

PART 2 Non-Ideal Flow

In PART I the reactors are all ideal. In fact reactors in reality are all behaves between them. This part we explore how to measure these flow pattern and apply them to reactor design.

PART 2 Non-Ideal Flow

Chap 11 Basics of Non-Ideal Flow

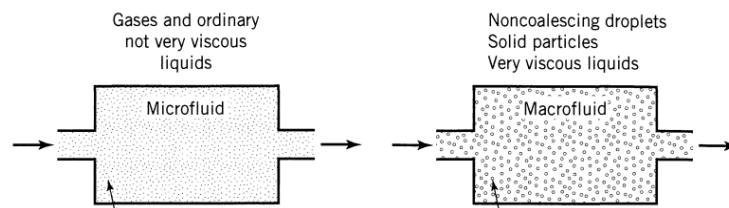
Contacting Pattern including 3 factors:

- State of Aggregation
- Residence Time Distribution
- Earliness of Mixing

— State of Aggregation

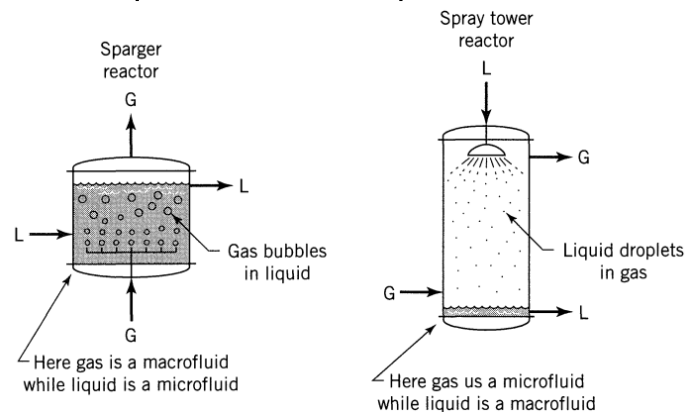
Microfluid : Individual molecules are all free to move and intermix

Macrofluid : Molecules are kept ground together in aggregates or packets
(molecules in one clump cannot jump to another)



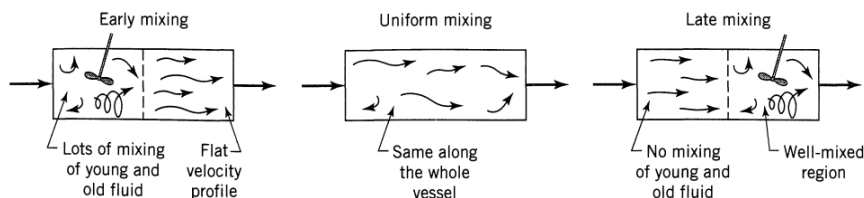
In Single-Phase Systems it depends on nature of fluids

In Two-Phase System it also depends on how it is operated

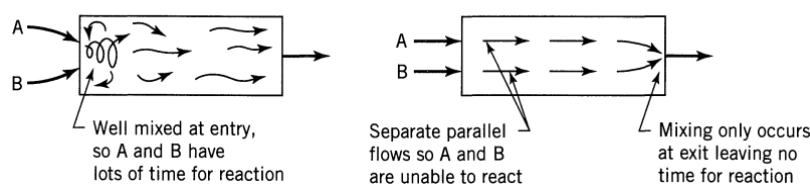


二 Earliness of Mixing

The fluid elements of a single flowing stream can mix with each other either early or later in their flow through the vessel.



For a system with two entering reactant streams it can be very important.



≡ RTD ※

To learn RTD, you need to review related mathematic concepts in Probability and Statics

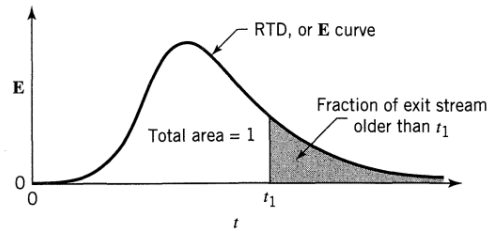
1. The Definition of RTD

① **Residence Time** (also called **age**)

Time between a element of fluid goes into the reactor and out of the reactor

These elements take different routes through the reactor thus may have different RT.

② **RTD** (Residence Time Distribution) **E** The probability density function of RT (time t)



Property : The fraction between t_1 and t_2 :

$$\int_{t_1}^{t_2} E dt$$

Total fraction

$$\int_0^{\infty} E dt = 1$$

mean residence time

$$\bar{t} = \int_0^{\infty} t E dt = \frac{V}{v}$$

variance

$$\sigma^2 = \int_0^{\infty} (t - \bar{t})^2 E(t) dt = \bar{t}^2 - \bar{t}^2$$

Transformation : Time based on mean RT

$$\theta = t / \bar{t}$$

RTD based on mean RT

$$E_{\theta} = \bar{t} E \quad \text{with} \quad \sigma_{\theta}^2 = \frac{\sigma^2}{\bar{t}^2}$$

Define

$$F = \int_0^t E dt$$

Then

$$E = \frac{dF}{dt}$$

2. Experiments of getting RTD

① The **Pulse** Experiment

At $t=0$, M units (mass or mole) of tracer are introduced into the fluid entering the vessel

→ only at $t=0$ does tracer go into vessel

At time t the tracer is detected at the exit, thus they have $RT = t$ and the concentrations

$C_{\text{pulse}}(t)$ shows the fraction.

∴

$$E(t) = \frac{C_{\text{pulse}}(t)}{M/v}$$

$$E(\theta) = \frac{V}{M} C_{\text{pulse}}(t)$$

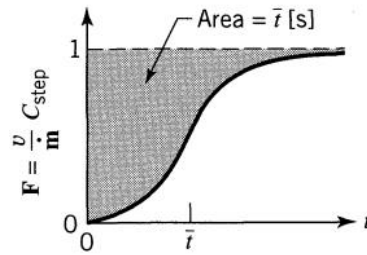
v : flow rate of fluid V : volume of vessel

② The **Step** Experiment

At $t=0$, the fluid which is still not going into the vessel is switched to fluid with tracer C_{max}

Then the concentration of tracer detected at exit at time t ($C_{\text{step}}(t)$) imply the fraction of fluid elements with residence time less than t

$$F(t) = \frac{C_{\text{step}}(t)}{C_{\text{max}}}$$



3. RTD of Ideal Reactors

	$E(t) = \delta(t - \bar{t})$		
	$E(t) = \frac{1}{\bar{t}} e^{-t/\bar{t}}$		

4. The Convolution Integral

- If C_{in} is an arbitrary function $C_{in}(t)$ instead of pulse or step function, with E already known, what would be shown at exit $C_{out}(t)$?
- Analysis : at time t , the fluid just go out of the vessel must went into vessel at time t' and have residence time $t - t'$, so among the $C_{in}(t')$, $E(t - t')$ of them leave the vessel at time t

So

$$C_{out}(t) = \int_0^t C_{in}(t') E(t - t') dt$$

This form of integration is called **Convolution**: $C_{out} = C_{in} * E$

* Dirac Delta Function (introduced to describe pulse)

$$\delta(t - t_0) = \begin{cases} 1 & t = t_0 \\ 0 & t \neq t_0 \end{cases}$$

四 Conversion of Macrofluid ※

For macrofluids, fluid elements are clumps acting as a little batch reactor individually.

So we need to calculate the relationship between conversion and time $(\frac{C_A}{C_{A0}})_{ele}(t)$

→ According to its kinetics

Then calculate mean conversion by adding them up according to RTD

$$\overline{\frac{C_A}{C_{A0}}} = \int_0^\infty (\frac{C_A}{C_{A0}})_{ele}(t) E(t) dt$$

Chap 12 Compartment Models

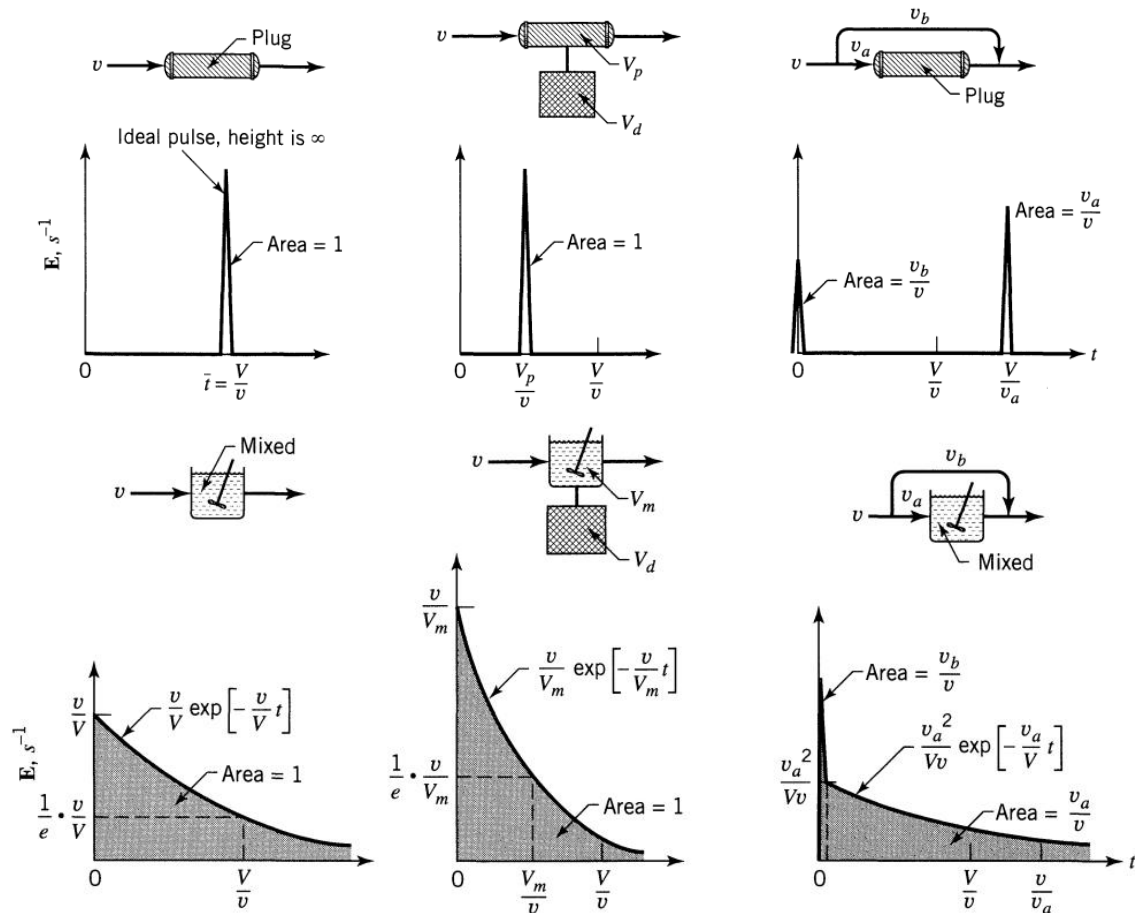
In Chapter 12 ~ 14 we are going to learn how to build reasonable model for a reactor according to known RTD.

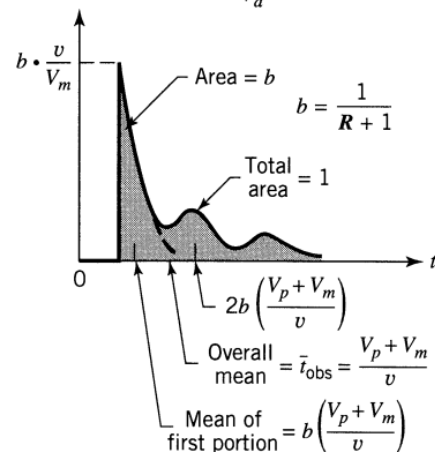
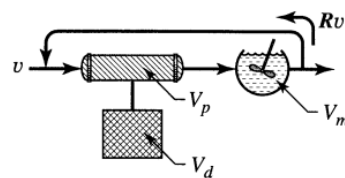
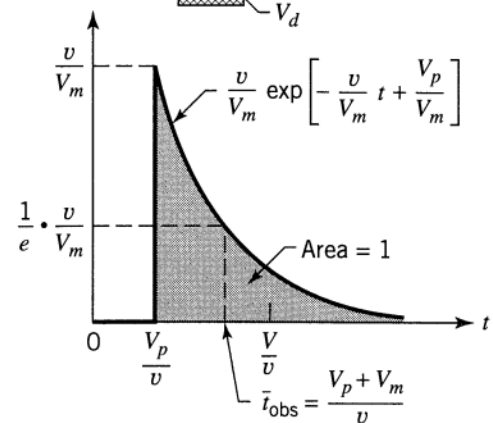
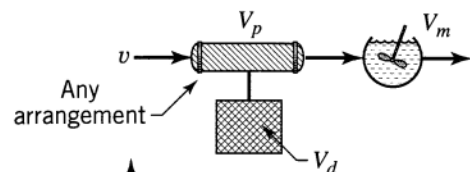
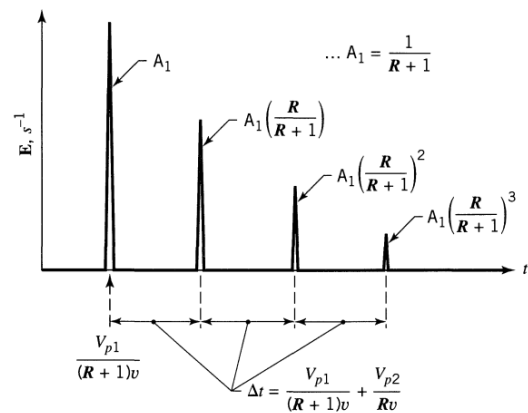
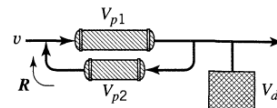
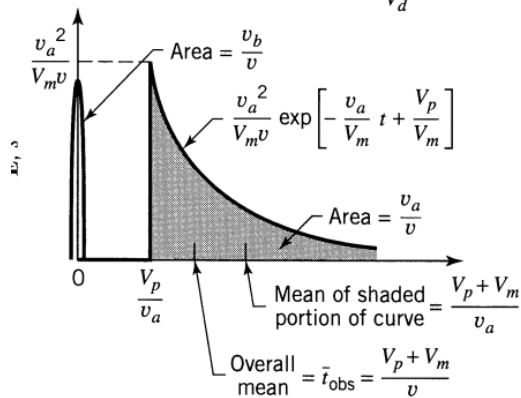
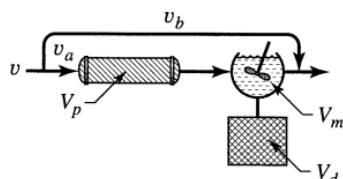
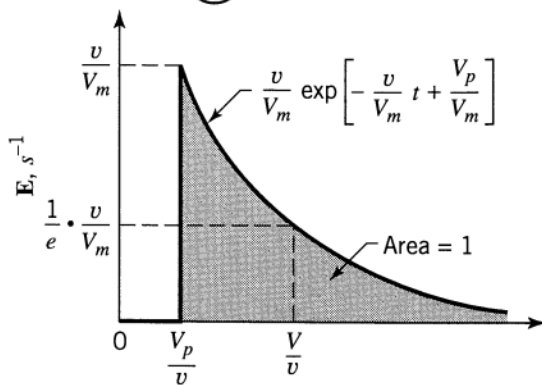
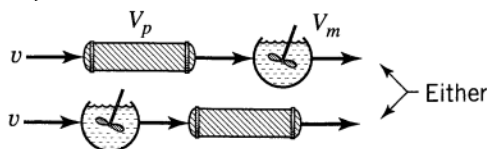
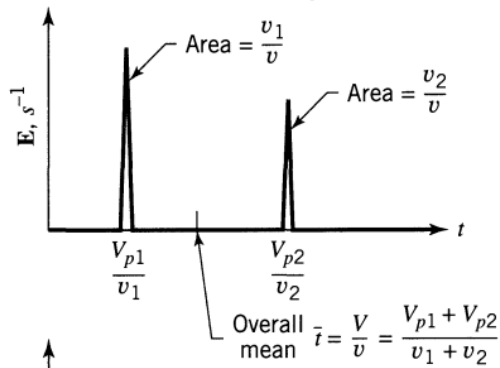
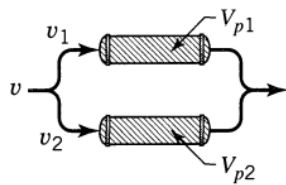
— Compartment Model

- Combine ideal reactors like PFR and MFR in parallel or in series along with dead region, bypass flow and recycle flow to acquire a complex model. The RTD of the model should fit the RTD of given vessel.
- Basic elements of compartment model :
 - V_a **Active Volume**, including V_p (**Plug Flow Region**) and V_m (**Mixed Flow Region**)
 - V_d **Dead or Stagnant Region**, there is no flow in it.
 - v_a **Active Flow**, that through active volume
 - v_b **Bypass Flow** it doesn't go through active volume
 - v_r **Recycle Flow** it goes from a PFR's exit to its entry

二 Typical Model and its RTD

- dead region causes ideal $\bar{t} = \frac{V}{v}$ greater than actual \bar{t}
- bypass makes $E(0) > 0$

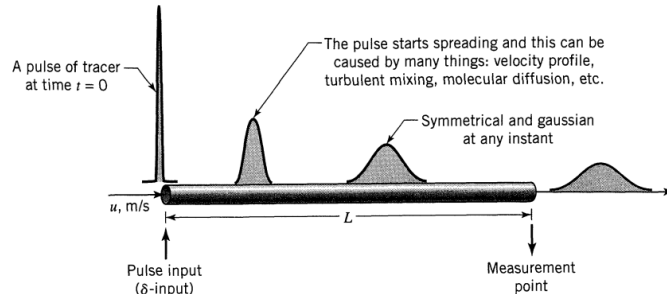




Chap 13 The Dispersion Model

Axial Dispersion

When an ideal pulse is introduced to fluid entering the vessel, it will spread as it passes through the vessel — a diffusion-like process happened, called dispersion



The larger the **dispersion coefficient** D , the more rapid the fluid spreads $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$

Its dimensionless form **Peclet Number** $Pe = \frac{uL}{D}$, and let $z = \frac{x}{L}$: $\frac{\partial C}{\partial \theta} = \frac{1}{Pe} \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z}$

• $Pe \rightarrow 0$: Mixed Flow $Pe \rightarrow \infty$: Plug Flow

Get Pe from RTD Data

1. $Pe > 100$

Pulse moves so fast that it can be considered as symmetrical curve

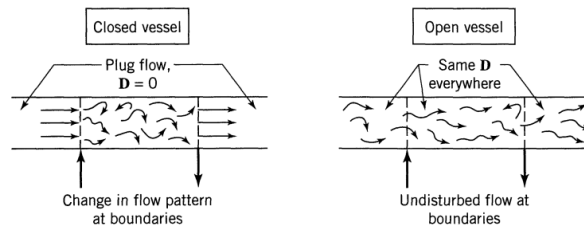
$$C = \frac{1}{2\sqrt{\pi/Pe}} e^{-\frac{Pe(1-\theta)^2}{4}}$$

$$\therefore \textcircled{1} \quad \bar{t} = \frac{V}{v} = \frac{L}{u} \quad \textcircled{2} \quad \sigma_{\theta}^2 = \frac{2}{Pe} \quad \text{and} \quad \sigma^2 = 2 \frac{DL}{u^3} \rightarrow \sigma^2 \propto L \quad \text{in dispersion model}$$

2. $Pe < 100$

Now what happens right at the entrance and exit of the vessel matters

- **Open Boundary Condition** Flow is undisturbed as it passes the boundary
- **Closed Boundary Condition** have plug flow outside the vessel up to the boundaries



	$\bar{\theta}$	σ_{θ}^2
Closed Vessel	$\bar{\theta} = 1$	$\sigma_{\theta}^2 = \frac{2}{Pe} - \frac{2}{Pe^2}(1 - e^{-Pe})$
Open Vessel	$\bar{\theta} = 1 + \frac{2}{Pe}$	$\sigma_{\theta}^2 = \frac{2}{Pe} + \frac{8}{Pe^2}$
Open-Closed Vessel	$\bar{\theta} = 1 + \frac{1}{Pe}$	$\sigma_{\theta}^2 = \frac{2}{Pe} + \frac{3}{Pe^2}$

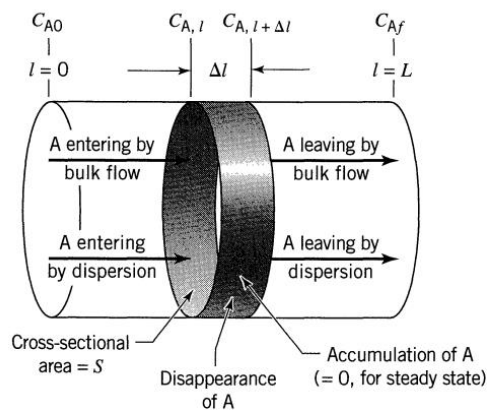
四 Chemical Reaction and Dispersion

Now we can build a model for chemical reactor in which material is mixing axially with a dispersion coefficient D . The dimensionless form of differential equation is

$$\frac{1}{Pe} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - k\tau C_A^n = 0 \quad z = l/L \quad \tau = L/u$$

Assume $n=1$: $\frac{C_A}{C_{A0}} = \frac{4ae^{Pe/2}}{(1+a)^2 e^{aPe/2} - (1-a)^2 e^{-aPe/2}} \quad a = \sqrt{1 + 4k\tau/Pe}$

How is That Done ?



Material Balance : input = output + reaction + accumulation

$$\rightarrow (\text{out} - \text{in})_{\text{bulk flow}} + (\text{out} - \text{in})_{\text{axial dispersion}} + \text{reaction} + \text{accumulation} = 0$$

Entering by bulk flow : $C_A(l) \times u \times S$ Leaving by bulk flow : $C_A(l + \Delta l)uS$

Entering by Dispersion : $-DS \frac{dC_A}{dl} \Big|_l$ Leaving by Dispersion : $-DS \frac{dC_A}{dl} \Big|_{l+\Delta l}$

Reaction : $(-r_A)S\Delta l = kC_A^n S\Delta l$

Thus $C_A(l + \Delta l)uS - C_A(l) \times u \times S - DS \frac{dC_A}{dl} \Big|_{l+\Delta l} + DS \frac{dC_A}{dl} \Big|_l + kC_A^n S\Delta l = 0$

Simplify : $u \frac{C_A(l + \Delta l) - C_A(l)}{\Delta l} - D \frac{\frac{dC_A}{dl} \Big|_{l+\Delta l} - \frac{dC_A}{dl} \Big|_l}{\Delta l} + kC_A^n = 0$

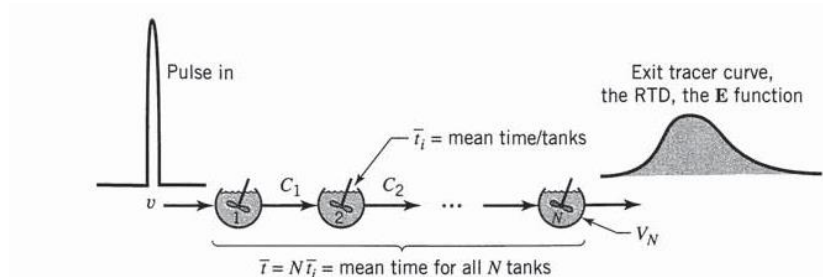
Make $\Delta l \rightarrow 0$: $D \frac{d^2 C_A}{dl^2} - u \frac{dC_A}{dl} - kC_A^n = 0$

Make $z = l/L \quad \tau = L/u \quad Pe = \frac{uL}{D}$

Dimensionless form : $\frac{1}{Pe} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - k\tau C_A^n = 0$

Chap 14 The Tanks-In-Series Model

— RTD for Tanks-In-Series



We define $\theta_i = \frac{t}{t_i}$ t_i : mean residence time per tank i

$\theta = \frac{t}{\bar{t}}$ \bar{t} : mean residence time in all tanks thus $\bar{t} = N t_i$ $\theta_i = N \theta$

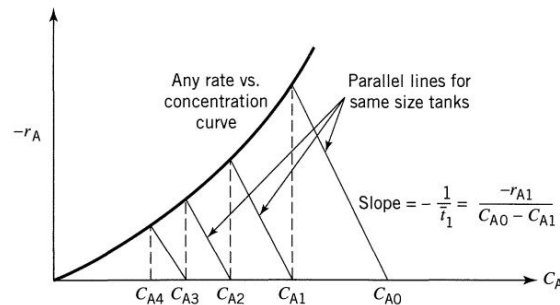
For $E = \frac{1}{t_i} e^{-\frac{t}{t_i}}$ → By Convolution $E_N = \underbrace{E * \dots * E}_N = \frac{t^{N-1}}{t_i^N (N-1)!} e^{-\frac{t}{t_i}}$

Thus $E_\theta = N \frac{(N\theta)^{N-1}}{(N-1)!} e^{-N\theta}$ $\sigma_\theta^2 = \frac{1}{N}$

二 Chemical Conversion

By performance equation of MFR : $\frac{C_A}{C_{A0}} = \frac{1}{(1 + \frac{k\bar{t}}{N})^N}$ (first-order)

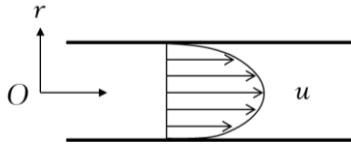
For other reactions graphical method can be used



Chap 15 The Convection Model and Its RTD

— The Convection Model and Its RTD

We have learned the Convection Model in Principles of ChemEng :



$$u(r) = u_0 \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad t = \frac{L}{u} = \frac{L}{u_0 [1 - (r/R)^2]}$$

So $\bar{t} = \frac{2L}{u_0}$ and $t_{\min} = \frac{L}{u_0} = \frac{\bar{t}}{2} \rightarrow E(t) = \begin{cases} 0 & t < \frac{\bar{t}}{2} \\ \frac{\bar{t}^2}{2t^3} & t \geq \frac{\bar{t}}{2} \end{cases} \quad E(\theta) = \begin{cases} 0 & \theta < \frac{1}{2} \\ \frac{1}{2\theta^3} & \theta \geq \frac{1}{2} \end{cases}$

Then we can use methods in Chap 11 (macrofluid) to solve problems, for there is no intermixing in this model.

— Which Model to Use ?

- If $\sigma^2 \propto L$ choose the Dispersion Model or Tanks-In-Series Model
- If $\sigma \propto L$ choose the Convective Model

Chap 16 Earliness of Mixing, Segregation and RTD

— Self-Mixing of a Single Fluid

- In BR and PFR, it makes no difference whether it is microfluid or macrofluid
- However, in MFR, microfluid acts differently from macrofluid (except for $n = 1$)

microfluid in MFR $\frac{C_A}{C_{A0}} = 1 - \frac{(-r_A)t}{C_{A0}} \quad (\text{uniform concentration})$

macrofluid in MFR $\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \frac{1}{\bar{t}} e^{-t/\bar{t}} dt \quad (\text{varying concentration})$

- Each flow pattern of fluid through a vessel has associated with it a definite clearly defined RTD or exit age distribution function E. The converse is not true, for different flow patterns may give the same RTD.

Summary

X_A or φ is affected by kinetics, RTD, degree of segregation, earliness of mixing

- The more RTD shifts from PFR to MFR, the more the Segregation plays role in.
- Late mixing and macrofluid favors reactions where $n > 1$
Early mixing and microfluid favors reactions where $n < 1$
- With the conversion level moving up, RTD gradually plays an important role, and seg & earliness have little effect until conversion rise to high level