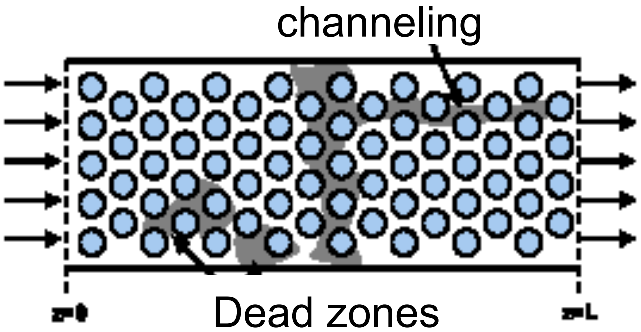
Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Nonideal Flow in a PBR

- **Ideal plug flow reactor**: all reactant and product molecules at any given axial position move at same rate in the direction of the bulk fluid flow
- **Real plug flow reactor**: fluid velocity profiles, turbulent mixing, & molecular diffusion cause molecules to move with changing speeds and in different directions







Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, n.

Residence Time Distribution (RTD)

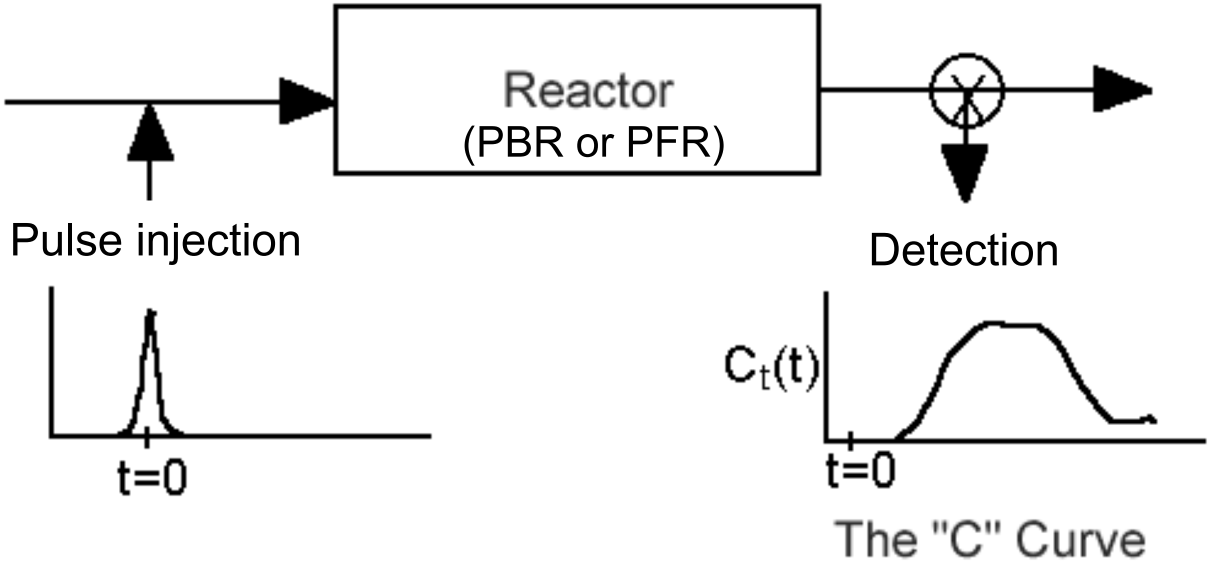
Flow through a reactor is characterized by:

1. The amount of time molecules spend in the reactor, called the RTD
2. Quality of mixing

RTD ≡ E(t) ≡ “residence time distribution” function

- RTD is measured experimentally by injecting an inert “tracer” at t=0 and measuring the tracer concentration C(t) at the exit as a function of time
- Tracer should be easy to detect & have physical properties similar to the reactant

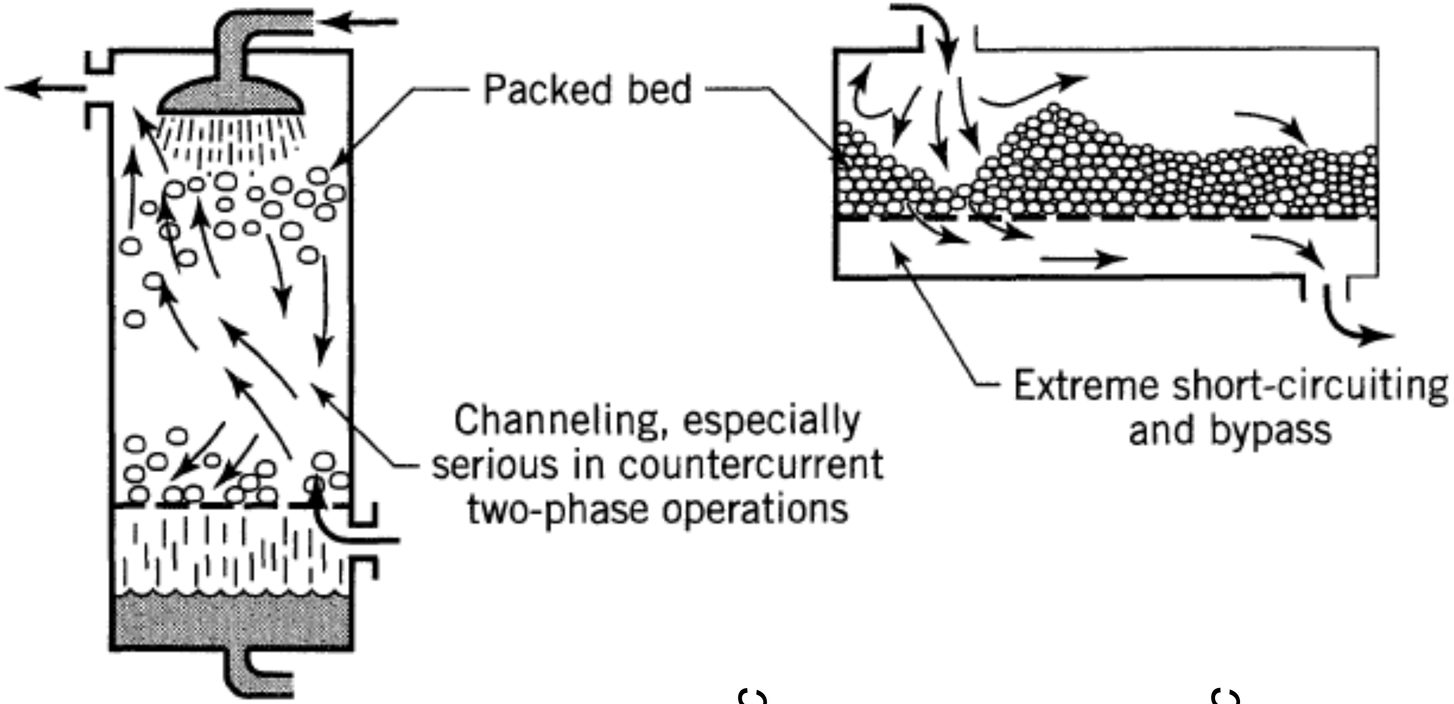
Measurement of RTD

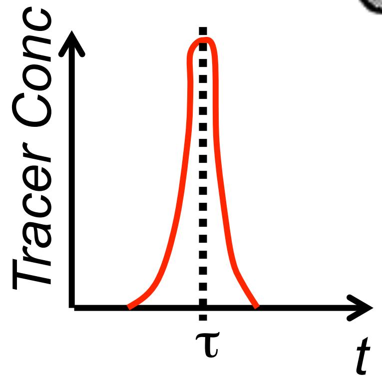


This plot would have the same shape as the pulse injection if the reactor had perfect plug flow

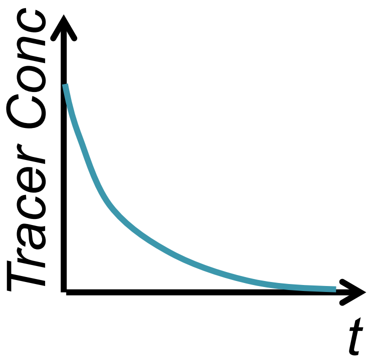
Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

RTD Profiles & Cum RTD Function F(t)

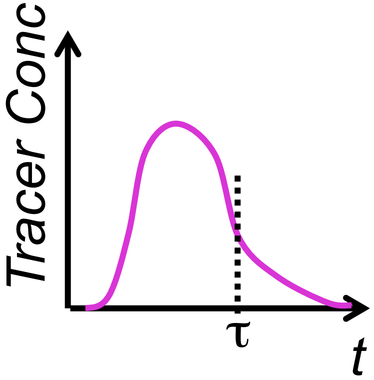




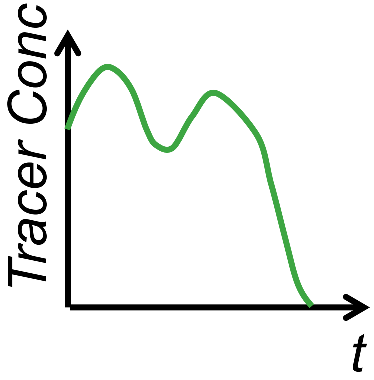
Nearly ideal PFR



Nearly ideal CSTR



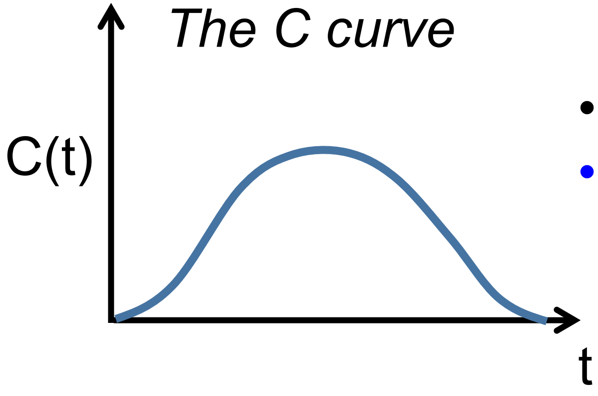
PBR w/ channeling & dead zones



CSTR with dead zones

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Calculation of RTD



- RTD ≡ E(t) ≡ “residence time distribution” function
- RTD describes the amount of time molecules have spent in the reactor

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} = \frac{\text{tracer concentration at reactor exit between time t and t+}\Delta\text{t}}{\text{sum of tracer concentration at exit for an infinite time}}$$

Fraction of material leaving the reactor that has resided in the reactor for a time between t_1 & t_2 $= \int_{t_1}^{t_2} E(t)dt$

$$\int_0^\infty E(t)dt = 1$$

E(t)=0 for t<0 since no fluid can exit before it enters

E(t)≥0 for t>0 since mass fractions are always positive

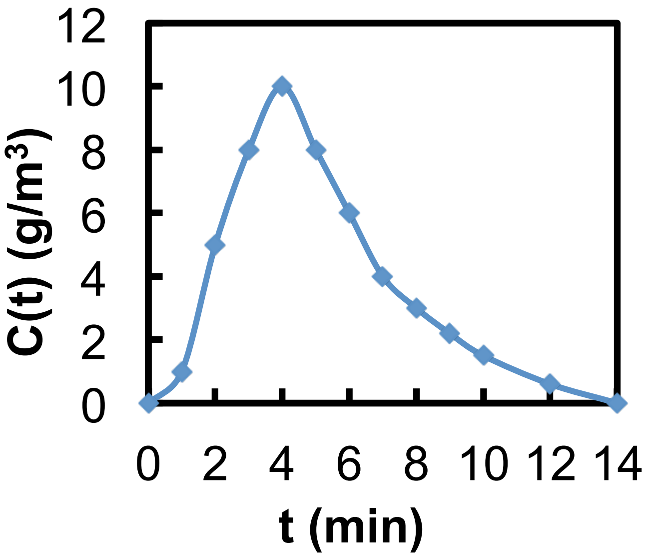
Fraction of fluid element in the exit stream with age less than t_1 is: $\int_0^{t_1} E(t)dt$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

A pulse of tracer was injected into a reactor, and the effluent concentration as a function of time is in the graph below. Construct a figure of C(t) & E(t) and calculate the fraction of material that spent between 3 & 6 min in the reactor

t min	0	1	2	3	4	5	6	7	8	9	10	12	14
C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0

Plot C vs time:



Tabulate E(t): divide C(t) by the total area under the C(t) curve, which must be numerically evaluated

$$\int_0^\infty C(t)dt = \int_0^{10} C(t)dt + \int_{10}^{14} C(t)dt$$

$$\int_{X_0}^{X_N} f(x)dx = \frac{\Delta t}{3}\left(f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 \ldots + 4f_{N-1} + f_N\right)$$

$$\int_0^{10} C(t)dt = \frac{1}{3}\begin{bmatrix} 0 + 4(1) + 2(5) + 4(8) + 2(10) + 4(8) \\ +2(6) + 4(4) + 2(3) + 4(2.2) + 1.5 \end{bmatrix}$$

$$\rightarrow \int_0^{10} C(t)dt = 47.4\,\frac{g\cdot min}{m^3}$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

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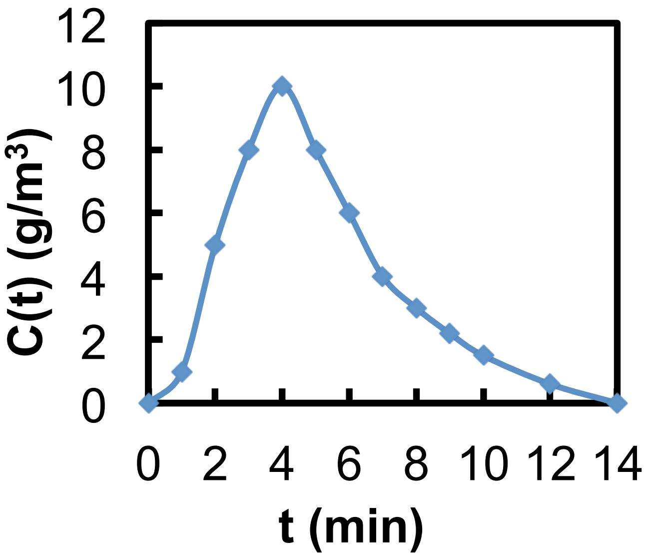

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$$\int_0^{\infty} C(t)dt = \int_0^{10} C(t)dt + \int_{10}^{14} C(t)dt$$

$$\int_{X_0}^{X_2} f(x)dx = \frac{\Delta t}{3}\left(f_0 + 4f_1 + f_2\right)$$

$$\int_{10}^{14} C(t)dt = \frac{2}{3}\left[1.5 + 4(0.6) + 0\right] = 2.6$$

$$\rightarrow \int_0^{\infty} C(t)dt = 47.4\frac{g\cdot min}{m^3} + 2.6\frac{g\cdot min}{m^3} = 50\frac{g\cdot min}{m^3}$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

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C g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E(t)	0	0.02	0.1	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

$$\int_0^\infty C(t)dt = 50\frac{g\cdot min}{m^3}$$

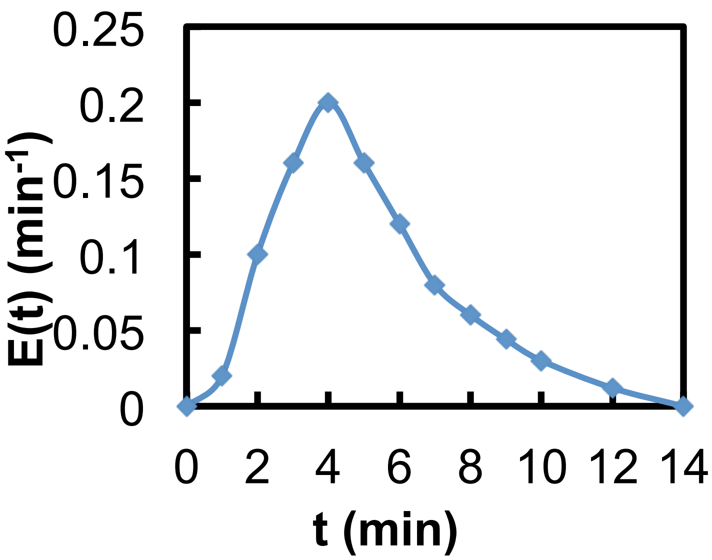
Tabulate E(t): divide C(t) by the total area under the C(t) curve:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt}$$

$$E(t_0) = \frac{0}{50} = 0 \qquad E(t_1) = \frac{1}{50} = 0.02$$

$$E(t_2) = \frac{5}{50} = 0.1 \qquad E(t_3) = \frac{8}{50} = 0.16$$

Plot E vs time:



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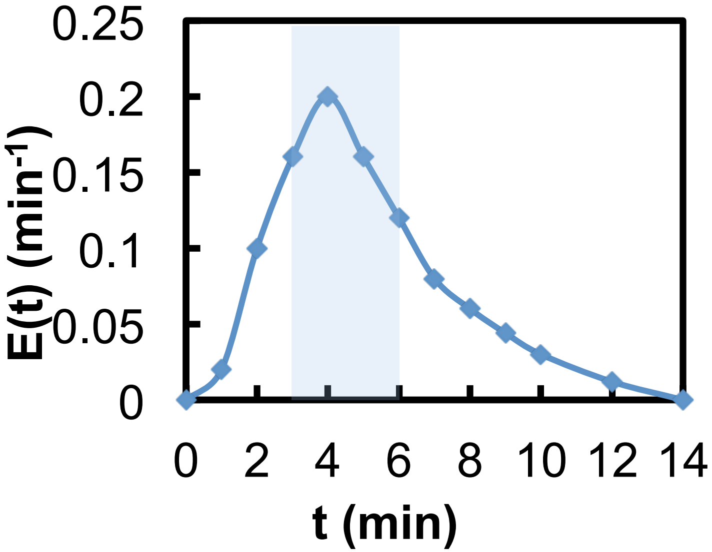
E vs time:



Fraction of material that spent between 3 & 6 min in reactor = area under E(t) curve between 3 & 6 min

Evaluate numerically:

$$\int_{X_0}^{X_3} f(x)\,dx = \frac{3}{8}\Delta t\left(f_0 + 3f_1 + 3f_2 + f_3\right)$$

$$\int_3^6 E(t) = \frac{3}{8}(1)\left(0.16 + 3(0.2) + 3(0.16) + 0.12\right)$$

$$\rightarrow \int_3^6 E(t) = 0.51$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

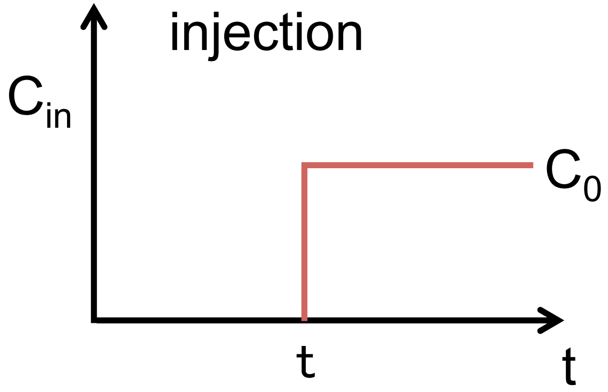
Step-Input to Determine E(t)

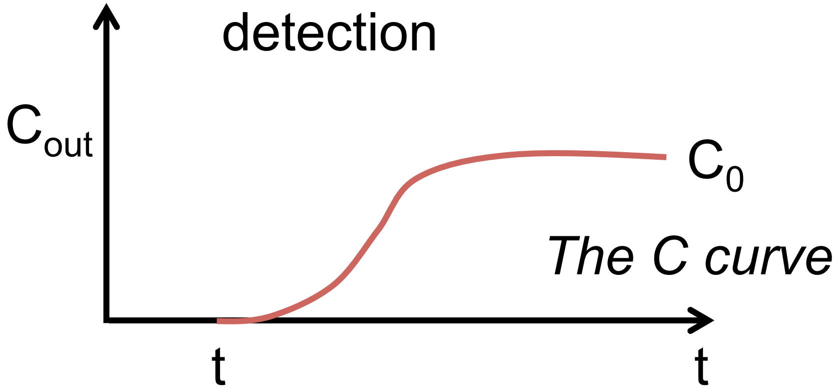
Disadvantages of pulse input:

- Injection must be done in a very short time
- Can be inaccurate when the c-curve has a long tail
- Amount of tracer used must be known

Alternatively, E(t) can be determined using a step input:

- Conc. of tracer is kept constant until outlet conc. = inlet conc.





$$C_{out} = C_0 \int_0^t E(t)\,dt$$

$$E(t) = \frac{d}{dt}\left(\frac{C(t)}{C_0}\right)_{step}$$

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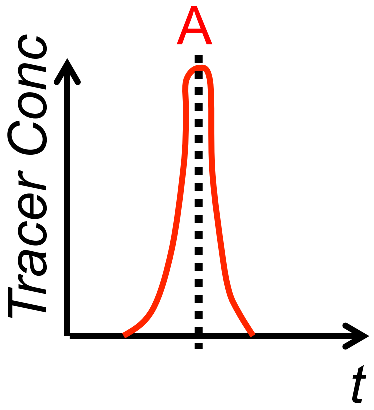
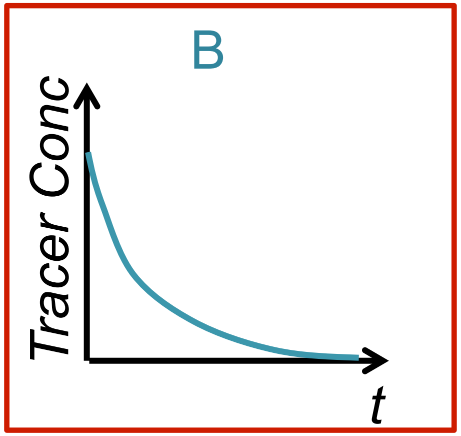
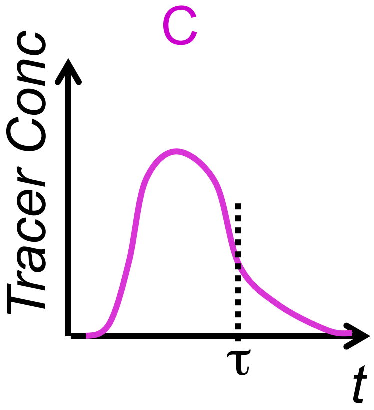
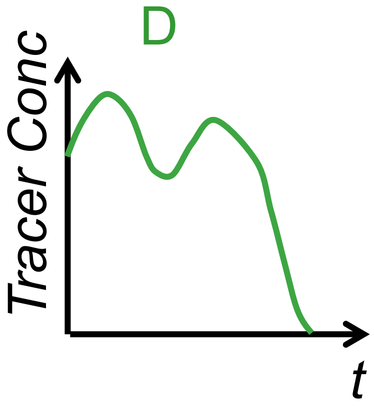
Questions

1. Which of the following graphs would you expect to see if a pulse tracer test were performed on an ideal CSTR?

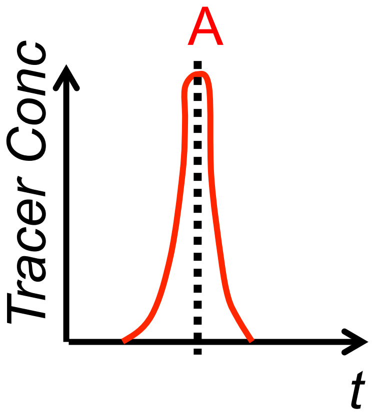


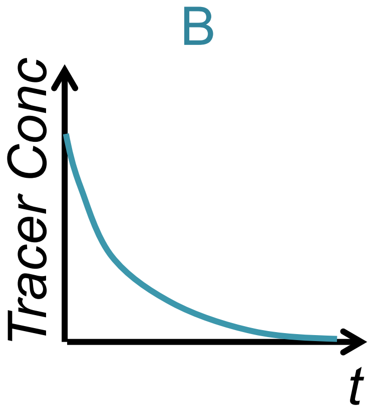


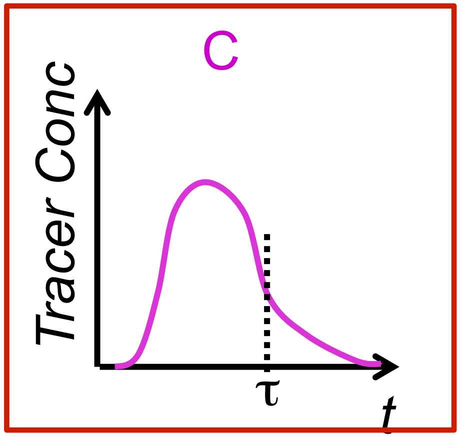


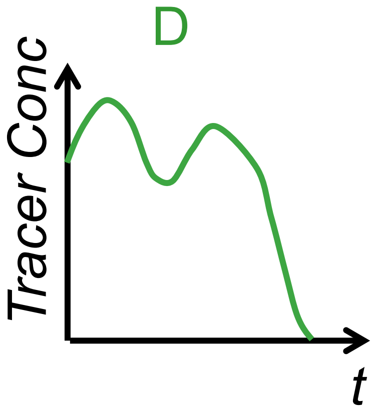


2. Which of the following graphs would you expect to see if a pulse tracer test were performed on a PBR that had dead zones?









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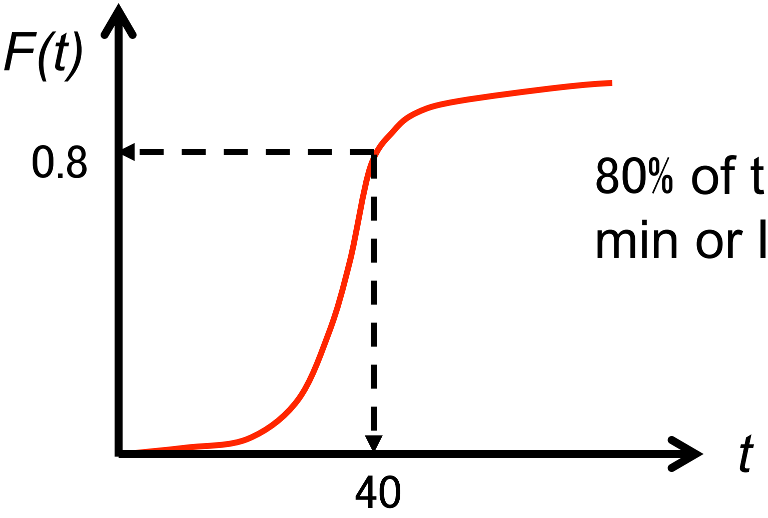
Cumulative RTD Function F(t)

F(t) = fraction of effluent that has been in the reactor for less than time t

$$F(t)=\int_0^t E(t)\,dt \qquad \begin{array}{l} F(t)=0 \text{ when } t<0 \\ F(t)\geq 0 \text{ when } t\geq 0 \\ F(\infty)=1 \end{array} \qquad 1-F(t)=\int_t^\infty E(t)\,dt$$



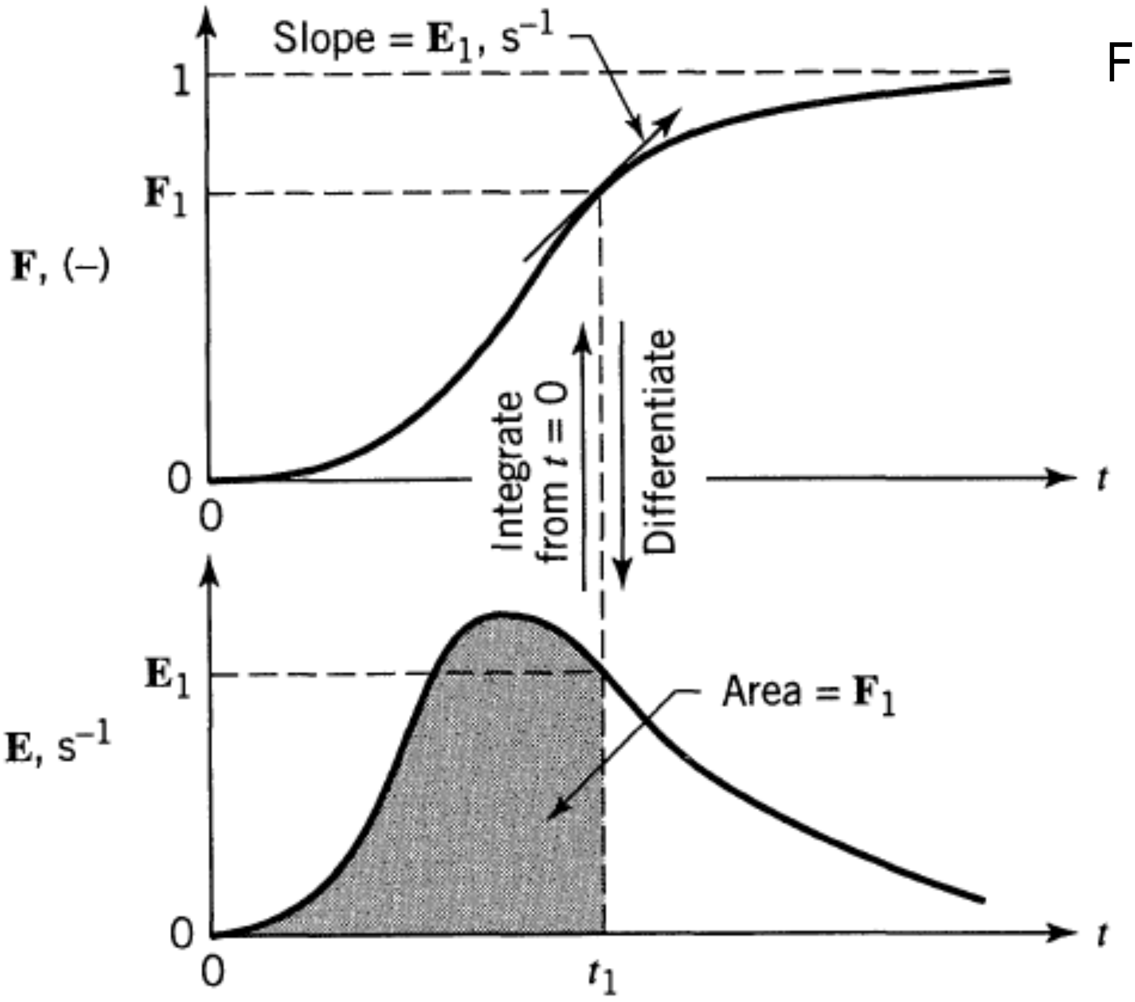
80% of the molecules spend 40 min or less in the reactor

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Relationship between E & F Curves

F(t) = fraction of effluent that has been in the reactor for less than time t

$$F(t) = \int_0^t E(t)\,dt$$



$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt}$$

E(t)= Fraction of material leaving reactor that was inside for a time between t_1 & t_2

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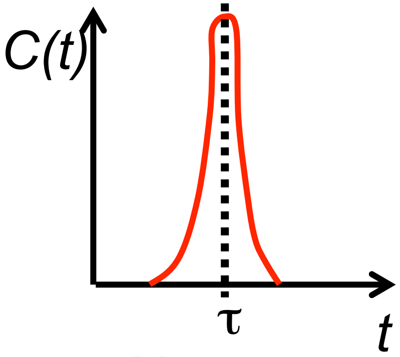
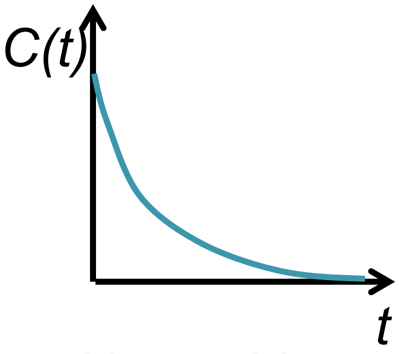
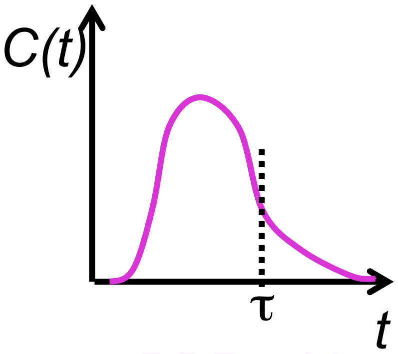
Boundary Conditions for the Cum RTD Function F(t)



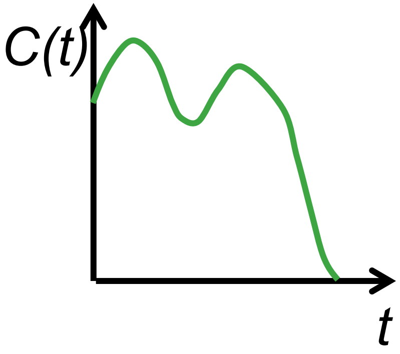
Nearly ideal PFR



Nearly ideal CSTR



PBR with channeling & dead zones



CSTR with dead zones

$$F(t)=\int_0^t E(t)\,dt$$

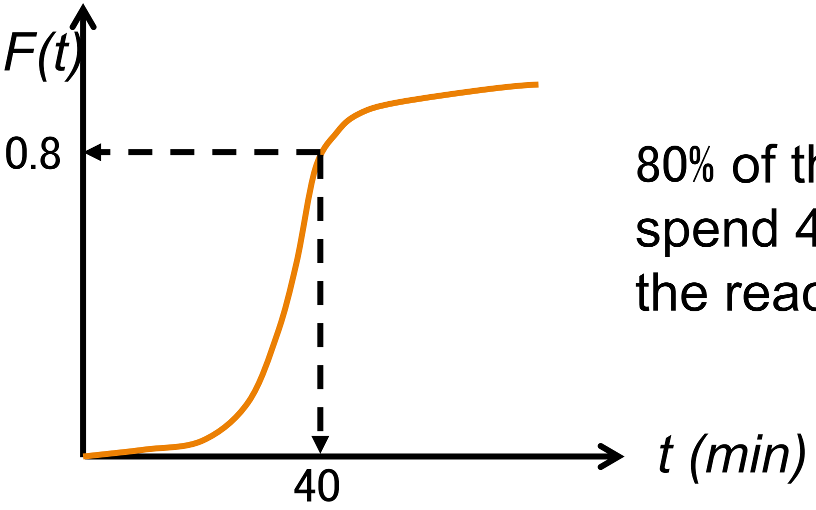
F(t)=fraction of effluent in the reactor less for than time t

$$F(t)=0 \text{ when } t<0$$

$$F(t)\geq 0 \text{ when } t\geq 0$$

$$F(\infty)=1$$

$$1-F(t)=\int_t^\infty E(t)\,dt$$



80% of the molecules spend 40 min or less in the reactor

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

Mean Residence Time, t_m

- For an ideal reactor, the space time τ is defined as V/υ_0
- The mean residence time t_m is equal to τ in either ideal or nonideal reactors

$$t_m = \frac{\int_0^\infty tE(t)dt}{\int_0^\infty E(t)dt} = \int_0^\infty tE(t)dt = \tau \qquad \frac{V}{\upsilon_0} = \tau = t_m$$

By calculating t_m, the reactor V can be determined from a tracer experiment

The spread of the distribution (variance): $\sigma^2 = \int_0^\infty (t - t_m)^2 E(t)dt$

Space time τ and mean residence time t_m would be equal if the following two conditions are satisfied:

- No density change
- No backmixing

In practical reactors the above two may not be valid, hence there will be a difference between them

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.

RTD in Ideal Reactors

All the molecules leaving a PFR have spent ~ the same amount of time in the PFR, so the residence time distribution function is:

$$E(t) = \delta(t-\tau) \quad \text{where } \tau = V/\upsilon_0$$

The Dirac delta function satisfies:

$$\delta(x) = \begin{cases} \infty & \text{when } x = 0 \\ 0 & \text{when } x \neq 0 \end{cases} \qquad \int_{-\infty}^{\infty} \delta(x)\,dx = 1 \qquad \int_{-\infty}^{\infty} g(x)\,\delta(x-\tau)\,dx = g(\tau)$$

Zero everywhere but one point

…but =1 over the entire interval

$$t_m = \int_0^{\infty} t\,\delta(t-\tau)\,dt = \tau$$

Slides courtesy of Prof M L Kraft, Chemical & Biomolecular Engr Dept, University of Illinois at Urbana-Champaign.